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Comparison of Equations of State in Thermodynamic Simulation of Multicomponent Natural Gas Using DWSIM

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Abstract :
The selection of a thermodynamic property package strongly affects the prediction of fluid properties in process simulation, particularly for non-ideal multicomponent natural gas systems. This study evaluates the influence of pressure on the compressibility factor (Z), density, heat capacity (Cp), and molar enthalpy of a natural gas mixture using several equations of state (EOS) in DWSIM. The gas mixture consisted of methane (CH_4), carbon dioxide (CO_2), ethane (C_2H_6), and nitrogen (N_2), simulated at 25 °C with pressure variations from 1 to 50 atm. An initial evaluation was performed on several DWSIM property packages to identify stable and relevant models. The analysis focused on five EOS models: Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), Peng-Robinson-Stryjek-Vera 2 (PRSV2-VL), Peng-Robinson/Lee-Kesler (PR/LK), and Peng-Robinson 1978 (PR78). Increasing pressure reduced Z from approximately 0.998 to 0.866 and increased density up to about 46 kg/m^3. Heat capacity increased to approximately 2.22 kJ/kg.K, while molar enthalpy became more negative at high pressure. PR and PR78 produced the most consistent predictions, whereas PRSV2-VL and PR/LK showed the largest deviations in Z and molar enthalpy, respectively.

Keywords: DWSIM; equation of state; natural gas; Peng-Robinson; thermodynamic simulation

1. Introduction

Accurate process simulation plays an important role in chemical engineering because it supports the analysis, design, and optimization of industrial processes before practical implementation. Through simulation, various operating conditions can be evaluated with lower cost and time requirements than experimental approaches while still providing valuable insight into process performance (Varandas et al., 2024). In addition, simulation tools facilitate the evaluation of thermodynamic behavior, heat transfer, mass transfer, and fluid-flow characteristics under different operating conditions (Oyegoke, 2025).

In process simulation, the accuracy of calculation results is strongly influenced by the selection of the thermodynamic model or property package (Wang et al., 2024). A property package is used to calculate fluid properties such as compressibility factor, density, enthalpy, heat capacity, and phase equilibrium based on a certain mathematical model (Tenenev and Koroleva, 2023). An inappropriate model may produce significantly different predictions, especially for non-ideal gas systems and high-pressure conditions (Brateau et al., 2024).

Natural gas is a multicomponent mixture generally dominated by methane, although carbon dioxide, ethane, and nitrogen are commonly present in varying concentrations. The presence of these components can significantly influence the thermodynamic behavior of the gas mixture, particularly under elevated pressure conditions where deviations from ideal-gas behavior become increasingly important (Mašláni et al., 2023). Carbon dioxide and nitrogen may affect density, compressibility factor, and phase behavior, thereby influencing the accuracy of process design calculations (Yu et al., 2025).

Equations of state are widely used to predict the behavior of hydrocarbon fluids and natural gas because they describe the relationship among pressure, temperature, and volume in real fluid systems (Simão et al., 2024). The Peng-Robinson (PR) model is one of the most frequently used EOS models for hydrocarbon and natural gas systems because it provides good prediction of vapor and liquid phase properties under various operating conditions (AlHammadi and Abutaqiya, 2023). The Soave-Redlich-Kwong (SRK) model is also commonly applied to hydrocarbon gas systems because its formulation is relatively simple and efficient for phase-equilibrium prediction (Malyshev et al., 2025).

In addition to PR and SRK, several EOS developments such as Peng-Robinson-Stryjek-Vera (PRSV), Peng-Robinson 1978 (PR78), and Peng-Robinson/Lee-Kesler (PR/LK) can be used to evaluate thermodynamic properties of gas mixtures under non-ideal conditions (Kuzmin et al., 2024). Differences in model formulation may lead to variations in predicted compressibility factor, density, heat capacity, and molar enthalpy (Manuel et al., 2023). Accordingly, comparison among property packages is needed to ensure that the selected model is suitable for the characteristics of the analyzed system.

