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Thermodynamic Property Package Selection in Chemical Process Simulators: A Critical Review

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Abstract-*Thermodynamic property package selection is a foundational yet frequently overlooked step in chemical process simulation. Simulators such as Aspen Plus, HYSYS, and DWSIM rely on property packages to compute vapor-liquid equilibrium, enthalpy, density, and transport properties and an incorrect selection makes even the most optimised process simulation unreliable. This paper reviews the four major families of thermodynamic models used in commercial simulators: equations of state (EOS), activity coefficient models, group contribution methods, and specialised models. The strengths, limitations, and appropriate application domains of each family are critically reviewed. A key original contribution of this paper is a structured decision framework enabling engineers to select the appropriate model based on system polarity, operating pressure, phase behaviour, and data availability. The role and validation of binary interaction parameters (BIPs) is examined in detail. Implementation differences across Aspen Plus, HYSYS, and DWSIM are compared. Case studies on natural gas processing and ethanol-water distillation demonstrates model selection in practice.*

Key Words: thermodynamic property packages, equation of state, Peng-Robinson, NRTL, activity coefficient models, binary interaction parameters, vapor-liquid equilibrium, process simulation, Aspen Plus, HYSYS

1. INTRODUCTION

1.1 Role of Thermodynamic Property Packages in Process Simulation

Chemical process simulation has become an indispensable tool in the design, optimisation, and troubleshooting of industrial plants. Every major commercial simulator Aspen Plus, Aspen HYSYS, ChemCAD, and the open-source DWSIM relies fundamentally on thermodynamic property packages to compute the physical and thermodynamic properties of process streams.

These packages underpin every calculation performed in a simulation: they determine the vapor-liquid equilibrium (VLE) that governs separation operations, the enthalpy and entropy changes that define heat exchanger and compressor duties, the molar volumes that control equipment sizing, and the transport properties that influence heat and mass transfer correlations. Without an accurate property package, no downstream simulation result regardless of how carefully the flowsheet is constructed can be considered reliable [1].

The selection of a thermodynamic property package is therefore not a routine software setting but a critical engineering judgement. It requires knowledge of the physical chemistry of the system, the operating conditions, and the assumptions embedded in each model family. Yet this decision receives disproportionately little attention in both academic curriculam and engineering practice, a gap that this review seeks to address.

1.2 Consequences of Wrong Model Selection

The practical consequences of selecting an inappropriate property package are significant and well-documented. A process that is otherwise fully optimised in terms of equipment selection, stream configuration, and operating conditions can be rendered essentially worthless if the underlying thermodynamic model does not accurately represent the system [2]. Specific consequences include: inaccurate VLE predictions leading to incorrect tray counts and reflux ratios in distillation columns, wrong heat exchanger duty calculations causing undersized or oversized equipment, false phase-split predictions that produce non-physical simulation results, and inaccurate density calculations affecting vessel sizing and hydraulic design. In severe cases, a simulation may converge to a result that appears physically plausible but is thermodynamically incorrect, making the error difficult to detect without independent validation.

1.3 The Default-Model Problem

A widely documented and persistent problem in industrial simulation practice is the uncritical acceptance of simulator default property packages. In the majority of commercial simulators, the default package is a variant of the Peng-Robinson (PR) equation of state a model designed primarily for nonpolar hydrocarbon systems.

Speranza (2017) documented that it remains standard practice in oil and gas design and operations to use this default without verification, producing silent errors in phase equilibrium and physical property predictions that are difficult to detect without direct comparison to experimental data [2]. The application of PR to polar mixtures, associating fluids, or electrolyte systems for which it is fundamentally

unsuitable represents a systematic and avoidable source of simulation error.

1.4 Scope and Objectives

This paper provides a critical review of thermodynamic property packages as implemented in commercial chemical process simulators.

The specific objectives are:

(1) to classify and describe the four major families of thermodynamic models in terms of their assumptions, mathematical structure, and applicable domains.

(2) to present a structured decision framework for systematic model selection based on published engineering heuristics.

(3) to evaluate the role of binary interaction parameters (BIPs) in model accuracy and to outline a validation procedure.

(4) to compare the property package implementations of Aspen Plus, Aspen HYSYS, and ChemCAD.

