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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 N_2, H_2, H_2S, and CO_2 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 CO_2, H_2, N_2, H_2S, 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., CO_2 + CH_4, H_2S + CH_4, CO_2 + N_2, CH_4 + CO_2 + H_2S, and CO_2 + H_2S + N_2) 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.

Keywords: gas hydrates; gas separation; phase equilibria; sour gases; CO_2 capture; process design

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1. Introduction

Gas hydrate formation offers versatile applications, including seawater desalination, CO_2 sequestration, hydrogen storage, natural gas transportation, and separation of gases from power plants or other chemical plants [1–7]. With increasing global warming and climate change, it is necessary to capture and sequester greenhouse gases (CH_4, CO_2) from flue gas mixtures. Existing processes for separation of CH_4 and CO_2 from a gas mixture are not efficient and economical and thus create a major roadblock in the sequestration of these greenhouse gases [8–14]. Depending on the composition of the gas mixture and the desired separation efficiency, different techniques can be employed to separate the mixture components. Examples of commonly used separation techniques include cryogenic distillation, polymer membranes, and adsorption and absorption-based processes [15–17]. High energy consumption, inefficient separation, and other economic factors limit the application of these separation techniques. Due to this, new energy-efficient separation processes (such as zeolites and metal–organic frameworks (MOFs)) are being aggressively researched. Gas separation using clathrate hydrates offers an attractive alternative with its selective separation and high efficiency compared to other available separation techniques. Unlike zeolite and MOFs, where different types of structures are needed for different gas mixtures, a wide variety of gas mixtures can be handled using the hydrate-based process.

Only temperature and pressure conditions need to be optimized depending on which component is getting enclathrated. The high concentration of gases stored in hydrate cages and the ability to tune cage occupancy by simply changing temperature or pressure provides a novel method for gas separation [8,18–24].

Separating components of a gas mixture by forming clathrate hydrates has been attempted by many researchers [1,3,7,21–23]. Figure 1 presents a pictorial representation and explains the fundamental concept behind hydrate-based separation. In Figure 1, a two-component gas mixture is separated by bringing the gas mixture in contact with water and subjecting the gas mixture plus water to hydrate formation and dissociation steps. In the hydrate formation step, T & P conditions are chosen such that HF-2 (a component that forms hydrate at lower pressure compared to HF-1) preferentially enters the solid hydrate phase. The gas phase (now richer in HF-1) is easily separated from the solid hydrate phase. The solid hydrate phase is then subjected to a hydrate dissociation step (increasing T and reducing P) such that the solid hydrate is dissociated forming a liquid water phase and a gas phase comprising only of HF-2. In a real application, it is possible that both components will go into the hydrate phase. However, concentration of different components will be different in gas vs. hydrate phase thus enabling separation in each step. In such cases, multiple hydrate formation and dissociation stages may be required to achieve the desired separation. Therefore, the careful selection of temperature and pressure for each step is essential to reduce the number of stages for optimal process design. In this work, process design calculations were performed for various binary and ternary gas mixtures (e.g., CO_2 + N_2, CH_4 + CO_2, CH_4 + H_2S, CH_4 + H_2S + CO_2, and N_2 + H_2S + CO_2 systems) over a range of feed compositions. In addition, the current work critically investigates the effectiveness of a hydrate-based gas separation process.