DWSIM is an open-source process simulation software that provides various property packages for thermodynamic analysis and chemical process simulation (Tangsriwong et al., 2020). DWSIM can serve as an alternative process simulator because it is open-source, flexible, and provides several thermodynamic models for fluid and hydrocarbon systems (Oyegoke, 2025). However, the availability of many property packages still requires evaluation because not all models have the same suitability for multicomponent natural gas systems (James et al., 2020). Studies comparing EOS models in multicomponent natural gas simulation using DWSIM remain relatively limited, particularly at medium to high pressure. Therefore, further evaluation is required to assess the capability of each model in predicting the thermodynamic properties of non-ideal gas mixtures.

This study was conducted to evaluate the sensitivity of several cubic EOS models to pressure changes in the simulation of multicomponent natural gas using DWSIM. In addition to comparing EOS prediction results, this study analyzes the effect of property package selection on thermodynamic parameters related to high-pressure gas process design. The analysis was performed at pressures of 1, 5, 10, 20, and 50 atm with a constant temperature of 25 °C. The parameters evaluated were compressibility factor, density, heat capacity, and molar enthalpy. The study also examined differences among the main EOS models and the limitations of selected non-EOS property packages for multicomponent natural gas simulation.

2. Method

Software

The simulation was performed using DWSIM version 9.0.5. Simulation data processing and graph preparation were carried out using Microsoft Excel. DWSIM was used to obtain the compressibility factor, density, heat capacity, and molar enthalpy at each pressure variation and property package.

System analyzed

The system analyzed in this study was a multicomponent natural gas mixture consisting of methane, carbon dioxide, ethane, and nitrogen. The mixture composition was defined based on the mole fraction of each component, as shown in Table 1.

Table 1. Composition of the multicomponent natural gas mixture

Component	Chemical formula	Mole fraction
Methane	CH_4	0.85
Carbon dioxide	CO_2	0.10
Ethane	C_2H_6	0.03
Nitrogen	N_2	0.02

The selected composition represents a methane-rich natural gas mixture containing methane as the major component together with carbon dioxide, ethane, and nitrogen, which are commonly encountered constituents in natural gas systems (Kuczyński et al., 2020).

The gas mixture was used as a material stream in DWSIM to evaluate the effect of pressure on the thermodynamic properties of a non-ideal gas system. The selected gas composition was chosen to represent a multicomponent natural gas system containing methane as the major component, along with carbon dioxide, ethane, and nitrogen as common accompanying components. This composition was used to evaluate the performance of different EOS models in predicting thermodynamic properties under varying pressure conditions.

Operating conditions

The simulation was conducted under isothermal conditions at a constant temperature of 25 °C. Pressure was varied to analyze changes in the thermodynamic properties of the gas mixture with increasing pressure. The pressure range of 1–50 atm was selected to represent pressure conditions commonly encountered in natural gas processing and transportation systems and to evaluate EOS performance under increasing non-ideal gas behavior.

Table 2. Pressure variation used in the simulation

No	Pressure (atm)
1	1
2	5
3	10
4	20
5	50

The fixed variables were a temperature of 25 °C and a mass flow rate of 1000 kg/s. The mass flow rate was used only as a simulation input and was not analyzed further because the observed parameters were intensive properties.

Simulation assumptions

The simulation was carried out under steady-state conditions by assuming a single vapor phase. Flash calculations and binary interaction parameters followed the default settings available in the DWSIM database. Phase equilibrium was calculated using the PT flash approach, with pressure and temperature as the main specified variables. For cubic EOS models, the mixing rule followed the standard van der Waals mixing rule implemented in the simulator.

Property packages

An initial screening was performed on several property packages available in DWSIM to determine the capability of each model in predicting the thermodynamic properties of a multicomponent natural gas mixture. The evaluated models included EOS-based models, activity coefficient models, ideal models, and specific property database models. The main discussion focused on five EOS models considered the most relevant and stable for natural gas systems: Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), Peng-Robinson-Stryjek-Vera 2 (PRSV2-VL), Peng-Robinson/Lee-Kesler (PR/LK), and Peng-Robinson 1978 (PR78).