(5) to critically analyse the limitations of each model family and common engineering errors.

(6) to illustrate model selection through industrial case studies. The paper is written at a level accessible to undergraduate chemical engineers and is intended to serve as a practical guide to property package selection.

2. CLASSIFICATION OF THERMODYNAMIC MODELS

Thermodynamic property packages in commercial process simulators are built upon one of four model families, each grounded in different physical assumptions and suited to different categories of chemical systems. Table 1 provides a comparative overview of these families across their primary examples, optimal application domains, and characteristic failure zones.

Table 1: Classification of thermodynamic model families

Model Family	Examples	Best For	Fails At
Equations of State (EOS)	PR, SRK, RKPR	Nonpolar, high-P, gas systems	Polar / associating fluids
Activity Coefficient Models	NRTL, UNIQUAC, Wilson	Polar, liquid-phase, low-P	High-pressure gas systems
Group Contribution	UNIFAC, PSRK,	Missing BIP data	Accuracy in critical
(UNIFAC)	mUNIFAC		systems
Specialised Models	CPA, SAFT, e-NRTL	Associating fluids, electrolytes	Computational cost

2.1 Equations of State (EOS)

Equations of state describe the relationship between pressure (P), molar volume (V), and temperature (T) for both vapor and liquid phases within a single mathematical framework. This unified treatment is a major practical advantage: a single EOS can handle phase equilibrium, enthalpy, entropy, and density calculations for both phases simultaneously, making EOS models the natural choice for systems where both phases must be described accurately over wide ranges of temperature and pressure.

The two cubic EOS that dominate industrial practice are the Soave-Redlich-Kwong (SRK) equation, proposed by Soave in 1972 as a modification of the earlier Redlich-Kwong (RK) equation, and the Peng-Robinson (PR) equation, introduced by Peng and Robinson in 1976 [5,6]. Both are two-parameter cubic equations with the general form,

$$p = \frac{RT}{V-b} - \frac{a(T)}{[V(V+b)+b(V-b)]}$$

where , a(T) is the temperature-dependent attractive term and b is the repulsive co-volume parameter. The PR equation differs from SRK in the denominator of the attractive term, a modification that improves liquid density predictions a known weakness of SRK while preserving computational simplicity [5].

The temperature dependence of the attractive parameter a(T) is governed by an alpha function α(T), which is the primary target of EOS modification efforts. The Soave alpha function, used in both SRK and the original PR equation, expresses α(T) as a function of the reduced temperature (T/T_c) and the acentric factor ω, a measure of molecular non-sphericity.

The alpha function and the Boston-Mathias (BM) modification offer improved extrapolation behaviour at high and low reduced temperatures. Since its introduction, the PR EOS has accumulated over 200 modifications for pure-component alpha functions and approximately 100 for mixture rules, the most significant being PR78 (a revised acentric factor correlation by Peng and Robinson themselves) and PRSV (the Stryjek-Vera modification, which introduces a compound-specific parameter for improved accuracy) [5].

The extension of EOS models to mixtures requires mixing rules that define the mixture parameters a_mix and b_mix as functions of the pure-component parameters and binary interaction parameters (BIPs, denoted k_{ij}). The classical van der Waals one-fluid mixing rules are the most widely used; the Wong-Sandler mixing rules offer improved accuracy for asymmetric mixtures by incorporating activity coefficient model data at the limit of infinite dilution. EOS models with classical mixing rules perform reliably for nonpolar and weakly polar systems at elevated pressures but fail increasingly for polar and hydrogen-bonding systems, for which the underlying assumption of random mixing in the liquid phase is physically incorrect [1].

2.2 Activity Coefficient Models

For polar, hydrogen-bonding, and strongly non-ideal liquid mixtures at low to moderate pressures, activity coefficient (γ) models provide a more physically appropriate description of liquid-phase non-ideality. These models do not describe the entire P-V-T surface; instead, they quantify deviations from Raoult's law through the activity coefficient γ_i, defined such that the fugacity of component i in the liquid phase is

$$f_i^L = x^i * \gamma^i * f_i^{(0,L)}$$

where $f_i^{(0,L)}$ is the standard-state fugacity of pure liquid i. In process simulation, activity coefficient models are combined with an EOS for the vapor phase (typically PR or SRK), yielding a so-called gamma-phi (γ-ϕ) approach to VLE calculation [7].

