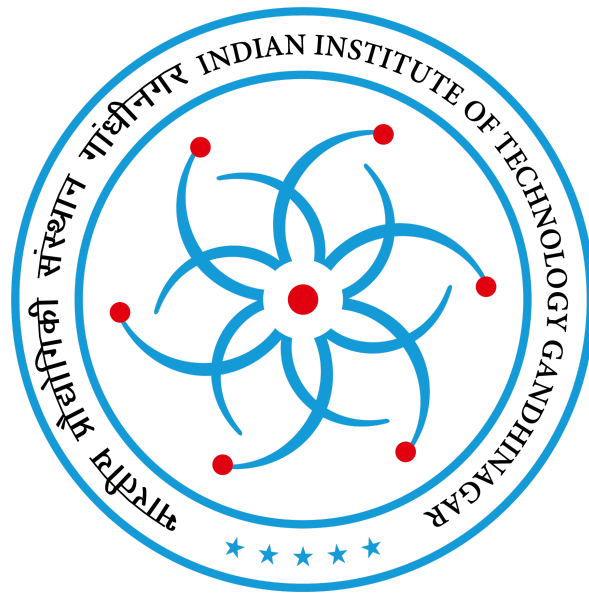


Indian Institute of Technology Gandhinagar



CL 317 Process Synthesis, Design, and Simulation

Final Project Report (End-Semester)

**Evaluation of Thermodynamic Models and Unit Performance in Aspen Plus for
CO₂-to-Methanol Conversion**

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Introduction

Modern process simulation tools such as **Aspen Plus** have become indispensable in chemical engineering for designing, optimizing, and analyzing complex industrial processes. At the heart of Aspen Plus lies its ability to accurately **predict thermodynamic behavior**, which is essential for simulating real-world systems involving multiple phases and components.

In Aspen, every simulation—from a basic flash separator to a complex reaction-distillation system—relies heavily on **thermodynamic models**. These models provide the mathematical foundation for calculating phase equilibria (like VLE and LLE), physical properties (such as enthalpy, entropy, and density), and reaction equilibria. The selection of the appropriate thermodynamic method is not arbitrary; it fundamentally affects the simulation's accuracy, especially when dealing with non-ideal systems, polar mixtures, or gas-liquid solubility.

Different models perform differently based on:

- Component type (polar vs. nonpolar)
- Phase behavior (ideal vs. non-ideal)
- System pressure/temperature range
- Intermolecular interactions (hydrogen bonding, polarity, etc.)

Thus, for accurate simulation and design, one must understand how these models work, when to use them, and what their limitations are.

This project is motivated by a desire to go beyond using Aspen as a black box. It explores the theory and implementation of thermodynamic models, both within Aspen Plus and independently via Python, to gain a deep understanding of model behavior. By comparing model outputs—like T-x-y and P-x-y diagrams, activity coefficients, and solubility predictions—the project emphasizes how thermodynamic methods influence the design and performance of key unit operations.

Objectives

The primary goal of this project is to evaluate and compare various thermodynamic methods for modeling methanol production from CO₂ in Aspen Plus. This includes:

- Investigating why different thermodynamic models are needed for different types of components and mixtures.
- Performing T-x-y and P-x-y analyses for binary systems such as methanol-water and CO₂-methanol.
- Implementing the NRTL model using Python to understand the backend of activity coefficient-based methods, and comparing the results with Aspen predictions.
- Simulating a complete methanol production flowsheet in Aspen Plus.
- Performing detailed unit-level analyses (reactor, flash, distillation column) to evaluate how sensitive they are to different thermodynamic methods.

Ultimately, the project aims to identify the most accurate and suitable thermodynamic approach.

Understanding Thermodynamic Models in Aspen Plus

Aspen Plus is a process simulation software widely used in chemical engineering to model and analyze chemical processes. At its core, Aspen Plus relies on thermodynamic models to predict the behavior of chemical mixtures under various conditions. These models are essential for:

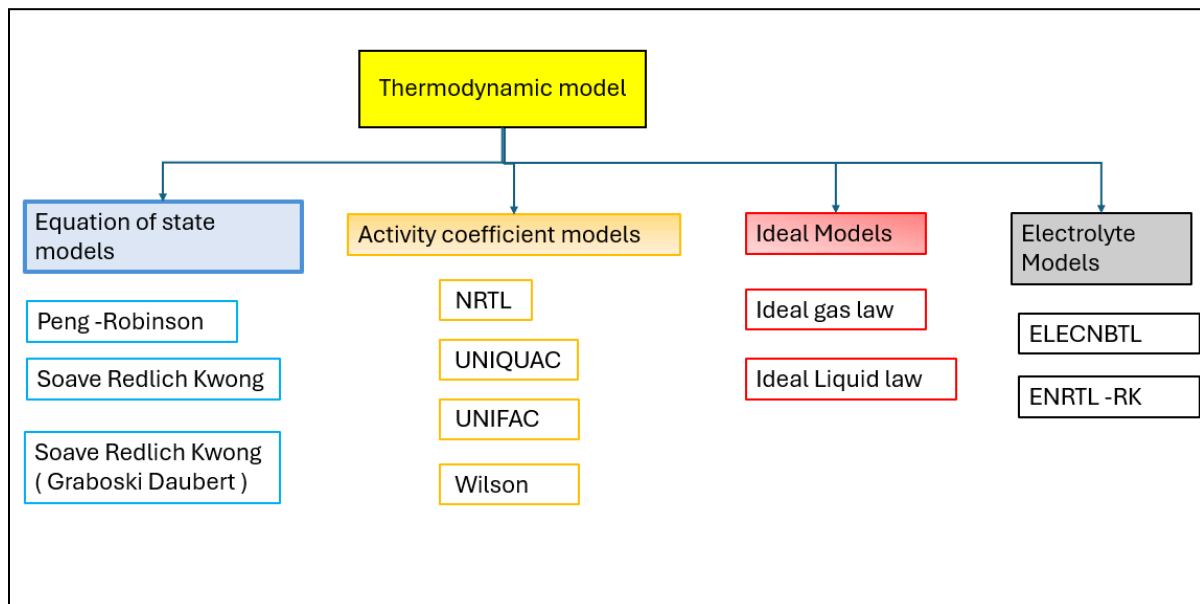
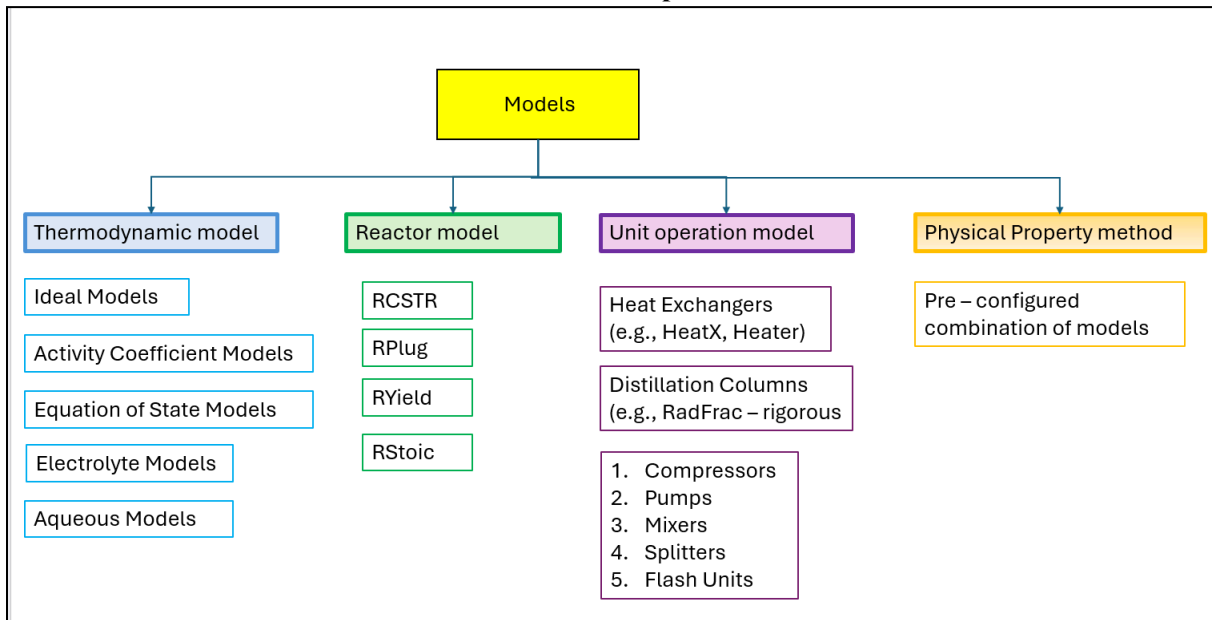
- **Phase Equilibria:** Determining vapor–liquid equilibrium (VLE), liquid–liquid equilibrium (LLE), and solid–liquid equilibrium (SLE).
- **Physical Properties:** Calculating properties like enthalpy, entropy, density, viscosity, heat capacity, surface tension, and thermal conductivity.
- **Reaction Equilibria:** Assessing the extent of chemical reactions based on Gibbs free energy minimization.
- **Mass and Energy Balances:** Ensuring accurate simulation results through precise thermodynamic data.