Table 3. Initial evaluation of DWSIM property packages for multicomponent natural gas simulation

Model group	Models	Initial evaluation	Decision
Cubic EOS	PR, SRK, PRSV2-VL, PR/LK, PR78	Stable and consistent	Main discussion
Activity coefficient	NRTL, Wilson, UNIQUAC, Modified UNIFAC	Less suitable for high-pressure gas	Not focused
Ideal model	Raoult's Law	Too ideal	Not focused
Specific database/properties	CoolProp	Unstable or not convergent	Not focused

The Peng-Robinson model is widely used in hydrocarbon and natural gas simulations because it provides reliable predictions for fluid properties at medium to high pressures. The SRK model has a simpler formulation and is frequently applied to light hydrocarbon gas systems. Meanwhile, PRSV2-VL, PR/LK, and PR78 are developments or combinations of the Peng-Robinson model that use different approaches for correction parameters and residual properties. Other property packages such as NRTL, Wilson, UNIQUAC, Modified UNIFAC, Raoult's Law, and CoolProp were included only as preliminary comparisons because they were less representative or less stable for high-pressure non-ideal gas simulation.

Equations of state

EOS models were used to predict the relationship among pressure, temperature, and molar volume in real gas systems. The Peng-Robinson equation was expressed as Equation (1).

$$P = \frac{R\,T}{V - b} - \frac{a\alpha}{V\,(V + b) + b(V - b)} \quad (1)$$

where P is pressure, T is temperature, V is molar volume, R is the universal gas constant, a and b are molecular interaction constants, and α is the temperature correction factor. The SRK equation was expressed as Equation (2).

$$P = \frac{R\,T}{V - b} - \frac{a\alpha}{V\,(V + b)} \quad (2)$$

The α parameter represents the attractive intermolecular force correction, while b represents the molecular volume of the fluid. The temperature correction factor is used to improve the accuracy of thermodynamic property prediction with respect to temperature changes. The Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations were selected because they are among the most widely used cubic EOS models for hydrocarbon and natural gas systems. These models have been extensively applied in thermodynamic studies and are commonly used for evaluating gas-phase properties under varying pressure conditions.

Parameters analyzed

The analyzed thermodynamic parameters were compressibility factor (Z), density (kg/m^3), heat capacity (Cp), and molar enthalpy (kJ/kmol). These parameters were selected because they represent the main thermodynamic characteristics of natural gas mixtures under different pressure conditions.

To determine the difference among thermodynamic model predictions, deviations were calculated relative to the Peng-Robinson model as the reference. Peng-Robinson was selected as the reference because it is widely used for natural gas and hydrocarbon systems and performs well at medium to high pressure. The deviation percentage was calculated using Equation (3).

$$\text{Deviasi (\%)} = \left|\frac{X_{EOS} - X_{PR}}{X_{PR}}\right| \text{ x } 100\% \quad (3)$$

A relative error was also calculated to compare DWSIM results with manual calculations at selected conditions using Equation (4).

$$\text{Error (\%)} = \left|\frac{X_{DWSIM} - X_{manual}}{X_{manual}}\right| \text{ x } 100\% \quad (4)$$

Simulation procedure

The simulation procedure started by creating a new case in DWSIM and adding all gas mixture components to the simulation basis. The selected property package was then assigned, and a material stream was created as the feed stream. Operating conditions including temperature, pressure, mass flow rate, and mixture composition were set according to the study variables. The simulation was run for each property

package at every pressure variation, and the resulting compressibility factor, density, heat capacity, and molar enthalpy were recorded for further analysis. The simulation procedure is illustrated in Figure 1.