The NRTL (Non-Random Two-Liquid) model, developed by Renon and Prausnitz in 1968, is the most widely used activity coefficient model in process simulation. It is based on the local composition concept, which accounts for the non-random arrangement of molecules in a liquid mixture by introducing a non-randomness parameter α_{ij} (typically fixed at 0.2 to 0.47). The NRTL model requires two binary interaction parameters per component pair, (τ_{12}, τ_{21}), regressed from experimental VLE data. It is capable of describing strongly non-ideal systems and can represent liquid-liquid equilibrium (LLE) as well as VLE, making it suitable for extraction and heterogeneous azeotrope systems [7].

The UNIQUAC (Universal Quasi-Chemical) model of Abrams and Prausnitz (1975) is based on a statistical mechanical treatment that accounts for molecular size and surface area through structural parameters r (volume parameter) and q (surface area parameter), derived from the chemical structure of each molecule. UNIQUAC also requires two BIPs per binary pair and is applicable to a wide range of systems including those with strong hydrogen bonding. However, it does not consistently fit experimental data across all system types and can exhibit thermodynamic inconsistencies when BIPs are extrapolated beyond their regression temperature range [1]. The Wilson equation, proposed in 1964, was the first activity coefficient model based on local compositions and performs well for fully miscible systems, but is fundamentally incapable of predicting liquid-liquid phase splitting (LLE) and is therefore unsuitable for two-liquid-phase systems [7].

The critical role of binary interaction parameters in activity coefficient models deserves emphasis. BIPs are regressed from experimental VLE or LLE data for each specific binary pair at specific conditions. When simulator databases provide default BIPs, these values may have been regressed from data at conditions far removed from the intended application. BIP errors propagate directly and non-linearly into column design: an error in the predicted relative volatility at the azeotrope composition leads to an incorrect reflux ratio, which leads to an incorrectly sized column a costly design error [1,8].

2.3 Group Contribution Methods

Group contribution methods estimate activity coefficients from the molecular structures of the components, without requiring experimentally regressed binary parameters. The most widely used is UNIFAC (Universal Functional Activity Coefficient), developed by Fredenslund et al. in 1975. UNIFAC decomposes each molecule into functional groups (e.g., CH3, OH, COOH, CH2=CH) and computes the activity coefficient from group-group interaction parameters that have been regressed from a large database of experimental VLE data. Because the same group parameters apply to all molecules containing those groups, UNIFAC can predict activity coefficients for mixtures where no direct experimental binary data exists [1].

UNIFAC is available as a predictive fallback in all major commercial simulators. It is particularly valuable in early-stage process design, when the component list is still evolving and experimental data is scarce. However, its accuracy is fundamentally lower than models with regressed BIPs, because the group additivity assumption ignores differences in the molecular environment of the same functional group in different molecules. Modified UNIFAC (Dortmund) and PSRK (Predictive Soave-Redlich-Kwong) offer improvements through temperature-dependent group parameters and integration with EOS mixing rules, respectively [3]. A critical practical point: simulators offer separate UNIFAC parameter sets for VLE and LLE prediction, and selecting the wrong option produces incorrect phase-split predictions. Engineers must explicitly verify which UNIFAC option is active before relying on predictive calculations for liquid-liquid systems.

2.4 Specialised Models

Certain categories of chemical systems exhibit physical behaviour that standard EOS and activity coefficient models

cannot adequately describe, necessitating specialised thermodynamic frameworks. Three specialised model families are particularly relevant to process simulation.

The Cubic Plus Association (CPA) equation of state, developed by Kontogeorgis et al. (1996), extends the SRK or PR equation with an explicit association term borrowed from the SAFT (Statistical Associating Fluid Theory) framework. The association term accounts for directional intermolecular hydrogen bonding between molecules such as water, alcohols, glycols, and carboxylic acids. CPA has become the industry standard for oil-water and gas-water systems, hydrate inhibitor design, and glycol dehydration processes. It is available in Aspen Plus and DWSIM [7].