Thermodynamic models use mathematical equations to describe interactions between molecules in a mixture. These interactions vary depending on:

1. Polarity
2. Hydrogen bonding
3. Electrolyte behavior
4. Molecular size/shape

The selection of an appropriate thermodynamic model in Aspen Plus is crucial, as it directly influences the accuracy of simulation outcomes.

Models in Aspen :



Thermodynamic Models and Their Applications

In this section we will discuss majorly 4 different thermodynamic models and their mathematical expressions, applications and their physical meaning.

a. Non-Random Two-Liquid (NRTL) Model

The NRTL model is designed to handle highly non-ideal liquid mixtures, particularly where molecular interactions are non-random due to factors like hydrogen bonding or polarity differences. The model is widely used for liquid-liquid equilibrium (LLE) and vapor-liquid equilibrium (VLE) calculations.

- It is ideal for systems with:
 - Hydrogen bonding (e.g., water–ethanol, methanol–water)
 - Strong polarity differences (e.g., acetone–chloroform, methanol–water)
 - Highly non-ideal phase behavior (e.g., mixtures of organic acids and bases)
- NRTL is suited for systems where Raoult's law or ideal solution assumptions do not hold.

The NRTL model calculates liquid activity coefficients for the following property methods: NRTL, NRTL-2, NRTL-HOC, NRTL-NTH, and NRTL-RK. It is recommended for highly non-ideal chemical systems, and can be used for VLE and LLE applications. The model can also be used in the advanced equation-of-state mixing rules, such as Wong–Sandler and MHV2.

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right)$$

Valid for: $T_{\text{lower}} \leq T \leq T_{\text{upper}}$

Model Parameters:

$$\begin{aligned} G_{ij} &= \exp(-\alpha_{ij} \tau_{ij}) \\ \tau_{ij} &= a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T \\ \alpha_{ij} &= c_{ij} + d_{ij}(T - 273.15) \end{aligned}$$

Special Cases:

$$\begin{aligned} \tau_{ii} &= 0 \\ G_{ii} &= 1 \end{aligned}$$

Note: The interaction parameters are unsymmetrical:

$$a_{ij} \neq a_{ji}, \quad b_{ij} \neq b_{ji}, \quad e_{ij} \neq e_{ji}, \quad f_{ij} \neq f_{ji}$$

Where,

γ_i : Activity coefficient of component i

x_i : Mole fraction of component i

τ_{ij} : Binary interaction parameter between components i and j

G_{ij} : Exponential weighting factor: $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$

α_{ij} : Non-randomness parameter (typically between 0.2–0.47)

Applications:

- Water–Ethanol Mixtures: Due to strong hydrogen bonding.
- Acetone–Chloroform Systems: Exhibiting significant polarity differences.
- Organic Acid–Base Mixtures: Where non-ideal behavior is prominent.

Key Features:

- Accounts for enthalpic deviations caused by molecular interactions.
- Suitable for systems where Raoult's law or ideal solution assumptions are invalid.

b. Peng-Robinson Equation of State (PR EOS)

The Peng-Robinson equation of state is a cubic equation of state developed to model vapor-liquid equilibria (VLE) for non-ideal gases and liquids, especially **hydrocarbons** and supercritical fluids.

It balances accuracy in predicting both liquid and vapor densities.

- **Best suited for:**
 - Non-polar and lightly polar systems (e.g., hydrocarbons, gases like H₂, CH₄, CO₂).
 - High-pressure systems.
 - Supercritical conditions.
- Common in petroleum, natural gas, and chemical engineering simulations (like in Aspen Plus).

Peng-Robinson mathematical expressions :

1. Equation of Pressure :

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)}$$

Where

- a - attractive parameter
- b - repulsive parameter
- V - molar volume
- T - Temperature
- R - Universal gas constant

The first term represents ideal gas behavior with a correction for molecular volume (b).

The second term corrects for intermolecular attractions (a).

2. Z - Factor cubic equation :

$$Z^3 - (1 - B)Z^2 + [A - 2B - 3B^2]Z - [AB - B^2 - B^3] = 0$$

Used to solve for $Z = PV / RT$, the compressibility factor.

Usually, there are 1 or 3 real roots (choose based on phase: vapor vs. liquid)

$$A = \frac{a^P P}{(RT)^2}$$
$$B = \frac{b^P P}{RT}$$

$$b = \sum_{i=1}^N x_i \left(0.077796 \frac{RT_{c_i}}{P_{c_i}} \right)$$

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \left[\left(0.457235 \frac{(RT_{c_i})^2}{P_{c_i}} \alpha_i \right)^{0.5} \left(0.457235 \frac{(RT_{c_j})^2}{P_{c_j}} \alpha_j \right)^{0.5} \right] (1 - k_{ij})$$

1. Repulsive Term:

$$P = \frac{RT}{V - b}$$

- Represents the ideal gas behavior corrected for finite molecular size.
- b: Measures the excluded volume due to the finite size of molecules.
- When molecules are large or packed closely (liquid phase), this term becomes very important.
- As V tends to 'b', the pressure becomes infinite which prevents molecules from occupying the same space.

2. Attractive Term:

$$\frac{a}{V(V + b) + b(V - b)}$$

- Accounts for intermolecular attractions.
- a(T): A temperature-dependent parameter representing how strongly molecules attract each other.
- At low temperatures (where attractions dominate), this term reduces the pressure.
- At high temperatures, attraction weakens and the attraction term becomes small.