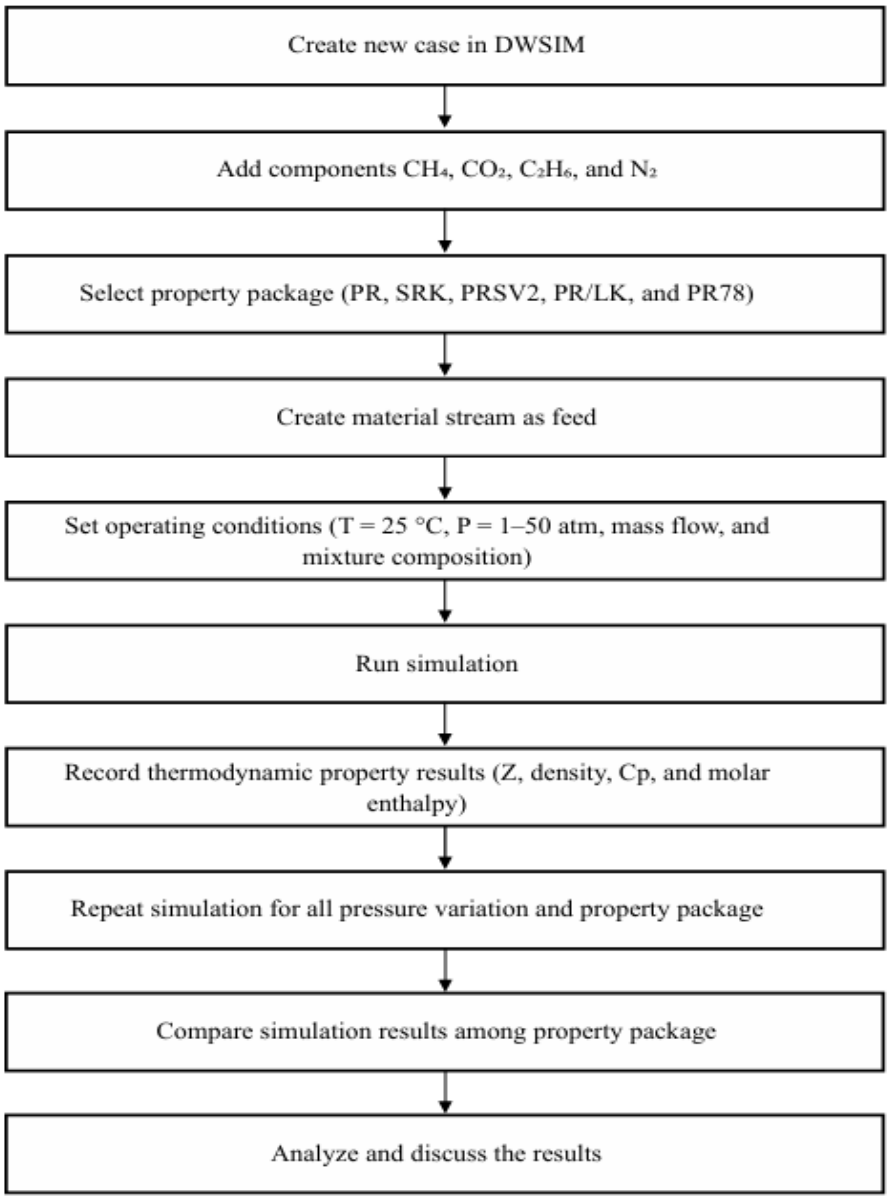

Figure 1. Flow diagram of the simulation procedure using DWSIM

3. Results and Discussion

Effect of pressure on compressibility factor (Z)

The compressibility factor (Z) decreased with increasing pressure for all analyzed models. The decrease became more significant above 20 atm, indicating a greater deviation of the gas mixture from ideal-gas behavior. As pressure increases, intermolecular attractive and repulsive forces become more significant because the distance between molecules decreases, causing the real-gas volume to deviate from ideal-gas predictions. Similar behavior has been reported for gas mixtures containing carbon dioxide under medium- and high-pressure conditions (Liu et al., 2021).