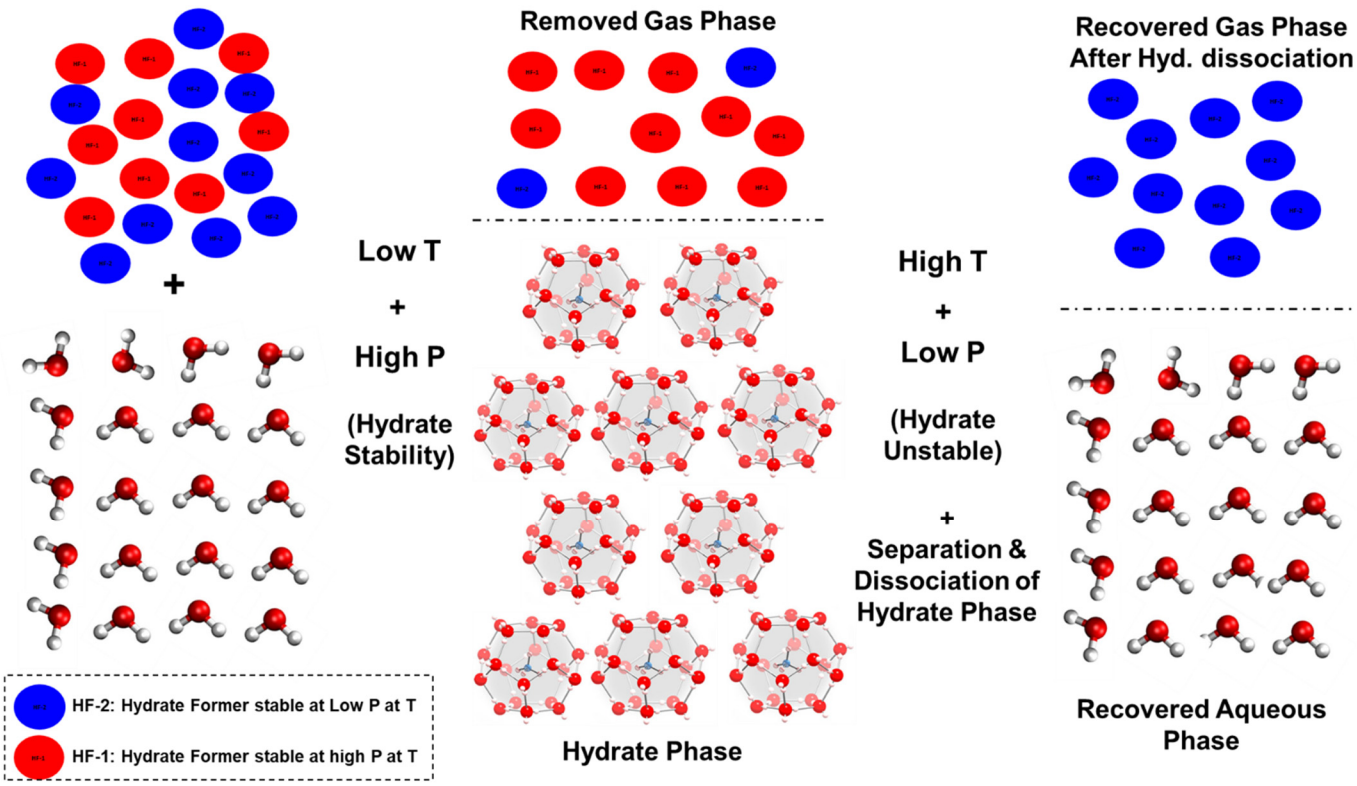


Figure 1. Pictorial representation of hydrate-based gas separation.

2. Theory

The hydrate phase equilibria for gas separation were calculated using the van der Waals and Platteeuw (vdWP) model coupled with the Gibbs energy minimization (GEM) algorithm. The coupled vdWP and GEM approach is a comprehensive gas hydrate thermo-

dynamic model based on a strictly statistical thermodynamic approach that can accurately predict hydrate phase equilibria [25]. For each component, equality of fugacity in all the phases (Equation (1)) is considered as the necessary and fundamental condition for hydrate phase stability [26–28].

$$f_i^H = f_i^\pi \tag{1}$$

The superscript H exemplifies the hydrate phase which can be s-I, s-II, or s-H; however, the superscript (π) describes the liquid, vapor, and ice phases. The Helgeson [29,30] equation (Equation (2)) is used to calculate the fugacity of water in the hydrate phase.

$$f_w^k = f_{wo} exp\left[\frac{\mu_w^k - g_{wo}}{RT}\right] \tag{2}$$

where:

f_w^k : fugacity of water in any phase k
f_{wo} : fugacity of water at standard conditions (T_o = 298.15 K and P = 1 bar)
u_w^k : chemical potential of water in any phase k
g_{wo} : Gibbs free energy of water at standard conditions (T_o = 298.15 K and P = 1 bar)
R : Gas constant.

The simplified algorithm has been shown in Figure 2 and a detailed procedure for phase equilibria calculations was discussed by Ballard and Sloan [30–34].