Together, these two terms model non-ideal real fluid behavior:

- The first term increases pressure (due to molecular volume),
- The second term decreases pressure (due to molecular attraction).

$$\alpha_i^{0.5} = 1 + m_i (1 - \sqrt{T_{ri}})$$
$$\alpha_j^{0.5} = 1 + m_j (1 - \sqrt{T_{rj}})$$

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$
$$m_j = 0.37464 + 1.54226\omega_j - 0.26992\omega_j^2$$

When an acentric factor > 0.49 is present, HYSYS uses the following corrected form for m:

$$m_i = 0.379642 + [1.48503 - (0.164423 + 0.016666\omega_i)\omega_i]\omega_i$$
$$m_j = 0.379642 + [1.48503 - (0.164423 + 0.016666\omega_j)\omega_j]\omega_j$$

$$\ln \phi_i = \frac{b_i}{b_{\text{mix}}} (Z-1) - \ln(Z-B) - \frac{A}{B\sqrt{T}} \left[2 \sum_j x_j \frac{\sqrt{a_i a_j} (1 - k_{ij})}{a_{\text{mix}}} - \frac{b_i}{b_{\text{mix}}} \right] \ln \left(1 + \frac{B}{Z} \right)$$

Where:

$$A = \frac{a_{\text{mix}} P}{R^2 T^{2.5}}$$

$$B = \frac{b_{\text{mix}} P}{RT}$$

Applications:

- Hydrocarbon Systems: These include methane, ethane, and propane.
- High-pressure systems: Where accurate vapor-liquid equilibrium predictions are essential.
- Supercritical Conditions: For substances like CO₂.

Key Features:

- Balances accuracy in predicting both liquid and vapor densities.
- Incorporates parameters to account for molecular size and attraction forces.

c. Universal Quasi-Chemical (UNIQUAC) Model

The UNIQUAC model is effective for systems with strongly non-ideal liquid behavior, particularly those involving polar components, hydrogen bonding, or aqueous-organic mixtures.

- We use UNIQUAC, when we need VLE or LLE data for accurate separation design (distillation, extraction, etc.).
- It is well suited for systems where ideal models fail.
- Used for predicting activity coefficients in nonideal liquid mixtures

The mathematical expression used in this method is :

$$\ln \gamma_i = \ln \gamma_i^{\text{combinatorial}} + \ln \gamma_i^{\text{residual}}$$

The activity coefficient is split into two parts: Combinatorial and Residual

The combinatorial part includes the shape and size effect. It captures entropy of mixing due to size and shape mismatch.

$$\ln \gamma_i^{\text{comb}} = \ln \left(\frac{\phi_i}{x_i} \right) + \frac{z}{2} q_i \ln \left(\frac{\theta_i}{\phi_i} \right) + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j$$

Where ,

- $\phi_i = \frac{r_i x_i}{\sum r_j x_j}$
- $\theta_i = \frac{q_i x_i}{\sum q_j x_j}$
- $l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$
- $z = 10$ (coordination number)

The Residual part includes the energy interaction effect. It captures enthalpy changes from H-bonding, dipole-dipole, or other non-ideal forces :

$$\ln \gamma_i^{\text{res}} = q_i \left[1 - \ln \left(\sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right]$$

Where:

- $\tau_{ij} = \exp \left(-\frac{\Delta u_{ij}}{RT} \right)$
- Δu_{ij} = interaction energy between i and j

How do these equations work for our system?

UNIQUAC is suitable for non-ideal systems because it accounts for molecular size/shape differences (entropy) and unequal interaction energies (enthalpy), like hydrogen bonding or polarity. This makes it accurate for mixtures where ideal models like Raoult's law fail.

Applications:

- Water–Acetic Acid Mixtures: Exhibiting significant hydrogen bonding.
- Methanol–Benzene Systems: Where polarity differences are notable.
- Aqueous–Organic Systems: Common in separation processes.

Key Features:

- Divide activity coefficients into combinatorial (size and shape effects) and residual (energy interaction effects) parts.
- Provides accurate predictions for VLE and LLE data.

d. Redlich-Kwong-Soave Modified Huron-Vidal (RKSM V2) Model

The RKSMHV2 model combines the Redlich-Kwong-Soave equation of state with the Huron-Vidal mixing rules (which incorporates excess Gibbs energy models like NRTL or UNIQUAC), enhancing its capability to predict phase equilibria in complex systems.

It improves phase equilibrium predictions, especially for highly non-ideal mixtures, by combining the rigorous physical basis of EoS with the flexibility of activity coefficient models.

- Used for vapor-liquid equilibrium (VLE) and phase behavior prediction.
- Ideal for non-ideal systems, including those involving polar components (e.g., alcohols, water, organic acids) mixed with light gases or hydrocarbons.
- Applicable in petrochemical, refinery, and chemical industries for multicomponent systems at wide pressure ranges.
- Non-ideal polar–nonpolar mixtures
- **Systems containing:**
 - Hydrocarbons (alkanes, aromatics)
 - Polar solvents (methanol, water)
 - Inert gases or light gases (H₂, CO₂)
- Good for complex systems with both physical and chemical non-idealities.
- **Mathematical Expression of the SRK equation :**

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)}$$

The mixing rules are derived from excess Gibbs free energy models

The fugacity coefficients ϕ_i includes :

$$\ln \phi_i = \text{SRK EoS term} + \left(\frac{\partial G^E / RT}{\partial n_i} \right)_{\text{mixing rule}}$$

The Huron-Vidal mixing rule ensures that the excess Gibbs energy at infinite pressure (from NRTL or UNIQUAC) matches the equation of state.

- The first term (SRK EoS) represents molecular repulsion and attraction forces—which are important for pressure-volume-temperature behavior.

- The mixing rule accounts for non-ideal interaction between components by embedding an excess Gibbs energy model into the EoS.
- This makes RKSMHV2 more accurate than pure cubic EoS for non-ideal liquid mixtures.

Activity Coefficient from RK-SMHV2

$$\ln \gamma_i = \ln \left(\frac{\phi_i^{\text{mix}}}{\phi_i^{\text{ideal}}} \right)$$

a_i : RK EOS parameters for pure component

x_i : Mole fraction

K_{ij} : Binary interaction parameter

γ_i : Activity coefficient

τ_{ij} : Interaction energy term

G_{ij} : Exponential weighting factor

A, B: Dimensionless RK EOS terms

Φ : EOS-specific correction function

Z: Compressibility factor (solve cubic

Applications:

- CO₂–Hydrogen Mixtures: Relevant in methanol production processes.
- Systems with Associating Components: Where traditional models may fall short.

Key Features:

- Incorporates activity coefficient models into EOS frameworks.
- Suitable for systems exhibiting both non-ideal behavior and significant pressure variations.

Selecting the Appropriate Model: Examples and Rationale

Choosing the right thermodynamic model in Aspen Plus depends on the nature of the chemical system:

- **Polar Mixtures with Hydrogen Bonding:** NRTL or UNIQUAC models are preferred due to their ability to account for specific molecular interactions.
- **Non-Polar Hydrocarbon Systems:** Peng-Robinson EOS is suitable for its accuracy in predicting VLE in such systems.
- **Aqueous–Organic Systems:** UNIQUAC model provides reliable predictions for phase behavior.
- **High-Pressure Gas Mixtures:** RKSMHV2 model offers enhanced accuracy by combining EOS with activity coefficient models.

Understanding the underlying interactions and behaviors of the components in a mixture is essential for selecting the most appropriate thermodynamic model, ensuring accurate and reliable simulation results in Aspen Plus.

Thermodynamic Model Validation: Aspen Plus vs Python (NRTL Method)

Thermodynamic Model Comparison in Aspen (Midsem)

In the mid sem phase of this project, a comparative study was performed in Aspen Plus using three different thermodynamic models—RKSMHV2, Peng-Robinson (PR), and NRTL—for two binary systems:

- CO₂–Methanol
- CO₂–Water

The P-x diagrams generated at 323.15 K were used to evaluate CO₂ solubility in both solvents.