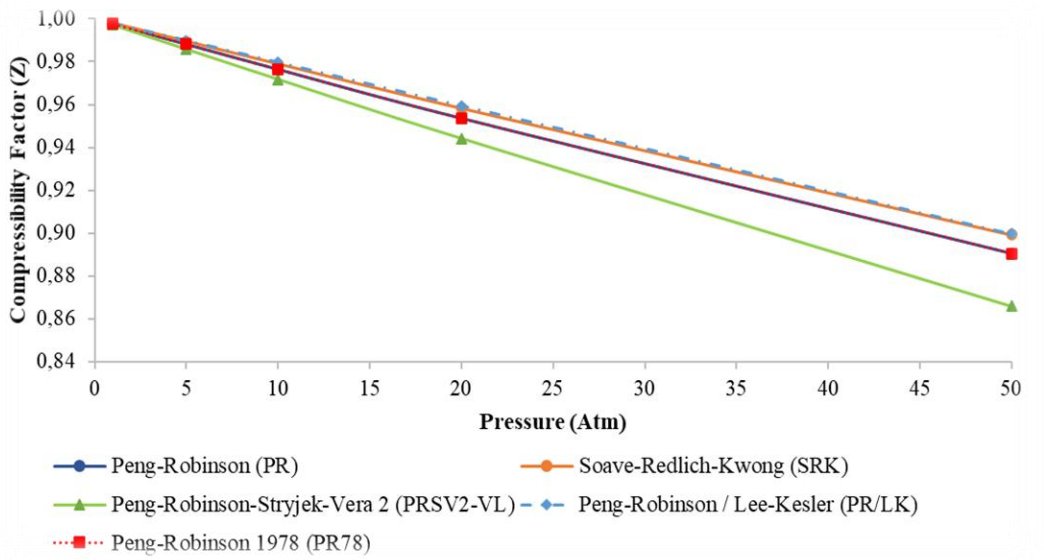

Figure 2. Relationship between pressure and compressibility factor (Z) of methane, carbon dioxide, ethane, and nitrogen mixture

Based on the graph, all EOS models showed a similar decreasing trend. PR, SRK, and PR78 produced relatively close values across the pressure range. PRSV2-VL exhibited the most significant decrease in Z, particularly at 50 atm, with a value of approximately 0.866. This indicates that PRSV2-VL is more sensitive to non-ideal fluid behavior than the other EOS models. The modified alpha function incorporated in PRSV2-VL appears to enhance the influence of intermolecular attractive forces, resulting in a stronger response to pressure-induced non-idealities.

In contrast, PR/LK yielded the highest Z value at high pressure compared with the other EOS models (Brateau et al., 2024). The combination of the Peng-Robinson approach with the Lee-Kesler correlation led to less pronounced changes in Z at high pressure. Overall, all EOS models consistently predicted a decrease in the compressibility factor with increasing pressure, although the degree of sensitivity differed among models.

Effect of pressure on density

Density increased almost linearly with pressure for the main EOS models. This increase became more apparent at high pressure due to volumetric compression of the gas mixture. As pressure rises, the occupied volume decreases while the mass remains constant, leading to a higher density. Similar behavior has been reported for non-ideal gaseous systems under elevated pressure conditions (Brateau et al., 2024).

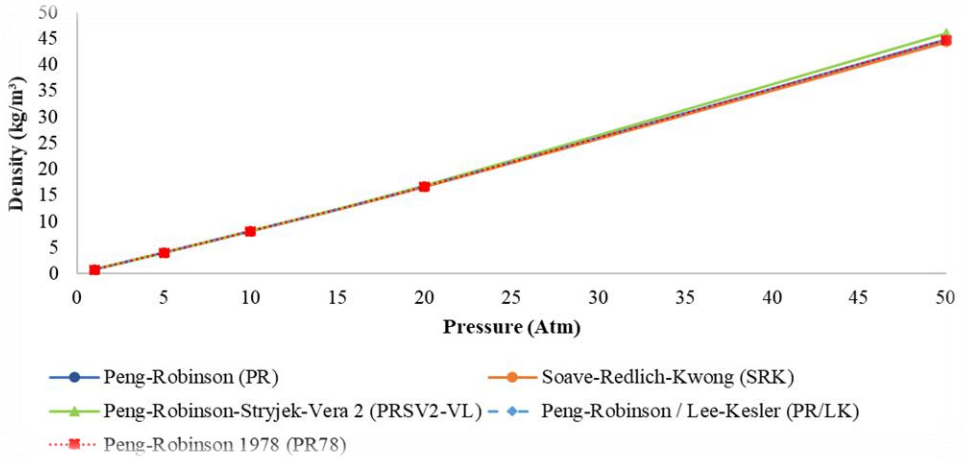

Figure 3. Relationship between pressure and density of methane, carbon dioxide, ethane, and nitrogen mixture

At 1 atm, all models yielded a density of approximately 0.79 kg/m^3. At 50 atm, density increased to about 44-46 kg/m^3 depending on the property package used. PRSV2-VL exhibited the highest density at high pressure, while SRK generated slightly lower values than the other EOS models. This indicates that each model uses a different approach to predict intermolecular interactions under high-pressure conditions (Wang et al., 2025).

Differences in density prediction are important in pipeline and gas compression simulations because density directly affects pressure drop, flow capacity, and compressor energy estimation. Therefore, selecting a suitable EOS becomes increasingly important for non-ideal gas simulation at high pressure because differences in density prediction may influence equipment sizing, pressure-drop estimation, and compressor power requirements. This trend is consistent with the decreasing compressibility factor observed at higher pressures, where lower Z values indicate greater deviation from ideal-gas behavior and contribute to higher gas density.