PC-SAFT (Perturbed-Chain Statistical Associating Fluid Theory), developed by Gross and Sadowski (2001), provides a rigorous molecular-level description of chain molecules and is particularly suited to polymer solutions, wax-forming crude oils, and complex multiphase systems. The electrolyte NRTL (e-NRTL) model, implemented in Aspen Plus as the ElecNRTL property method, extends the NRTL framework to handle the long-range electrostatic interactions between ions in aqueous electrolyte solutions. It is essential for CO_2 capture with amine solvents, acid gas scrubbing, and any process involving dissolved salts or ionic species. The use of standard NRTL or PR for these systems produces physically meaningless results because the electrostatic contribution to excess Gibbs energy is entirely neglected [7,9].

3. MODEL SELECTION FRAMEWORK AND DECISION GUIDELINES

3.1 The First Step: System Characterisation

Systematic property package selection begins not with the simulator but with a thorough characterisation of the chemical system. This step must be completed before the simulation software is opened. The engineer must establish answers to four diagnostic questions:

(i) Are the components polar or nonpolar? Polarity arising from dipole moments and hydrogen bonding, is the single most important determinant of model family selection.

(ii) What are the operating temperature and pressure ranges? Elevated pressures favour EOS approaches; near atmospheric conditions broaden the applicability of activity coefficient models.

(iii) Which phases are present in the system: vapor-liquid (VLE), liquid-liquid (LLE), or three-phase vapor-liquid-liquid (VLLE)?

(iv) Is experimental phase equilibrium data available for validation or BIP regression? The answer determines whether a predictive or regressed model should be used as the starting point [1,4].

3.2 Engineering Heuristics: The Decision Framework

Based on the system characterisation, engineering heuristics drawn from published guidelines [1,4,7] direct the selection to the appropriate model family and specific model. Table 2 synthesises these heuristics into a structured decision framework, it consolidates guidance from multiple published sources into a single, accessible reference for practising engineers and students. Each row should be interpreted as a starting recommendation, to be refined through BIP validation and sensitivity analysis.

Table -2: Model selection decision framework (synthesised from [1,4,7])

System Type	Recommended Model	Typical Application
Nonpolar; high pressure > 10 bar	EOS: PR or SRK	Oil & gas, natural gas processing
Polar; hydrogen-bonding; low-P	NRTL or UNIQUAC	Alcohol-water, azeotropic distillation
No BIP data available	UNIFAC (predictive)	Novel solvents, early-stage design
Electrolytes / ionic species	e-NRTL, Pitzer	CO_2 capture, acid gas scrubbing
Associating fluids (OH, COOH groups)	CPA or SAFT	Water, alcohols, carboxylic acids
Cryogenic systems	SRK or GERG-2008	LNG processing, air separation
Near-critical / supercritical	PR or RKPR	Supercritical extraction, dense gas

Several principles supplement Table 2. First, EOS models are preferable whenever the system is nonpolar and high-pressure conditions prevail, because they provide a consistent description of both phases with good accuracy and no requirement for liquid-phase activity data. Second, activity coefficient models (NRTL, UNIQUAC) are required whenever strong polarity or hydrogen bonding is present at near-atmospheric pressures, particularly for azeotropic systems and liquid-liquid extraction. Third, UNIFAC should be used only as a starting estimate; it should be replaced with regressed BIPs as soon as experimental data becomes available. Fourth, for associating or electrolyte systems, specialised models are not optional, applying a standard EOS or activity coefficient model to these systems produces fundamentally incorrect results [1,3,7].

3.3 Role and Validation of Binary Interaction Parameters (BIPs)

Binary interaction parameters are the numerical values that tune thermodynamic models to match experimental data for a specific binary component pair. In activity coefficient models, BIPs (τ_{ij}) directly scale the excess Gibbs energy expression and are the primary determinant of predicted VLE and LLE behaviour. In EOS mixing rules, BIPs (k_{ij}) correct the unlike-pair interaction energy. Both types are dimensionless and system-specific, BIPs regressed for ethanol-water at 25°C are not valid for ethanol-water at 100°C or for methanol-water at any condition [1,8].

