

Hydrate-Based Separation for Industrial Gas Mixtures

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Abstract: The removal of acidic gases and impurities from gas mixtures is a critical operation in the oil and gas industry. Several separation techniques, e.g., cryogenic fractionation, polymeric membranes, zeolites, and metal–organic frameworks, are employed to treat gas mixtures depending upon the nature of separation and contaminants present in the gas mixtures. However, removing N₂, H₂, H₂S, and CO₂ contents from industrial gas mixtures is a challenging step due to economic factors, high energy consumption, and effective separation. Hydrate-based separation for selective gas removal is a promising and efficient separation technique over a range of temperatures, pressures, and acidic gas contents. The enclathration of CO₂, H₂, N₂, H₂S, and other natural gas constituents effectively removes acidic gases and other contaminants from process gas streams. This work presents a novel process design to remove acidic gases and other contaminants from industrial waste gases and natural gas mixtures to achieve the desired selectivity in gas mixtures. Multi-phase equilibria calculations were also performed for various binary and ternary gas mixtures (e.g., CO₂ + CH₄, H₂S + CH₄, CO₂ + N₂, CH₄ + CO₂ + H₂S, and CO₂ + H₂S + N₂) over a range of compositions and T, P conditions. The former calculations established the suitable region in terms of temperature and pressure for adequate separations. To determine the optimal process conditions (T & P) for efficient separation, fractional cage occupancy and gas mole fraction in each phase were also computed. A detailed analysis of the hydrate-based separation shows that the number of stages necessary for desired separation efficiency depends on the nature of the gas mixture and hydrate stability.

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Supplementary Information

While doing hydrate phase equilibria calculations, while imposing equilibrium criteria for C # of components and π phases, objective function in each phase is as shown in Equation S1:

$$E_K = \sum_{i=1}^c \frac{z_i \left(\frac{x_{ik}}{x_{ir}} - 1 \right)}{1 + \sum_{\substack{j=1 \\ j \neq r}}^{\pi} \alpha_j \left(\frac{x_{ij}}{x_{ir}} - 1 \right)} \quad (1)$$

Where:

x_{ik} mole fraction of component i in any phase k

x_{ir} mole fraction of component i in reference phase r

α_j Normalized molar amount.

z_j Overall mole fraction.

the fugacity coefficient ratios are utilized here for $\frac{x_{ik}}{x_{ir}}$ and it was calculated by Equation S2:

$$\frac{x_{ik}}{x_{ir}} = \frac{\phi_{ir}}{\phi_{ik}} e^{\theta_k} = K_{ik} e^{\theta_k} \quad (2)$$

Where:

K_{ik} fugacity coefficient ratio for component i between phase k and reference phase r

ϕ_{ik} fugacity coefficient of component i in phase k

ϕ_{ir} fugacity coefficient of component i in reference phase r

θ_k stability variable for phase k .

The natural log of fugacity ratio is stability of phase k and calculated by Equation S3

$$e^{\theta_k} = \ln \frac{f_{ik}}{f_{ir}} \quad (3)$$

Where:

f_{ik} fugacity of component i in phase k

f_{ir} fugacity of component i in reference phase r

This is equivalent to the Gibbs energy minimization with the constraint (Equation S4):

$$S_k = \frac{\theta_k \alpha_k}{\theta_k + \alpha_k} \quad (4)$$

The generalized algorithm for thermodynamic equilibrium is given in Figure 2 of the manuscript. Moreover, the adopted Newton-Raphson procedure for minimizing Gibbs energy of a system for set of distribution ratios is discussed in detail of the Adam Ballard Ph.D. thesis [1].

While minimizing Gibbs free energy at calculated values of distribution coefficients and checking phase stability criteria (Table S1), the mole fractions are updated using below Equation S5 and the algorithm (Figure 2 of the manuscript).

Table S1. Phase Stability criteria for GEM algorithm.

Normalized molar amount (α_k)	Stability Variable (θ_k)	Phase stability
> 0	0	Phase k is present
= 0	$\neq 0$	Phase k absent

$$x_{ik} = \frac{z_i K_{ik} e^{\theta_k}}{1 + \sum_{\substack{j=1 \\ j \neq r}}^{\pi} \alpha_j (K_{ij} e^{\theta_j} - 1)} \quad (5)$$

To initialize the Gibbs energy minimization algorithm the $\theta_k = 0$ and $\alpha_k = \frac{1}{\pi}$ are initialized with the former values with the assumption that all phases are available with equal amounts. Moreover, GEM calculations for ternary gas mixture of $N_2 + H_2S + CO_2$ were also carried out, and the mole fraction of nitrogen for each stage is presented in Figure S1.