Effect of pressure on heat capacity (Cp)

Heat capacity (Cp) showed an increasing trend with increasing pressure for all property packages. This behavior suggests that non-ideal thermodynamic effects become increasingly important as pressure increases. Under these conditions, part of the supplied energy is associated with intermolecular interactions in addition to molecular motion, resulting in a greater heat requirement for a given temperature increase (Simão et al., 2024).

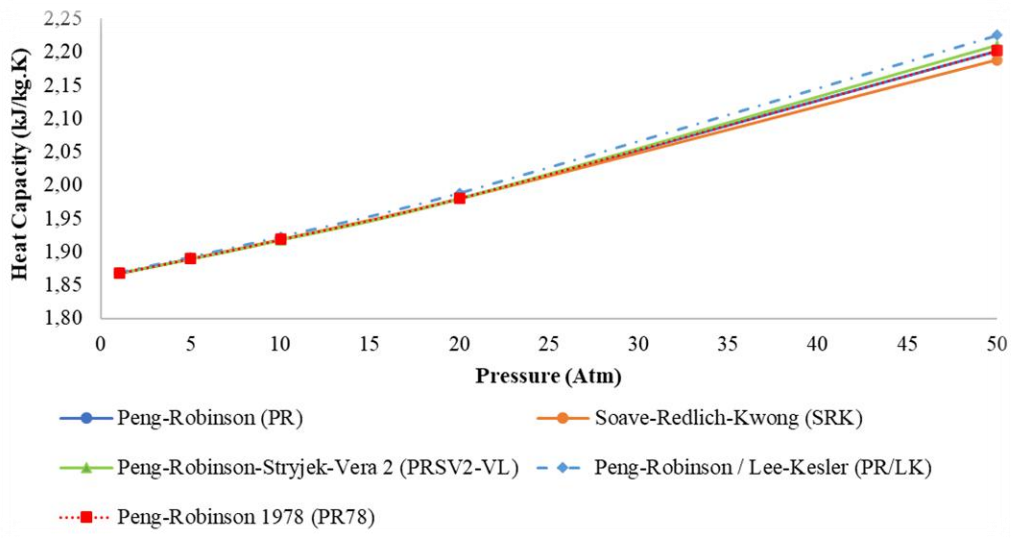

Figure 4. Relationship between pressure and heat capacity (Cp) of methane, carbon dioxide, ethane, and nitrogen mixture

At 1 atm, Cp values for all models were around 1.86-1.87 kJ/kg.K. When pressure increased to 50 atm, Cp increased to approximately 2.18-2.23 kJ/kg.K. PR/LK demonstrated the highest Cp value at high pressure, whereas SRK yielded the lowest value. Nevertheless, all EOS models showed a similar increasing trend. Differences in heat capacity estimation may affect heat-duty calculations in heat exchangers, especially for high-pressure gas processing systems that are sensitive to temperature changes. Consequently, the choice of EOS may influence thermal design calculations, particularly in processes involving high-pressure gas heating or cooling.

Effect of pressure on molar enthalpy

All EOS models showed a decreasing trend in molar enthalpy with increasing pressure. More negative enthalpy values indicate that the residual enthalpy contribution becomes more dominant at high pressure. This behavior reflects the increasing influence of intermolecular interactions in the compressed gas phase, causing

the thermodynamic properties to deviate further from ideal-gas assumptions (Burgoyne et al., 2025). At high pressure, gas molecules experience greater compression, causing intermolecular potential energy to become more dominant and leading to more negative enthalpy values.