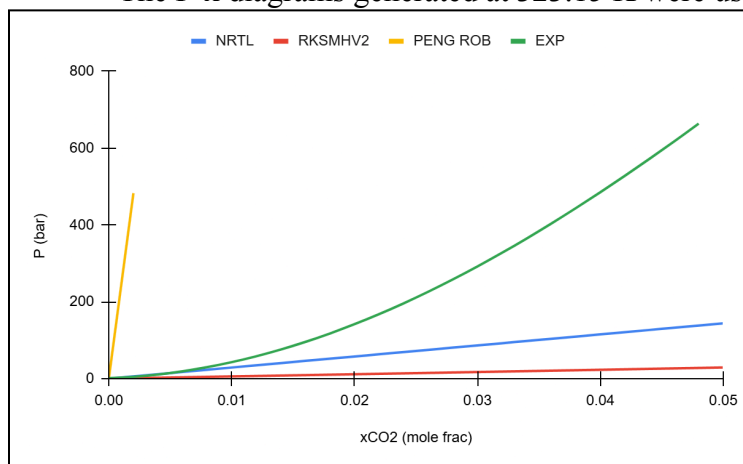


Figure: P-x of CO₂ in CH₃OH(Methanol) at 323.15K

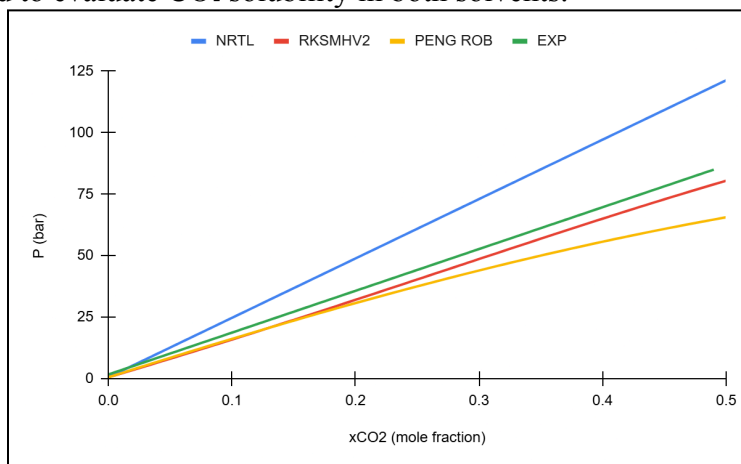


Figure: P-x of CO₂ in H₂O(water) at 323.15K.

Key Observations from Mid-Sem Analysis:

- RKSMHV2 gave the most accurate prediction for CO₂ solubility in methanol.
- PR underpredicted solubility in most cases, especially in polar systems.
- NRTL performed well when Henry's constants were specified, showing the importance of parameter tuning in activity coefficient models.

Similarly, for the Methanol–Water system, Aspen was used to generate T-x-y diagrams using:

- RKSM V2
- NRTL
- NRTL-RK
- Peng-Robinson

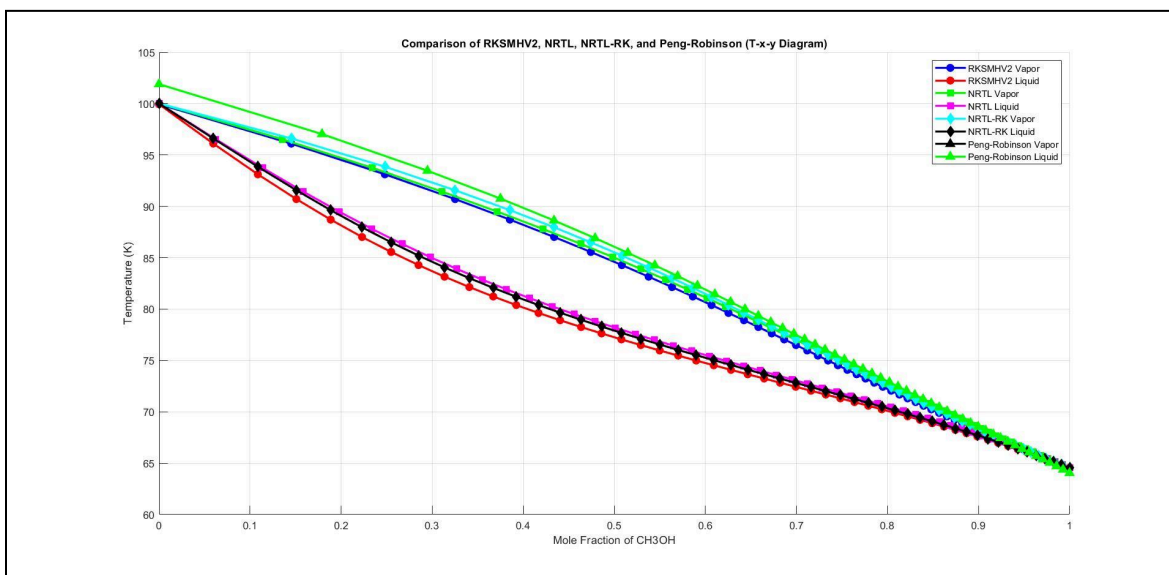


Figure: Comparison of RKSMHV2, NRTL, NRTL-RK, and Peng Robinson(T-xy diagram).

Key Observations from T-x-y Diagrams:

- RKSMHV2 predicted slightly lower bubble point temperatures but was computationally efficient.
- NRTL/NRTL-RK provided better accuracy in liquid phase due to detailed interaction modeling.
- PR showed deviations in vapor phase composition due to limitations in handling polarity.

These diagrams allowed visual comparison of how models treat non-ideality, hydrogen bonding, and phase equilibrium.

Activity Coefficient Modeling in Python

To build on the Aspen-based results and understand how the NRTL model works behind the scenes, a Python script was developed.

```
import numpy as np

import matplotlib.pyplot as plt

from scipy.optimize import minimize

# ----- NRTL Activity Coefficients ----- #

def nrtl_activity_coefficients(alpha, tau, x):

    n = len(x)

    G = np.exp(-alpha * tau)

    gamma_ln = np.zeros(n)

    for i in range(n):

        sum1 = np.sum(G[:, i] * x)

        sum2 = 0.0

        for j in range(n):

            sum_tauG = np.sum(G[:, j] * x)

            term = G[i, j] * (tau[i, j] - np.sum(x * tau[:, j] * G[:, j]) / sum_tauG)

            sum2 += x[j] * term / sum_tauG

        gamma_ln[i] = (np.sum(tau[:, i] * G[:, i] * x) / sum1) + sum2

    return np.exp(gamma_ln)
```

```
# ----- Antoine Equation ----- #

def antoine_pressure(component, T_C):

    params = {

        "methanol": [8.08097, 1582.271, 239.726],
```

```

    "water": [8.07131, 1730.63, 233.426]

}

A, B, C = params[component]

return 10 ** (A - B / (T_C + C)) * 133.322 # mmHg → Pa

```

```

# ----- Bubble Point via NRTL ----- #

def bubble_point_nrtl(P_guess, x, Psat, alpha, tau):

    def objective(P):

        gamma = nrtl_activity_coefficients(alpha, tau, x)

        y = x * gamma * Psat / P

        return abs(np.sum(y) - 1)

    result = minimize(objective, P_guess, method='Nelder-Mead')

    P_bubble = result.x[0]

    gamma = nrtl_activity_coefficients(alpha, tau, x)

    y = x * gamma * Psat / P_bubble

    return P_bubble, y / np.sum(y)