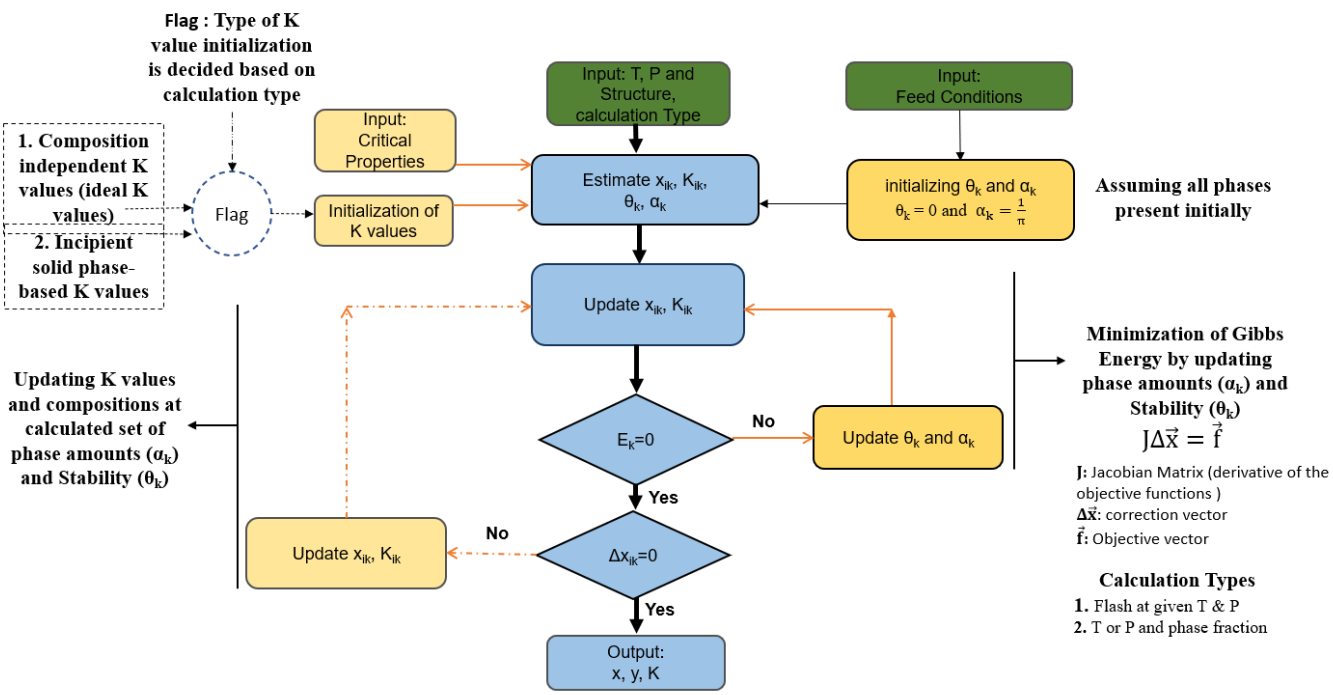


Figure 2. Gibbs free energy minimization (GEM) algorithm. Reproduced with permission from ref. [28]. 2021 Elsevier Science and Technology Journal.

3. Results and Discussions

The following section presents phase equilibria calculation results and process design for separation of different gas mixtures.

3.1. Process Design for CH_4 + H_2S Mixture

Figure 3 shows the CH_4 + H_2S hydrate phase equilibria predicted using the vdWP and GEM model over a range of temperatures and compositions. It can be observed that H_2S forms hydrate at much milder conditions (lower P/higher T) compared to CH_4. At the

same temperature, with increasing H_2S concentration in the mixture, the pressure required to form hydrate decreases, i.e., hydrate phase boundary shifts to a lower pressure. Due to this significant difference in the CH_4 vs. H_2S hydrate stability region, their mixture can be easily separated.