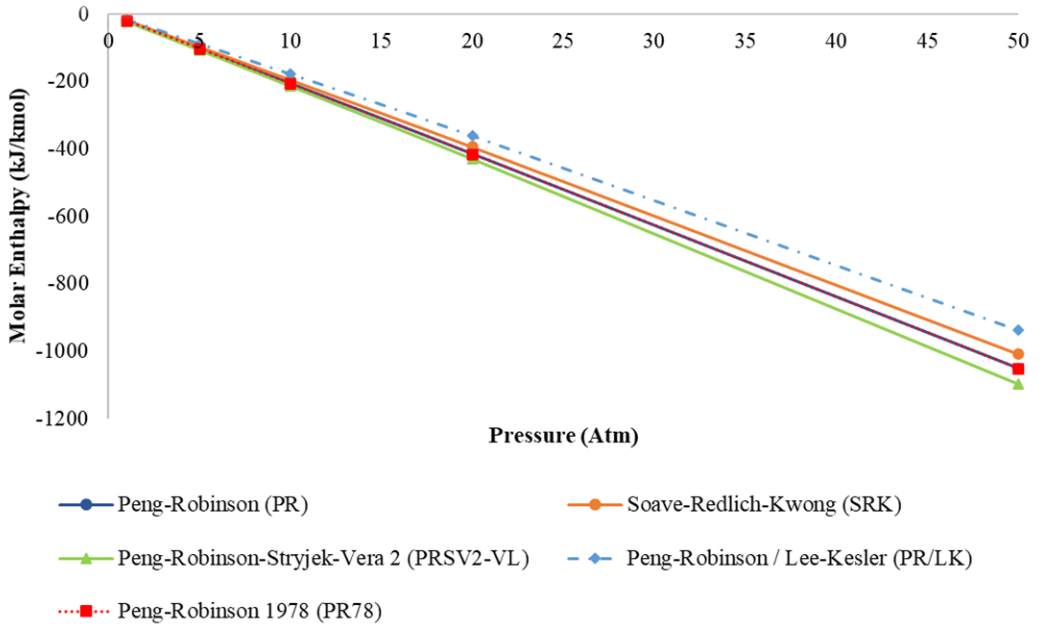

Figure 5. Relationship between pressure and molar enthalpy of methane, carbon dioxide, ethane, and nitrogen mixture

At low pressure, molar enthalpy was approximately -20 to -21 kJ/kmol. At 50 atm, the enthalpy became more negative, reaching approximately -937 to -1097 kJ/kmol depending on the EOS model used. PRSV2-VL produced the lowest enthalpy value, while PR/LK produced the highest value compared with the other models. These results show that the sensitivity of each model to pressure leads to different energy predictions in non-ideal gas systems (Salhi et al., 2024). The interpretation of absolute enthalpy should be performed carefully because DWSIM enthalpy values are affected by the reference state and residual property calculation method applied by each EOS. Therefore, this discussion focuses mainly on the trend of enthalpy change with pressure.

Comparison among property packages

Based on the initial evaluation, not all property packages available in DWSIM were appropriate for high-pressure multicomponent natural gas simulation. Therefore, the discussion focused on five main EOS models: PR, SRK, PRSV2-VL, PR/LK, and PR78. These models were selected because they generated more consistent thermodynamic property trends with increasing pressure than non-EOS models.

Although all EOS models predicted similar trends with increasing pressure, differences in numerical values were observed. These differences arise from variations in equation formulation, correction parameters, and residual property calculations used by each model. PR and PR78 produced almost identical values for all parameters, indicating that the parameter modifications introduced in PR78 did not significantly alter the overall thermodynamic predictions within the investigated pressure range. This finding suggests that the fundamental behavior of the Peng-Robinson formulation remains largely unchanged despite the parameter refinement.

SRK produced relatively stable predictions, although it showed slightly different values from PR for some parameters. PRSV2-VL showed higher sensitivity to pressure changes, especially for the compressibility

factor. This greater sensitivity may be attributed to the modified attractive-term formulation used in PRSV2-VL, which enhances the response of the EOS to non-ideal intermolecular interactions at elevated pressure. PR/LK displayed distinct behavior in molar enthalpy because of the combination of Peng-Robinson and Lee-Kesler approaches. These differences indicate that each EOS has a different sensitivity level in predicting non-ideal gas behavior at high pressure.

Table 4. Deviation of compressibility factor from the Peng-Robinson model at 50 atm

EOS	Z value	Deviation from PR (%)
Peng-Robinson (PR)	0.89051	0
Soave-Redlich-Kwong (SRK)	0.89917	0.97
PRSV2-VL	0.86589	2.76
PR/LK	0.89971	1.03
PR78	0.89051	0

Based on Table 4, PR78 produced an identical value to the PR model, resulting in 0% deviation. PRSV2-VL showed the largest deviation, 2.76% from PR at 50 atm. This confirms that PRSV2-VL is more sensitive to fluid non-ideality than the other EOS models. Meanwhile, SRK and PR/LK produced relatively small deviations, indicating consistent predictions relative to PR.