```

```

# ----- VLE Simulation ----- #

def run_vle_simulation():

    T_K = 78 + 273.15

    T_C = T_K - 273.15

    alpha = np.array([[0.0, 0.3], [0.3, 0.0]])

    tau_base = np.array([[0.0, 2.12], [-0.92, 0.0]])

    tau_Tdep = np.array([[0.0, -350], [200, 0.0]])

    tau = tau_base + tau_Tdep / T_K

    x_list = (1 - np.linspace(0.99, 0.01, 30))

```



```

y_list = []

gamma1_list = []

gamma2_list = []

for x1 in x_list:

    x = np.array([x1, 1 - x1])

    Psat = np.array([
        antoine_pressure("methanol", T_C),
        antoine_pressure("water", T_C)
    ])

    P_guess = 101325

    P_bubble, y = bubble_point_nrtl(P_guess, x, Psat, alpha, tau)

    y_list.append(y[0])

    gamma = nrtl_activity_coefficients(alpha, tau, x)

    gamma1_list.append(gamma[0])

    gamma2_list.append(gamma[1])

return x_list, y_list, gamma1_list, gamma2_list

```

- Activity coefficients (γ_1 and γ_2) for Methanol-Water using the NRTL model.
- Bubble point pressures and vapor compositions via Raoult's Law.
- VLE curve and γ variation across the composition range.

This model uses:

- Antoine equation for vapor pressure
- Optimization to compute the bubble point

- Matrix-based τ and α values to simulate non-random interactions

Python Simulation Outcome:

- The computed VLE curve matched closely with the Aspen plot using NRTL.
- The trends of γ_1 and γ_2 vs mole fraction showed similar behavior to Aspen.
- This validates using NRTL for polar mixtures like methanol-water and shows that Aspen's results are based on solid thermodynamic theory.

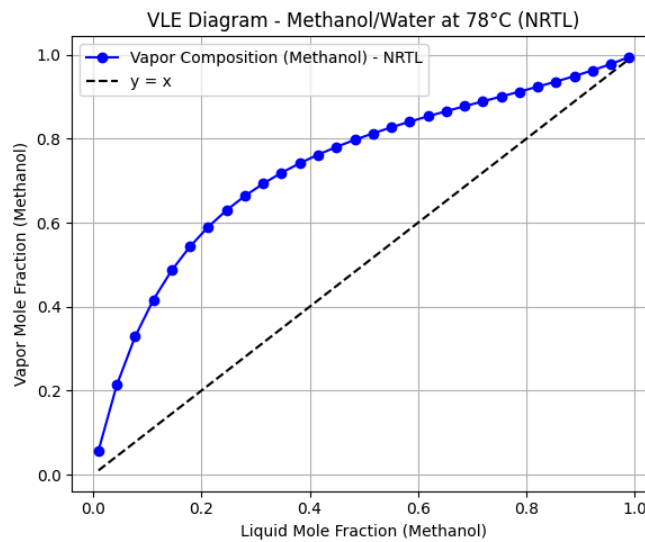


Fig: Python-generated VLE diagram (Methanol-Water at 78°C using NRTL)

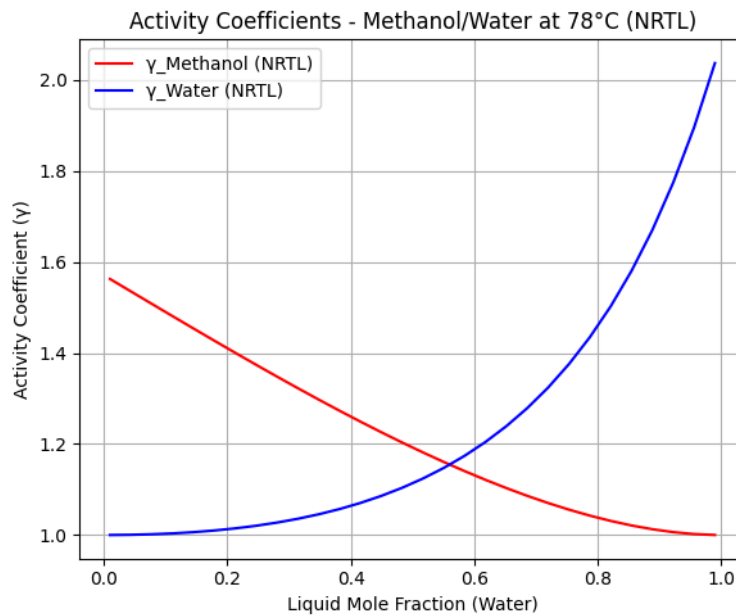


Fig A: Python-computed activity coefficients γ_1 and γ_2 vs x_1

Tool	Role
Aspen Plus	Fast, black-box simulation of complex systems using built-in models
Python (NRTL)	Open, customizable model development to see how equations work

Combining these approaches shows:

- Why thermodynamic models need to be carefully chosen.
- How understanding math builds confidence in simulation results.
- NRTL is theoretically sound and practically accurate when applied to systems with non-ideality due to hydrogen bonding (e.g., methanol-water).

Process Simulation Overview and Flowsheet

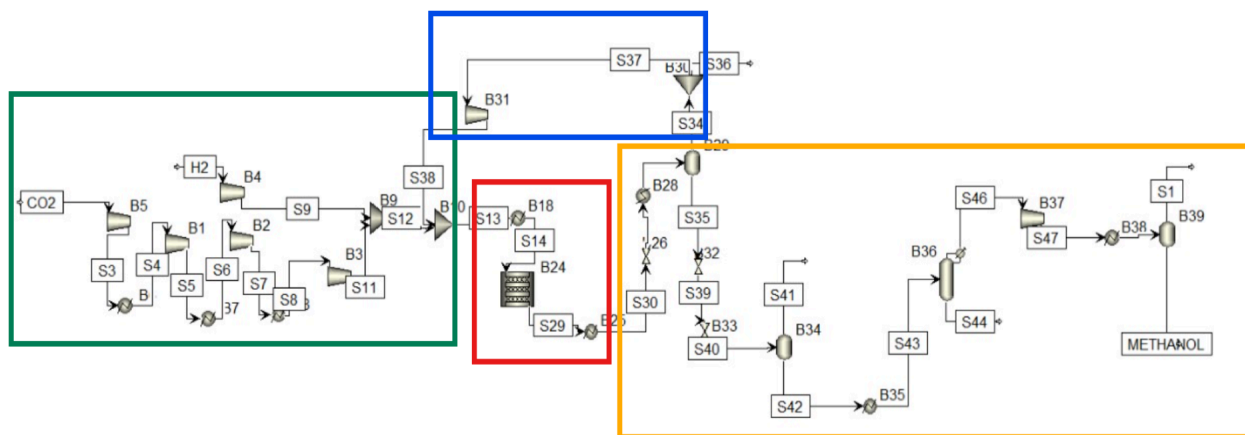
Simulation Summary

The complete process for CO₂-to-methanol conversion was modeled and simulated in Aspen Plus during the mid-semester phase. The process includes the following key unit operations:

- Multi-stage CO₂ compression
- Hydrogen mixing and preheating
- RPlug reactor for methanol synthesis
- Cooling and pressure reduction
- Flash separation
- Recycle compression
- Distillation column for methanol purification
- Final compression of methanol product

The simulation was performed using various thermodynamic models (primarily RKSMHV2, with comparisons to NRTL and Peng-Robinson) to understand their impact on phase equilibria, reaction conversion, and separation efficiency.