Commercial simulators maintain databases of pre-regressed BIPs derived from experimental data collections such as the DECHEMA Vapor-Liquid Equilibrium Data Collection. When a simulator provides BIPs for a given binary pair, the engineer must verify that these values were regressed from data at conditions relevant to the intended application. When no BIPs are available, the simulator silently assigns $k_{ij} = 0$ (EOS) or $\tau_{ij} = 0$ (activity models), which is equivalent to assuming ideal mixing in the liquid phase an assumption that is frequently wrong for polar systems [1].

The standard procedure for BIP validation is as follows:

(1) identify all binary component pairs in the mixture.

(2) check BIP availability in the simulator database for each pair.

(3) predict bubble-point pressures or VLE compositions with the selected model and compare against experimental data from DECHEMA or peer-reviewed literature

(4) compute the Average Relative Deviation as,

$$ARD = 100\% \times \sum \frac{y\_pred - y\_exp}{y\_exp / N}$$

(5) if ARD exceeds 5%, perform BIP regression using the simulator's regression module and re-validate. Jaiswal et al. [8] demonstrated that systematic BIP redressing in CHEMCAD significantly reduces ARD for binary systems, with improvements in predicted bubble-point pressures of up to 15-25% relative to default parameters.

3.4 Validation against Experimental Data

Validation is a mandatory step that follows model and BIP selection. It establishes the predictive accuracy of the chosen property package for the specific system and operating conditions of the simulation. The primary source of experimental VLE and LLE data for validation is the DECHEMA Chemistry Data Series, a comprehensive multi-volume collection that remains the gold standard for phase equilibrium data. For systems where DECHEMA data is unavailable, peer-reviewed literature should be consulted. An ARD below 5% in bubble-point pressure prediction is generally considered acceptable for engineering calculations, though tighter tolerances may be required for azeotropic systems where small errors in relative volatility have a disproportionate effect on column design [7]. The outcome of validation including the model selected, the BIPs used, and the achieved ARD should be documented in the simulation basis and all associated design reports.

4. IMPLEMENTATION IN MAJOR PROCESS SIMULATORS

The three major commercial process simulators Aspen Plus, Aspen HYSYS, ChemCAD and DWSIM implement the same thermodynamic model families but differ in terminology, interface, default settings, available models, and BIP database coverage. Understanding these implementation differences is essential to using each simulator effectively. Table 3 provides a side-by-side comparison.

4.1 Aspen Plus

In Aspen Plus, thermodynamic property package selection is called Property Method selection, performed in the Properties environment before any flowsheet elements are defined. Aspen provides a Property Method Selection Guide within the software that maps process type (e.g., OIL-GAS, CHEMICALS, ELECTROLYTES) to recommended property methods. Oil and gas processes default to PR or SRK; chemical processes with polar components default to NRTL or UNIQUAC. A key feature is the Data Regression System (DRS), which allows engineers to regress custom BIPs from experimental data entered directly into the Aspen environment.

Aspen Plus maintains one of the largest built-in BIP databases among commercial simulators, drawing from NIST, DECHEMA, and proprietary sources. UNIFAC and modified UNIFAC (Dortmund, Lyngby) serve as predictive fallbacks when experimental BIPs are unavailable. For electrolyte systems, the ElecNRTL property method provides full speciation of ionic equilibria [9].

4.2 Aspen HYSYS

Aspen HYSYS uses the term Fluid Package for its property package selection, which is the first action required when creating any new simulation case. Unlike Aspen Plus, the fluid package cannot be changed after streams or unit operations have been added to the flowsheet a design decision that enforces thermodynamic consistency throughout the simulation but requires the engineer to make the correct selection upfront. HYSYS is the dominant simulator in oil and gas and upstream processing industries, and its default modified PR (PR78) has been extensively

validated for hydrocarbon systems. The Sour PR fluid package handles H_2S and CO_2 containing streams through modified BIPs that improve accuracy for sour gas systems.

HYSYS also provides the Kent-Eisenberg amine package for gas treating simulations involving MEA, DEA, MDEA, and blended amine solvents. NRTL and UNIQUAC are available for chemical process simulations, though HYSYS's BIP database coverage for these models is less extensive than that of Aspen Plus [2].