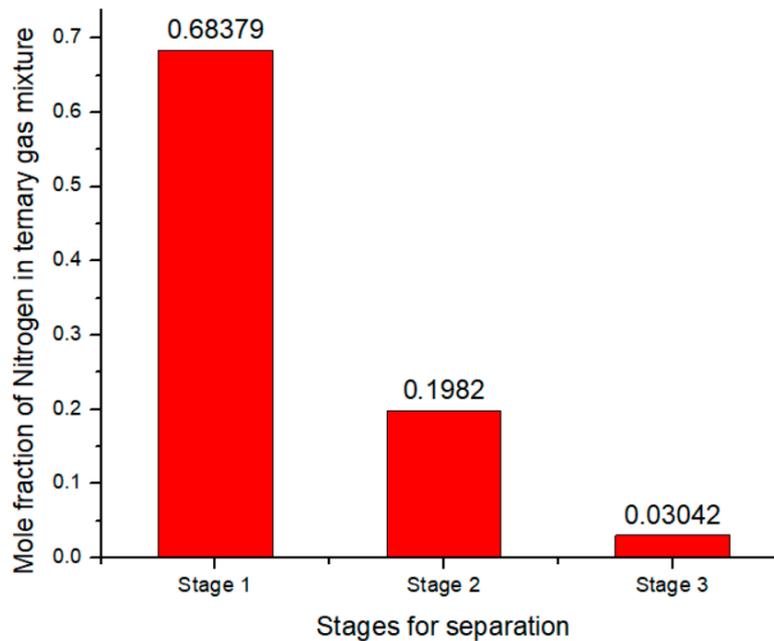
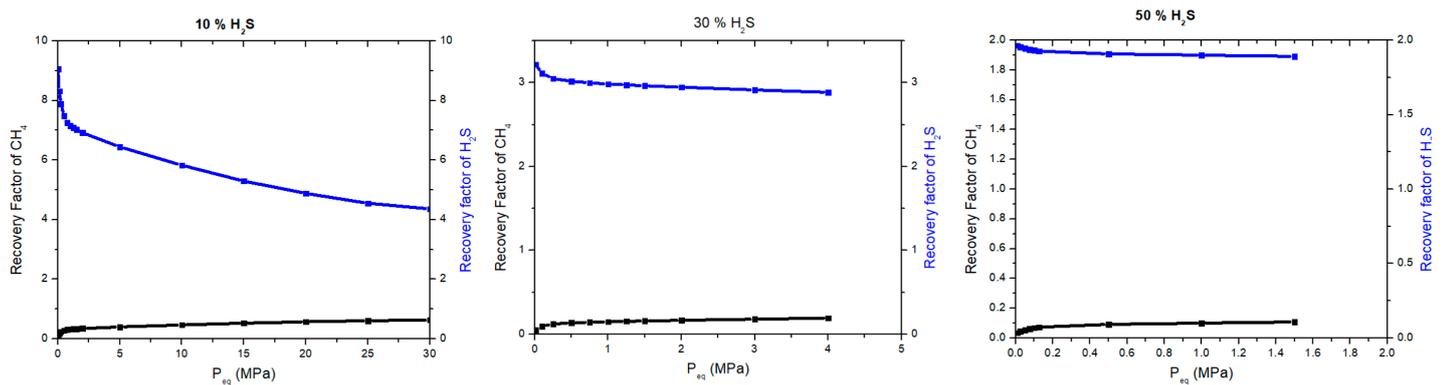


Figure S1. Case study for hydrate-based Separation for the ternary gas mixture of $CO_2 + N_2 + H_2S$ (Feed: 86.36 mol. % $N_2 + 4.54$ mol. % $CO_2 + 9.09$ mol. % H_2S).

In addition, recoveries of CH_4 and H_2S in binary hydrate systems for a range of H_2S concentrations were calculated and shown in Figure S2.



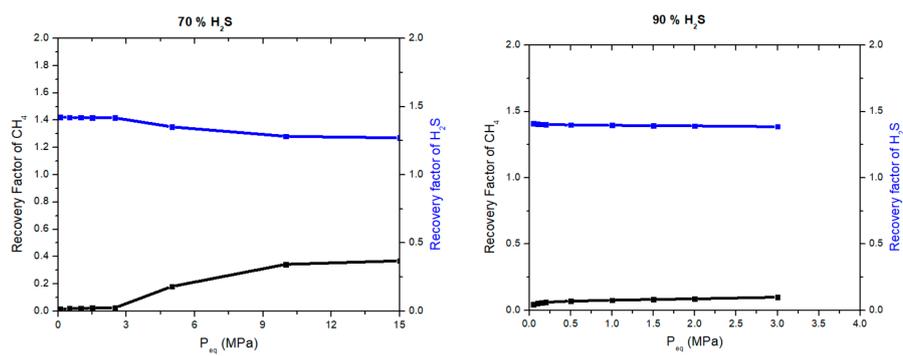


Figure S2. Predicted Recoveries of CH₄ and H₂S in binary hydrate systems for a range of H₂S concentrations.

References

1. Ballard, A.L. Non-Ideal Hydrate Solid Solution Model for a Multi-Phase Equilibria Program, A. Doctoral Dissertation, Colorado School of Mines, Golden, CO, USA, 2002.