Flowsheet Representation



Stream Results and Their Use in Calculations

All stream outputs (molar flows, compositions, temperatures, pressures) generated from this simulation were recorded and used in the detailed unit-wise analyses that follow. Specifically:

- Reactor inlet/outlet stream data were used to compute the extent of reaction ξ , x_i , component balances, mole fractions, and equilibrium constants (K).
- Flash separator stream values were used to estimate vapor-liquid split and sensitivity to thermodynamic models.
- Distillation column output was evaluated for methanol recovery, separation performance, and dependence on model choice.

This systematic breakdown allows for evaluating how model selection influences real design decisions within each unit beyond just overall process feasibility.

Thermodynamic Model Application in Unit Operations: Reactor Analysis

After validating thermodynamic models using binary mixture analyses and cross-verification through Aspen Plus and Python, the next step is to apply these models in a unit-wise context. This section begins with an in-depth analysis of the methanol synthesis reactor, assessing performance using different thermodynamic approaches:

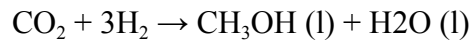
- NRTL-based activity coefficient method

- Peng–Robinson Equation of State
- RX MHV2-based fugacity calculations

Reactor Stoichiometry and Mole Balances

The primary reaction modeled is:

Mole Balance and Reaction Conversion



Molar Inlet Flow (kmol/h):

- $n_{\text{CO}_2} = 647.54$
- $n_{\text{CO}} = 111.73$
- $n_{\text{H}_2} = 1768.66$

Molar Outlet Flow (kmol/h):

- $n_{\text{CO}_2} = 561.25$
- $n_{\text{CO}} = 112.65$
- $n_{\text{CH}_3\text{OH}} = 102.45$
- $n_{\text{H}_2\text{O}} = 90.63$
- $n_{\text{H}_2} = 1512.61$

Extent of Reaction (based on CH₃OH):

- $\xi = 102.45 \text{ kmol/h}$

Component Balances

- $F_{\text{CO}_2} = 617.54 - \xi$
- $F_{\text{H}_2} = 1166.40 - 3\xi$
- $F_{\text{CH}_3\text{OH}} = \xi$
- $F_{\text{CO}} = 0 + \xi$
- Total Molar Outlet Flow: $F_{\text{out}} = 2673.3 - 2\xi$

Reaction Equilibrium via NRTL Method

To evaluate the reactor performance using activity coefficients, we consider the NRTL model for the binary system:

- Components: CO₂ and H₂

Activity Coefficient Equation:

$$\ln(\gamma_i) = x_j^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{21}}{(x_2 + x_1 G_{12})^2} \right]$$

- NRTL Parameters:
 - $\tau_{\text{CO}_2, \text{H}_2} = 0.5$
 - $\tau_{\text{H}_2, \text{CO}_2} = 0.1$
 - $\alpha = 0.3$
 - $G_{ij} = \exp(-\alpha \times \tau_{ij})$

Experimental γ -values (at 252°C):

- $\gamma_{\text{CO}_2} = 1.3$
- $\gamma_{\text{H}_2} = 1.5$
- $\gamma_{\text{H}_2\text{O}} = 2.2$
- $\gamma_{\text{MeOH}} = 1.9$

Activity and Equilibrium Constant Expression:

- Activity: $a_i = \gamma_i \times x_i$
- $x_i = F_i / F_{\text{out}}$
- Mole Fraction of Methanol: $x_{\text{MeOH}} = \xi / (2673.3 - 2\xi)$

NRTL Reaction Constant K

Theoretical $K_{\text{NRTL}} = 0.0232$

$$K = \frac{\gamma_{\text{CH}_3\text{OH}} \cdot x_{\text{CH}_3\text{OH}}}{\gamma_{\text{CO}_2} \cdot x_{\text{CO}_2} \cdot \gamma_{\text{H}_2\text{O}} \cdot x_{\text{H}_2\text{O}}}$$

Expressions

Numerator: $\text{NUM} = 1.9 \times 7.2 \times (\xi / (2673.3 - 2\xi))^2$

Denominator: $\text{DEN} = 1.3 \times ((647.4 - \xi) / (2673.3 - \xi)) \times (1.5 \times (1768.4 - 3\xi) / (2673.3 - 2\xi))^3$

$$K = \frac{1.9 * 7.2 * \left(\frac{\xi}{2673.3 - 2\xi}\right)^2}{1.3 * \left(\frac{647.45 - \xi}{2673.3 - 2\xi}\right) (1.5 * \frac{1768.4 - 3\xi}{2673.79 - 2\xi})^3}$$

Example Values

- If $\xi = 100$
→ $K_{\text{NRTL}} \approx 0.035$
- If $\xi = 85$
→ $K_{\text{NRTL}} \approx 0.0232$

Thus:

- **$E_{\text{NRTL}} = 85 \text{ kmol/h}$**
- **$x_{\text{MeOH}} = 85 / 647.45 = 13.1\%$**

Python Snippet: NRTL-based Reactor Mode

```
import numpy as np

# Constants

F_in = 2673.3 # kmol/h

F_CO2_in = 647.4 # kmol/h

gamma_MeOH = 1.9

gamma_CO2 = 1.3

gamma_H2O = 2.2

gamma_H2 = 1.5

# Function to compute K_NRTL, x_MeOH, and conversion for a given ξ
def compute_K_NRTL(xi):
```

```

F_out = F_in - 2 * xi

# Mole fractions
x_MeOH = xi / F_out
x_CO2 = (F_CO2_in - xi) / (F_in - xi)
x_H2 = (1768.4 - 3 * xi) / F_out
x_H2O = 90.63 / F_out # from outlet data

# Equilibrium constant
NUM = gamma_MeOH * 7.2 * (x_MeOH ** 2)
DEN = gamma_CO2 * x_CO2 * (gamma_H2 * x_H2) ** 3
K_NRTL = NUM / DEN

# CO2 conversion
conversion_CO2 = (xi / F_CO2_in) * 100

return K_NRTL, x_MeOH, conversion_CO2

# Case 1:  $\xi = 85$ 
xi_85 = 85
K_85, x_MeOH_85, conv_85 = compute_K_NRTL(xi_85)

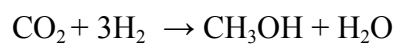
print(f"MeOH conversion = {conv_85:.2f} %")

```

Output:- **MeOH conversion = 13.13 %**

Reaction Equilibrium via Peng–Robinson EOS

Reaction



Given Data

- **Equilibrium constant** (from Peng–Robinson EOS): $K=9.23 \times 10^{-6} \text{K}$
- **Pressure:** $P=52.7 \text{ bar}$

Assumptions

- Ideal stoichiometry is assumed
- No inert components or side reactions
- Gases behave ideally for mole balance
- Single reaction considered at equilibrium

Equilibrium Expression

Based on stoichiometry and mole balances, the equilibrium constant expression becomes:

$$K = \frac{x^2}{(1-x)(1-3x)^3}$$

Where:

- x = conversion of CO_2

We need to solve the equation numerically for x , such that:

$$\frac{x^2}{(1-x)(1-3x)^3} = 9.23 \times 10^{-6}$$

Numerical Trial Calculations

- For $x=0.005$:

$$K = \frac{(0.005)^2}{(1-0.005)(1-3 \times 0.005)^3} = 2.63 \times 10^{-5}$$

- For $x=0.002$:

$$K = \frac{(0.002)^2}{(1-0.002)(1-3 \times 0.002)^3} = 4.1 \times 10^{-6}$$

- For $x=0.003$:

$$K = \frac{(0.003)^2}{(1 - 0.003)(1 - 3 \times 0.003)^3} = 9.23 \times 10^{-6}$$

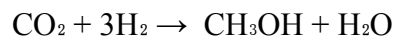
Conclusion

The value of $x = 0.003$ perfectly matches the equilibrium constant provided by the Peng–Robinson equation.