4.3 ChemCAD and DWSIM

ChemCAD (by Chemstations) provides a K-Value Wizard that guides the engineer through property package selection based on the component list and operating conditions. The wizard classifies systems into EOS, activity coefficient, empirical, and special method categories, and selects UNIFAC as the predictive fallback when BIPs are insufficient. ChemCAD's thermodynamic method descriptions, documented in detail by Edwards [4], represent one of the most practically oriented published guides to property package selection available in the open literature. DWSIM, a free and open-source process simulator developed in .NET, offers comparable thermodynamic coverage to commercial tools including EOS models (PR, SRK, PRSV), NRTL, UNIQUAC, UNIFAC, CPA, and PC-SAFT, making it a valuable platform for academic use where commercial licenses are unavailable [3].

Table -3: Property package implementation comparison across major simulators

Feature	Aspen Plus	Aspen HYSYS	ChemCAD / DWSIM
Default EOS	Peng-Robinson	Peng-Robinson (PR78)	Peng-Robinson
Activity models	NRTL, UNIQUAC, Wilson	NRTL, UNIQUAC	NRTL, UNIQUAC, Wilson
Predictive model	UNIFAC, PSRK, mUNIFAC	UNIFAC	UNIFAC
Selection tool	Property Method wizard	Fluid Package dialog	K-Value Wizard
BIP regression	Data Regression System	Regression module	Data regression utility
Specialised models	e-NRTL, Pitzer, CPA	Sour PR, Amine pkg	CPA, SAFT (DWSIM)
BIP database source	NIST, DECHEMA, PURE	Internal databank	DECHEMA-derived

5. LIMITATIONS AND COMMON PITFALLS

5.1 Limitations of Equations of State

Despite their wide industrial adoption, cubic EOS models carry fundamental limitations that engineers must understand. The most significant is their inability to represent strongly polar and hydrogen-bonding systems accurately. The van der Waals-type attractive term in PR and SRK assumes isotropic, non-directional intermolecular forces, an assumption that fails completely for molecules such as water, alcohols, amines, and carboxylic acids, where hydrogen bond directionality dominates the liquid-phase structure [5,6].

For CO_2, the PR EOS gives inaccurate predictions in the condensed phase and below the triple point, which is relevant for cryogenic CO_2 capture and liquefaction processes [6].

A more fundamental limitation is the two-parameter cubic structure itself. Lopez-Echeverry et al. [5] demonstrated that the intrinsic accuracy of any two-parameter cubic EOS regardless of the alpha function chosen is limited by the mathematical constraint that the critical compressibility factor Z_c is a fixed constant (Z_c = 0.307 for PR, 0.333 for SRK), whereas real substances have Z_c values ranging from approximately 0.23 to 0.29. This structural limitation means that no modification of the alpha function can simultaneously reproduce the correct critical point, subcritical VLE, and liquid density for all substances.

The liquid density error of SRK (typically 10-20% for light hydrocarbons) is the primary reason PR was developed: PR reduces this error to approximately 2-4% for nonpolar systems, though it remains significant for polar compounds [5].

5.2 Limitations of Activity Coefficient Models

Activity coefficient models are restricted to the liquid phase and require a separate EOS or correlation for the vapor phase, introducing additional uncertainty when both phases are present.

The accuracy of NRTL and UNIQUAC is entirely dependent on the quality of the BIPs used, BIPs regressed from data at one temperature may be unreliable at another, and the temperature extrapolation behaviour of both models can be thermodynamically inconsistent at conditions far from the regression range [1].

UNIQUAC in particular has been shown to not consistently fit experimental data across all system types, even with optimal

BIPs, due to the limitations of its physical model for certain molecular geometries [1].

Wilson's model cannot predict LLE, applying it to a system with partial miscibility will produce a single liquid phase in the simulation where two phases actually exist a qualitatively incorrect result that may not trigger any error message in the simulator [7].

UNIFAC suffers from systematic errors arising from the group additivity approximation. The model cannot distinguish between structural isomers that contain the same functional groups, and its accuracy degrades for highly asymmetric mixtures, for mixtures containing multiple hydrogen-bonding groups on the same molecule, and for systems far from the conditions of the regression database.

Published ARD values for UNIFAC predictions typically range from 5-15% for bubble-point pressures, compared to 1-3% for well-regressed NRTL or UNIQUAC models [1,3].