Table 5. Deviation of molar enthalpy from the Peng-Robinson model at 50 atm

EOS	Molar enthalpy (kJ/kmol)	Deviation from PR (%)
Peng-Robinson (PR)	-1050.96	0
Soave-Redlich-Kwong (SRK)	-1007.80	4.11
PRSV2-VL	-1097.59	4.44
PR/LK	-937.17	10.83
PR78	-1050.96	0

Based on Table 5, PR78 again produced an identical enthalpy value to PR. PR/LK showed the largest deviation, 10.83% from PR at 50 atm. This significant enthalpy deviation indicates that the Lee-Kesler correlation provides a different residual property estimation compared with conventional cubic EOS at high pressure. SRK and PRSV2-VL still produced predictions close to PR, although their pressure sensitivity began to differ under certain conditions.

The difference in EOS sensitivity is influenced by the attractive term, alpha function correction, and residual property approach in each model (Simão et al., 2024). Differences among EOS models become more apparent at high pressure, when attractive and repulsive intermolecular forces contribute more strongly to predicted thermodynamic properties. This finding emphasizes that property package selection affects thermodynamic predictions and must be adjusted to the fluid characteristics and simulation operating conditions.

Comparison between DWSIM simulation and manual calculation

A comparison between DWSIM simulation results and manual calculations was conducted to evaluate the consistency of the simulation results with the equations of state used. Manual calculations were performed at 1 atm and 25 °C with mixture composition of CH_4 = 0.85, CO_2 = 0.10, C_2H_6 = 0.03, and N_2 = 0.02. Compressibility factor values were obtained by solving the PR and SRK cubic equations, while density was calculated using the real gas relationship.

Table 6. Comparison of compressibility factor and density between DWSIM and manual calculations at 1 atm

Parameter	EOS	Manual	DWSIM	Error (%)
Z	PR	0.99738	0.99760	0.024
Z	SRK	0.99792	0.99786	0.006
Density (kg/m^3)	PR	0.79911	0.79897	0.018
Density (kg/m^3)	SRK	0.79868	0.79876	0.010

The comparison revealed very good agreement between DWSIM and manual calculations. The errors for compressibility factor and density were below 0.1%, indicating that DWSIM results are consistent with EOS-based calculations. Minor differences are likely associated with parameter rounding, database implementation, and binary interaction parameters applied by the simulator. Manual validation was performed at 1 atm because all EOS models produced nearly identical results under near-ideal conditions, allowing consistency between DWSIM and analytical calculations to be verified.

Limitations and future prospects

This study was limited to isothermal conditions at 25 °C, so the influence of temperature on thermodynamic properties was not analyzed in depth. The simulation results were not validated using direct industrial experimental data, and therefore the findings remain predictive based on the thermodynamic models available in DWSIM. Furthermore, only one gas composition and one operating temperature were investigated. Additional studies involving different gas compositions and temperature ranges are required to evaluate the robustness of the selected EOS models under broader operating conditions. In addition, not all DWSIM property packages could be directly compared because some models produced unstable predictions or did not converge at high pressure. Future studies may investigate the influence of temperature variation, different natural gas compositions, and experimental validation to further evaluate the reliability of EOS models under broader operating conditions.

4. Conclusion

Based on the DWSIM simulation results, pressure significantly influenced the thermodynamic behavior of the multicomponent natural gas mixture. Increasing pressure caused stronger deviations from ideal-gas behavior, reflected by decreasing compressibility factor and molar enthalpy values as well as increasing density and heat capacity.

Among the evaluated EOS models, Peng-Robinson (PR) and Peng-Robinson 1978 (PR78) provided the most consistent predictions throughout the investigated pressure range. In contrast, PRSV2-VL showed greater sensitivity in compressibility-factor prediction, whereas PR/LK produced the largest deviation in molar enthalpy prediction at high pressure.

The results indicate that differences among EOS models become more apparent at elevated pressure, highlighting the importance of selecting a suitable property package for natural gas simulation. Therefore, PR and PR78 may be considered reliable options for preliminary simulation and thermodynamic evaluation of multicomponent natural gas systems using DWSIM.

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