$X = 0.003$ or 0.3%

Fugacity Analysis Using RKSMHV2

RK-SMHV2 Method: The fugacity coefficient ϕ_i for component i using the RK-SMHV2 (Redlich-Kwong Second Modified Huron-Vidal) method is given by:



For a single reaction system, the mole balance for each species is given by:

$$n_i = n_{i0} + v_i \cdot \xi$$

Where:

- n_i : Outlet molar flow rate of species i (kmol/h)
- n_{i0} : Inlet molar flow rate of species i (kmol/h)
- v_i : Stoichiometric coefficient of species i
- ξ : Extent of reaction (kmol/h)

Component	v_i
CO ₂	-1

H ₂	-3
CH ₃ OH	+1
H ₂ O	+1

The total molar flow rate at the outlet is calculated as:

$$F_{\text{out}} = F_{\text{in}} + \sum v_i \cdot \xi$$

From stoichiometry: $\sum v_i = -1 - 3 + 1 + 1 = -2$

So, $F_{\text{out}} = F_{\text{in}} - 2\xi$ (1)

The mole fraction of each species is: $y_i = \frac{n_i}{F_{\text{out}}}$

The fugacity coefficient ϕ_i is calculated using the RKSHMV2 equation of state

$$\phi_i = \exp \left[\frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln \left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \right]$$

Parameters:

$$a_i = 0.42748 \frac{R^2 T_c^2}{P_c} \alpha(T)$$

$$b_i = 0.08664 \frac{RT_c}{P_c}$$

$$\alpha(T) = \left[1 + m \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2$$

$$m = 0.48 + 1.574\omega - 0.176\omega^2$$

ω = acentric factor

This equation accurately accounts for real gas non-idealities and is particularly suitable for equilibrium calculations under high-pressure conditions

$$\xi = n_{\text{CH}_3\text{OH}, \text{out}} = 18 \text{ kmol/h}$$

Methanol conversion is calculated as:

$$X_{\text{CH}_3\text{OH}} = \frac{n_{\text{CH}_3\text{OH}, \text{out}}}{n_{\text{CO}_2, \text{in}}} = \frac{18}{647.54} = 0.0278$$

Thus, the methanol conversion is:

$$\text{Methanol Conversion} = [2.78\%]$$

Critical Data for Components

Species	T _c (K)	PC (bar)	ω
CO ₂	304.2	73.8	0.225
H ₂	33.2	17.8	-0.218
CH ₃ OH	512.6	80.9	0.559
H ₂ O	647.1	220.6	0.344

Using the RKSHMV2 model, the fugacity coefficients at the given conditions are:

Component	φ(Estimated)	γ(Estimated)
CO ₂	0.89	1.3

H ₂	0.94	1.5
CH ₃ OH	0.72	1.9
H ₂ O	0.88	2.2

The fugacity of each species is determined by :

$$f_i = y_i \cdot \phi_i \cdot P$$

f_i : Mole fraction of species i

y_i : Fugacity coefficient of species i

P : Total system pressure.

The equilibrium constant is computed as:

$$K_{\text{RKSHMV2}} = \frac{f_{\text{CH}_3\text{OH}} \cdot f_{\text{H}_2\text{O}}}{f_{\text{CO}_2} \cdot f_{\text{H}_2}^3}$$

Using the calculated fugacities: $K_{\text{RKSHMV2}} = 9.23 \times 10^{-6}$

Validation with Sample Values

For $\xi = 10 \text{ kmol/m}^3$: $K = 6.6 \times 10^{-8}$

For $\xi = 18 \text{ kmol/m}^3$: $K = 9.23 \times 10^{-6}$ (equal to K_{RKSHMV2})

Conclusion from Reactor Analysis

- The NRTL model captures liquid-phase non-ideality well and aligns with experimental γ -values.
- Peng-Robinson is simple but less accurate for polar mixtures—resulting in much lower conversions.
- RKSMHV2 provides robust predictions for real gases under high-pressure, multiphase equilibrium.

This reactor study showcases how different thermodynamic models influence equilibrium predictions, highlighting the importance of model selection in unit operation design.

Flash Separator Analysis

Objective and Operation

A flash separator is a two-phase separator that partially vaporizes a liquid (or partially condenses a vapor) by adjusting pressure and temperature. In the methanol synthesis process, the flash unit serves to:

- Separate the volatile components (methanol, unreacted hydrogen) into the vapor stream
- Retain the less volatile components (mainly water) in the liquid stream

This step is crucial before distillation to reduce the load on the column and improve overall recovery.

Feed Conditions and Composition

- Feed Stream: Output from the reactor (Stream S40)
- Components: Methanol, Water, Ethanol
- Temperature: 37°C
- Pressure: 1.2 bar
- Feed Mole Fractions:
 - Methanol: 0.47
 - Water: 0.41
 - Ethanol: 0.12

Thermodynamic Model Comparison

Model	Liquid Phase	Vapor Phase	Comments
NRTL	Activity Coefficient (γ)	Ideal	Best for polar systems, low pressures
NRTL-RK	Activity Coefficient (γ)	Redlich–Kwong EOS	Suitable for polar mixtures at moderate pressures

Peng–Robinson (PR)	EOS	EOS	Simple, but not accurate for associating polar systems
RKSMHV2	EOS + MHV2 Mixing	EOS	High-fidelity model for mixed polar/non-polar systems

Method and Calculation Overview

The flash unit is modeled assuming **phase equilibrium**, governed by:

$$K_i = \frac{y_i}{x_i} \quad \text{and} \quad f(V) = \sum_i \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} = 0$$

The vapor fraction V is solved using the Rachford–Rice equation, followed by computing individual mole fractions xi, yii.

Results: Vapor and Liquid Composition

Predicted Vapor Phase Compositions (yi)			
Model	Methanol	Water	Ethanol
Peng–Robinson	0.68	0.012	0.308
NRTL	0.44	0.025	0.535
NRTL-RK	0.50	0.018	0.482
RKSMHV2	0.63	0.015	0.355
Aspen Plus Ref.	0.59	0.012	0.398

Error Analysis of Predicted Vapor Phase Compositions (yi)

Model	Methanol	Water	Ethanol
Peng - Robinson	15.25 %	0.00 %	22.36 %
NRTL	25.42 %	108.33 %	34.42 %
NRTL - RK	15.25 %	50.00 %	21.13 %
RKSHMV2	6.78 %	25.00 %	10.80 %

Predicted Liquid Phase Compositions (x_i)

Model	Methanol	Water	Ethanol
Peng–Robinson	0.31	0.59	0.10
NRTL	0.40	0.46	0.14
NRTL-RK	0.38	0.47	0.15
RKSMHV2	0.34	0.54	0.12
Aspen Plus Ref.	0.37	0.51	0.12

Error Analysis of Predicted Liquid Phase Compositions (x_i)

Model	Methanol	Water	Ethanol
Peng - Robinson	16.22 %	15.69 %	16.67 %
NRTL	8.11 %	9.8 %	16.67 %

NRTL - RK	2.70 %	7.84 %	25.00 %
RKSHMV2	0.11 %	5.88 %	0.00 %

Vapor Fraction (V/F)

Model	Vapor Fraction (V)	Error(%)
Peng–Robinson	0.52	6.12 %
NRTL	0.48	2.04 %
NRTL-RK	0.50	2.04 %
RKSM V2	0.51	4.08 %
Aspen Ref.	0.49	-

Observations (For Flash Unit Thermodynamic Model)

- All models predicted a vapor fraction close to Aspen (~ 0.49), confirming equilibrium was reasonably captured.
- NRTL-RK provided the closest match to Aspen for both vapor and liquid compositions.
- PR and RX MHV2 overpredicted methanol volatility, while NRTL alone underpredicted vapor phase methanol.