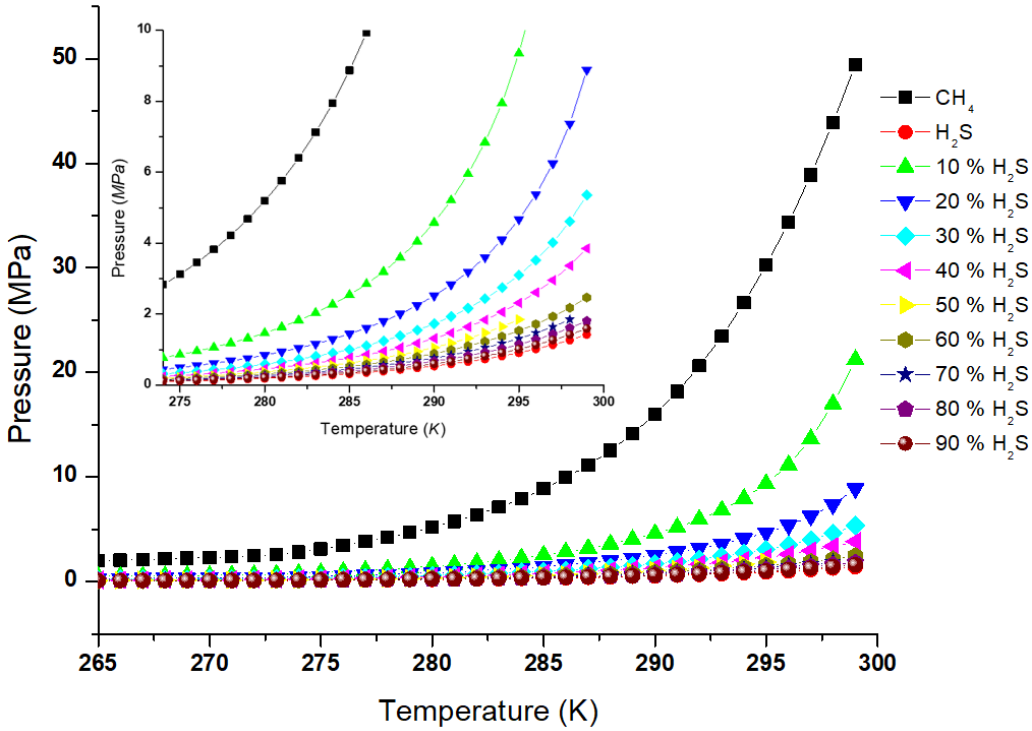


Figure 3. Hydrate phase equilibria predictions for CH_4+H_2S mixture over a range of temperatures. Inset shows the expanded view. Reproduced with permission from ref. [9]. 2015 M.N. Khan, Ph.D. Thesis.

Figure 4 shows predicted composition in the hydrate phase for different concentrations of H_2S in the CH_4 + H_2S gas mixture. For the case of 70:30 H_2S:CH_4, there is very clear separation with the hydrate phase almost entirely comprising H_2S (recoveries calculated in Figure S2). A similar conclusion was observed for other binary gas mixtures with the appropriate *P* and *T* conditions selection. Separation becomes challenging at higher CH_4 concentrations, as both gases compete for enclathration. This concept was applied for an industrially relevant composition (Bab Field, UAE—~70 mol.% CH_4 + 30 mol.% H_2S), and the process design for separating such a gas mixture is shown in Figure 5.

Figure 5 reveals the process design calculation for 70 mol.% CH_4 + 30 mol.% H_2S gas mixture in a hydrate crystallizer and dissociator (two-column). The effluent from Stage 1 upon hydrate dissociation results in a gas stream with 90/10% (H_2S/CH_4) mole fraction. The product stream from Stage 1 is then subjected to the second hydrate crystallization stage, which results in a gas stream that is 99% CH_4. Gas produced after the decomposition of hydrate formed in the second stage is 99% H_2S. The calculations of fractional cage occupancies (Figure 6) and mole fraction establish the optimal process condition to achieve the desired separation. The calculated recovery and separation factors for gas mixtures depends on the feed composition and T & P conditions. In addition, thermodynamic calculation shows that the appropriate selection of specific T, P conditions can provide clear and efficient separation. Novel process designs were also developed for other gas mixtures. The number of stages needed for desired separation efficiency was assessed and was found to be strongly dependent on the process T & P and hydrate stability region. Recovery and selectivity for gaseous mixtures were significantly dependent on the hydrate former polarity and process conditions.