5.3 The Default-Model Trap

The most pervasive and consequential error in industrial process simulation is the uncritical acceptance of the simulator's default property package. This error is documented across multiple industries and simulation environments [1,2].

Engineers who accept the Peng-Robinson default for a system containing water, alcohols, or ionic species will obtain simulation results that appear numerically convergent but are physically incorrect. The difficulty is that simulators rarely warn the user when an inappropriate model is applied, the simulation converges, streams have properties, and equipment sizes are computed but the underlying thermodynamics is wrong.
Detection requires independent validation against experimental data, which is frequently omitted in time pressured engineering environments. The consequences range from inaccurate energy balances (recoverable at the detailed engineering stage) to completely wrong phase behaviour predictions (which can propagate undetected through an entire process design).

5.4 Missing BIPs and Extrapolation Errors

A significant practical limitation of activity coefficient models is incomplete BIP database coverage. For novel solvents, specialty chemicals, ionic liquids, and bio-based compounds, experimental VLE data is often unavailable, and simulator databases contain no BIPs for these component pairs.

As discussed in Section 3.3, simulators assign BIP = 0 for missing pairs, the ideal mixing assumption which can be severely wrong. A silent BIP = 0 assumption in a mixture that exhibits strong non-ideality (e.g., a water-hydrocarbon pair) will produce a completely incorrect VLE prediction with no error flag [3,4].

5.5 Transport Property Oversight

Engineers frequently select a property package that correctly represents phase equilibrium but overlook the transport property correlations viscosity, thermal conductivity, and diffusivity that are calculated by a separate set of correlations within the same property package.

A correct EOS for VLE does not guarantee accurate viscosity predictions. For example, the PR EOS with standard mixing rules gives poor viscosity predictions for heavy oils and high-viscosity solvents, requiring separate viscosity correlation selection (e.g., Twu correlations for petroleum fractions, Letsou-Stiel for polar liquids). Inaccurate transport properties propagate into heat exchanger design (incorrect U values), column hydraulics (incorrect tray flooding predictions), and pipeline pressure drop calculations [4].

6. CASE STUDIES: MODEL SELECTION IN PRACTICE

The following case studies illustrate correct and incorrect property package selection across four representative industrial systems. All cases are drawn from published literature, no independent simulations were conducted for this review.

6.1 Natural Gas Processing: PR vs. SRK

Natural gas processing : dehydration, acid gas removal, NGL recovery, and liquefaction, involves multicomponent hydrocarbon mixtures (predominantly methane, ethane, propane, butanes) with varying amounts of CO_2, H_2S, N_2, and water. For pure hydrocarbon VLE in this pressure range (typically 20-100 bar), both PR and SRK give reliable predictions and similar accuracy. PR is generally preferred because its improved liquid density accuracy reduces error in NGL recovery calculations and stream composition predictions.

For CO_2-rich streams (CO_2 > 5 mol%), both standard PR and SRK give increasingly inaccurate phase envelope predictions, particularly near the CO_2 critical point (T_c= 304.2 K, P_c = 73.8 bar). In HYSYS, the Sour PR fluid package which uses specially regressed BIPs for the CO_2-CH_4 and CO_2-H_2S binary pairs provides significantly improved accuracy.

Speranza [2] documented cases in oil and gas simulation where the choice between standard PR and Sour PR changed the predicted dew point of a gas stream by 5-10°C, a difference with significant consequences for hydrate formation risk and separator design.

6.2 Ethanol-Water Distillation: EOS Failure vs. Activity Model

The ethanol-water binary system is the canonical example of EOS model failure and activity coefficient model necessity. At atmospheric pressure, ethanol and water form a positive azeotrope at approximately 89.4 mol% ethanol and 78.1°C. The Peng-Robinson EOS with standard van der Waals mixing rules and $k_{12} = 0$ predicts an essentially ideal VLE diagram for this system, completely failing to reproduce the azeotrope. This is a direct consequence of the EOS's inability to capture the strong and directional hydrogen bonding between ethanol and water molecules in the liquid phase.

NRTL and UNIQUAC with BIPs regressed from DECHEMA experimental data accurately reproduce the azeotrope, the shape of the VLE diagram, and the composition-dependent relative volatility throughout the composition range.