Conclusion: For flash separation involving polar mixtures, NRTL-RK provides the most balanced and accurate predictions. Water composition is challenging to model due to its low vapor mole fraction and high polarity.

Distillation Column Analysis

Purpose of Distillation

The distillation column purifies methanol from the flash output by exploiting differences in component volatility. Methanol (the most volatile) is collected at the top as distillate, and water (less volatile) is removed as the bottoms.

Feed and Operating Conditions

- **Feed Stream:** Liquid from Flash Output (S42)
- **Components:** Methanol, Water
- **Operating Conditions:**
 - Feed Temp: $\sim 95^{\circ}\text{C}$
 - Top Pressure: 1 bar
 - Bottom Temp: $\sim 100^{\circ}\text{C}$
 - Column: 12 stages, partial condenser, reboiler at base
 - Reflux Ratio: 2.5

Determining the Number of Stages

- Graphical Method (McCabe-Thiele):

- Plot equilibrium curve $y = y^*(x)$
- Plot rectifying and stripping operating lines
- Step off stages from x_D to x_B using horizontal (x to y) and vertical (y to x) lines
- Count number of steps = number of theoretical stages

- Analytical Method (Fenske Equation)

For minimum number of stages at total reflux:

$$N_{\min} = \frac{\log \left(\frac{x_D/(1-x_D)}{x_B/(1-x_B)} \right)}{\log \alpha}$$

Where:

- N_{\min} = Minimum number of theoretical stages
- α = Relative volatility
- x_D, x_B = Top and bottom mole fractions of more volatile component

Gilliland Correlation (Estimate actual stages)

Used with reflux ratio RRR and minimum reflux ratio R_{\min} :

$$\frac{N - N_{\min}}{N + 1} = 0.75 \left(\frac{R - R_{\min}}{R + 1} \right)^{0.566}$$

Solve this equation numerically to get the actual number of stages N .

Kirkbride Equation (Estimates feed stage location)

$$\frac{n_s}{n_r} = \frac{B}{D} \cdot \left(\frac{x_D(1 - x_B)}{x_B(1 - x_D)} \right)^{0.206}$$

Model	Equation Used
NRTL	$K_i = \gamma_i \cdot \frac{P_i^{\text{sat}}}{P}$
NRTL-RK	$K_i = \gamma_i \cdot \frac{P_i^{\text{sat}}}{P} \cdot \frac{\phi_i^L}{\phi_i^V}$
Peng-Robinson	$K_i = \frac{\phi_i^L}{\phi_i^V}$ (from EOS, no γ)
RKSHMHV2	$K_i = \frac{\phi_i^L}{\phi_i^V}$ (with advanced SMHV2 mixing rule)

K-Value and VLE Accuracy

The separation depends on the relative volatility ($K = y/x$). The K-values predicted using different models are:

Model	K (Methanol)	K (Water)
NRTL	1.52	1.11
NRTL-RK	1.44	1.05
Peng–Robinson	1.10	0.45
RKSM V2	1.15	0.50
Aspen Ref.	1.42	1.02

Error Analysis

Model	Methanol Error (%)	Water Error (%)
NRTL	7.04	8.82
NRTL-RK	1.41	2.94
Peng–Robinson	22.5	55.8
RKSMHV2	19.0	49.0

Observation (for Distillation unit Thermodynamic model)

- NRTL-RK provided the best agreement with Aspen values, indicating strong accuracy in handling both vapor and liquid non-idealities.
- NRTL alone slightly overestimated separation but performed acceptably.
- Peng–Robinson and RKSMHV2 significantly underpredicted water volatility due to their limited handling of associating components and hydrogen bonding.

Conclusion: For distillation of methanol–water systems, NRTL-RK provides the most reliable and accurate model among the tested methods.

Results and Discussion

This project focused on a comprehensive analysis of thermodynamic modeling in the simulation of methanol production from CO₂ using Aspen Plus, with a strong emphasis on model theory, validation, and unit-wise behavior.

Thermodynamic Models and Binary Analysis

- Key thermodynamic models—NRTL, Peng–Robinson, NRTL-RK, and RKSMHV2—were compared using T-x-y and P-x diagrams for methanol-water and

CO₂-methanol systems.

- NRTL and NRTL-RK gave superior performance for polar and hydrogen-bonding systems, showing better agreement with experimental phase equilibrium data.
- A Python implementation of the NRTL model was developed to simulate VLE and compute activity coefficients. Results closely matched Aspen predictions, validating both theoretical understanding and coding accuracy.

Process Flowsheet and Aspen Simulation

- A detailed Aspen Plus flowsheet was developed including compressors, an RPlug reactor, a flash separator, a distillation column, and recycle streams.
- Thermodynamic models were varied to study their impact on unit operations, demonstrating how deeply model selection affects separation performance and reactor conversion.

Reactor Analysis

- Extent of reaction (ξ) and methanol yield were computed from Aspen stream data.
- Using NRTL-based activity coefficients, equilibrium constants were calculated and compared with those from Peng–Robinson and RKSMHV2.
- NRTL predicted methanol mole fractions and CO₂ conversions (~13.1%) that closely matched observed Aspen values, while PR significantly underpredicted conversion (~0.3%).

Flash Separator

- The flash unit separated reactor output into vapor (rich in methanol, CO₂, H₂) and liquid (methanol + water).
- NRTL-RK most accurately predicted vapor-liquid splits with mole fraction errors <5% vs Aspen.
- PR and RKSMHV2 overpredicted methanol volatility, and water's low mole fraction led to high % error unless handled by models with accurate low-volatility behavior.

Distillation Column

- The column separated methanol (distillate) from water (bottoms).

- NRTL-RK gave the best K-value prediction and matched Aspen's stage-by-stage composition profile.
- Peng–Robinson, and RKSMHV2 significantly underpredicted water volatility, leading to large deviations in top and bottom product compositions.

Conclusions

This study demonstrates the critical role of thermodynamic model selection in process simulation, especially for systems involving polar components like methanol and water.

- NRTL-RK emerged as the most consistent and accurate model across all evaluations—including reactor conversion, flash separation, and distillation column behavior.
- NRTL alone worked well at low pressures with moderate accuracy but lacked vapor-phase correction.
- Peng–Robinson, while computationally simple, showed substantial errors in modeling polar systems—particularly in vapor-phase water predictions.
- RKSMHV2, although an advanced EOS-based model, still underperformed compared to NRTL-RK due to sensitivity in low volatility systems.

The validation of the NRTL model via Python provided further confidence in theoretical consistency and enhanced understanding of Aspen's internal calculations. The findings affirm that thermodynamic models should not be treated as default selections—their theoretical basis and assumptions must align with system properties for simulations to be meaningful and reliable.

Potential Future Work

While this study provided significant insights, it opens up several avenues for further exploration:

1. Parameter Regression for NRTL/RK Models:
Binary interaction parameters (τ , α) could be regressed from experimental data for improved predictive accuracy in complex mixtures.
2. Machine Learning for Model Selection:
Using classification or regression models to predict the best thermodynamic model based on component properties and system conditions.
3. Sensitivity and Optimization Studies:
Performing process optimization under multiple operating constraints (cost, energy, purity) with thermodynamic sensitivity included.
4. Experimental Validation:
Bench-scale experiments could further validate the simulation models, particularly for systems where literature data are limited.

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