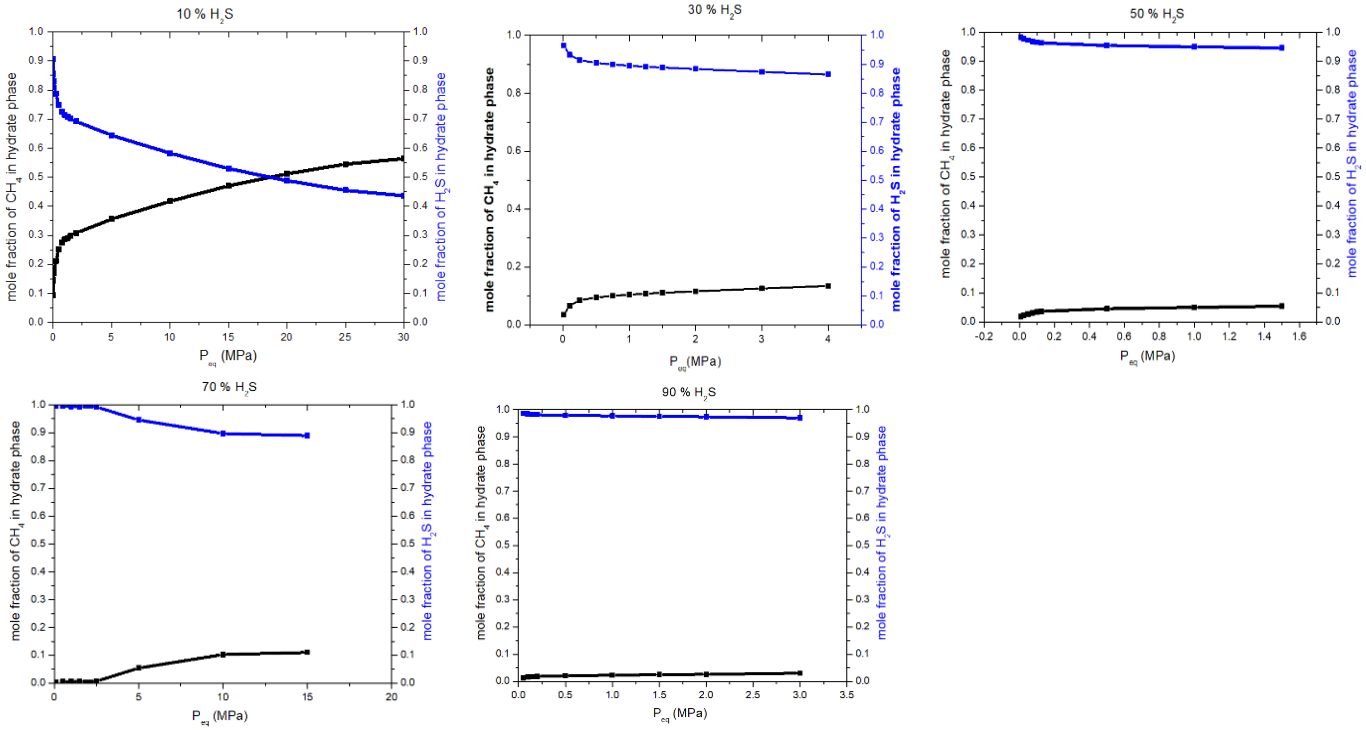


Figure 4. Predicted hydrate phase composition for CH_4 + H_2S mixture for a range of H_2S concentrations. Reproduced with permission from ref. [9]. 2015 M.N. Khan, Ph.D. Thesis.