For a distillation column designed to concentrate ethanol from 10 mol% feed to 85 mol% product, using PR instead of NRTL yields an incorrect relative volatility profile that produces wrong theoretical stage counts and a non-convergent simulation near the azeotrope. The design based on NRTL is validated against the extensive experimental VLE database for this system in DECHEMA with ARD < 2% on bubble-point pressures. This case demonstrates unambiguously why activity coefficient models are not optional for polar azeotropic systems [1,7].

6.3 CO_2 Capture with Amine Absorption: Specialised Models

Post-combustion CO_2 capture using monoethanolamine (MEA) or other amine solvents is a system of industrial importance and thermodynamic complexity. The CO_2-MEA-water system involves simultaneous chemical reactions (CO_2 hydration, carbamate formation), ionic equilibria (bicarbonate, carbonate, carbamate ions), and strongly non-ideal liquid-phase thermodynamics. Standard PR or NRTL cannot represent any of these features: PR neglects liquid-phase non-ideality entirely, while NRTL lacks the speciation and electrostatic terms needed for ionic systems.

Accurate simulation of MEA scrubbing requires either the electrolyte NRTL (e-NRTL) property method in Aspen Plus, which models the full ionic speciation with activity coefficients for both molecular and ionic species, or the Kent-Eisenberg amine package in HYSYS, which uses an empirical correction to the equilibrium constants to account for the non-ideal liquid phase.

Published simulation studies using e-NRTL report good agreement with pilot plant CO_2 loading data (ARD < 5% on CO_2 partial pressure), while simulations using standard NRTL without electrolyte corrections show systematic deviations exceeding 30% [7,9].

This case illustrates that for certain system types, model selection is not a matter of preference or accuracy optimisation but of physical correctness: applying a standard model produces thermodynamically nonsensical results.

6.4 BIP Sensitivity: Default vs. Regressed Parameters

Jaiswal et al. [8] reported a systematic study of BIP redressing in CHEMCAD for binary mixtures of propionic acid with 2-ethoxyethanol, a system representative of specialty chemical production. Using the default UNIQUAC BIPs from the simulator database, bubble-point pressure predictions showed ARD values of 8-15% compared to experimental DECHEMA data, indicating that the default BIPs were regressed from data at significantly different conditions. After regressing new UNIQUAC BIPs from the same experimental dataset used for validation, ARD reduced to 1.5-3.2%, within the acceptable range for engineering calculations.

This quantitative demonstration confirms that default BIPs must not be assumed accurate: they provide a starting estimate that must be validated and, where necessary, replaced with condition-specific regressed values before the simulation is used for equipment design [8].

7. CONCLUSIONS

This review has examined thermodynamic property package selection in chemical process simulation from the perspectives of model classification, decision methodology, simulator implementation, model limitations, and industrial application.

The central conclusion is that property package selection is a systematic engineering decision with significant consequences for simulation accuracy, and it should be treated as a preliminary start and not as a default software setting.

The four major model families (EOS, activity coefficient, group contribution, and specialised) each have well-defined domains of applicability, and no single model is appropriate for all systems.

The following seven recommendations are offered as practical guidance for engineers and students:

- Always characterise the chemical system in terms of polarity, hydrogen-bonding capacity, operating pressure, and phases present before selecting a property package. This step must precede simulator use.
- Never accept the simulator's default property package without verifying its suitability for the specific system. The default (typically Peng-

Robinson) is appropriate only for nonpolar hydrocarbon systems.

- Use the decision framework presented in Table 2 as the starting point for model selection, applying the heuristics systematically and documenting the selection rationale.
- Check binary interaction parameter (BIP) availability for all component pairs in the mixture. Do not assume that BIP = 0 is a safe default; verify explicitly and use UNIFAC as a predictive estimate when BIPs are absent.
- Validate VLE and LLE predictions against experimental data from DECHEMA or peer-reviewed literature. Compute the ARD for bubble-point pressures and accept only those models achieving ARD < 5% for standard engineering calculations.
- Do not neglect transport property correlations. Verify that the viscosity, thermal conductivity, and diffusivity correlations within the chosen property package are appropriate for the system, separately from the VLE model selection.
- Document the property package selection, the BIPs used, and the achieved ARD in the simulation basis and all associated process design reports, to enable independent review and future modification.

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