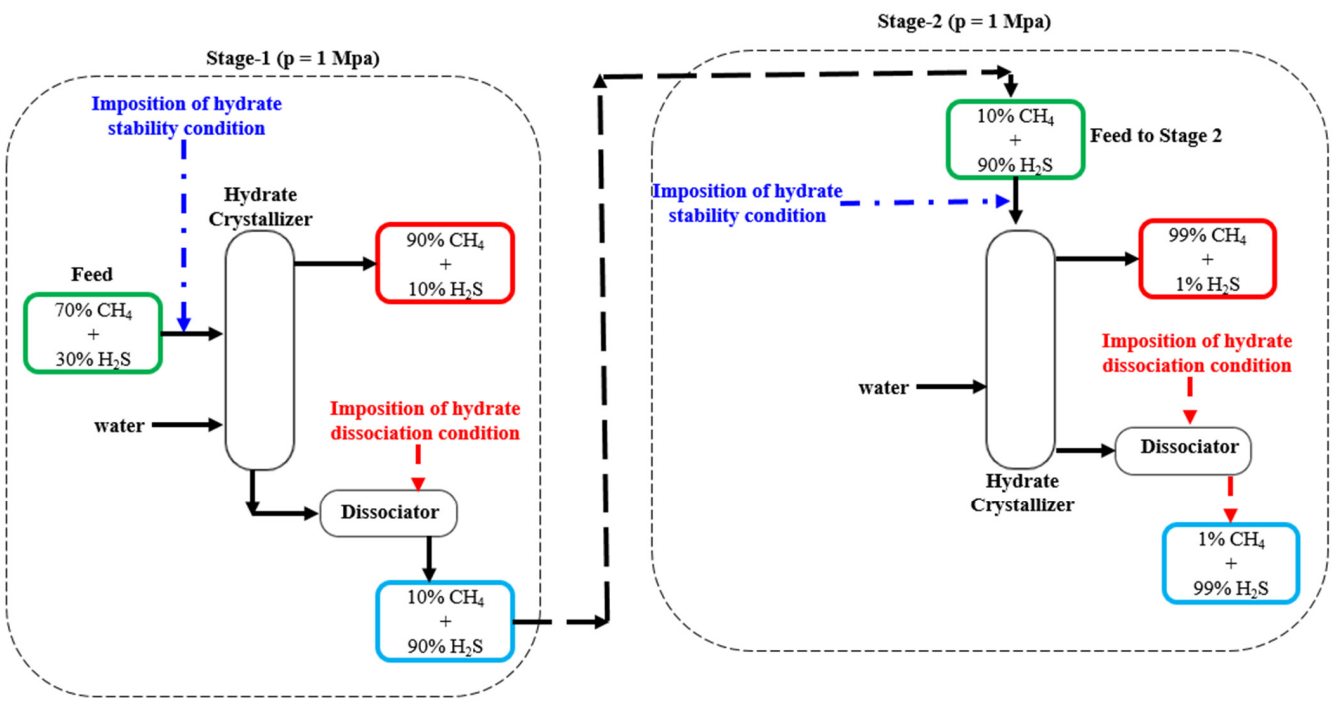
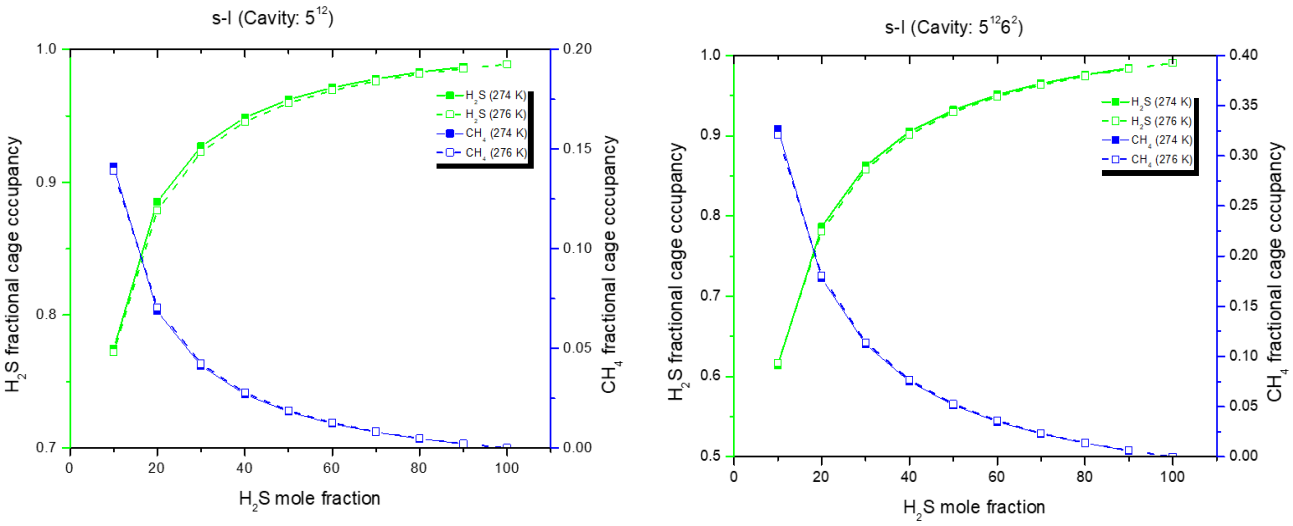


Figure 5. Separation process scheme for a gas composition from the Bab Field, UAE (~70 mol.% CH_4 + 30 mol.% H_2S). Reproduced with permission from ref. [9]. 2015 M.N. Khan, Ph.D. Thesis.



(a) **(b)**

Figure 6. Fractional cage occupancy of hydrate formers in CH_4 + H_2S binary gas mixture (**a**) Small Cavity and (**b**) Large Cavity at 1 MPa.

3.2. Process Design for CH_4 + CO_2 Mixture

Predicted hydrate phase boundaries for CH_4 and CO_2 mixture are shown in Figure 7. CH_4 + CO_2 hydrate phase equilibria is rather complex and increasing CO_2 concentration has different effects at different T/P. CO_2 hydrate is more stable at lower pressures at given temperature than CH_4 hydrate, and with CO_2 liquification (at higher temperatures and pressures), CH_4 is relatively stable.

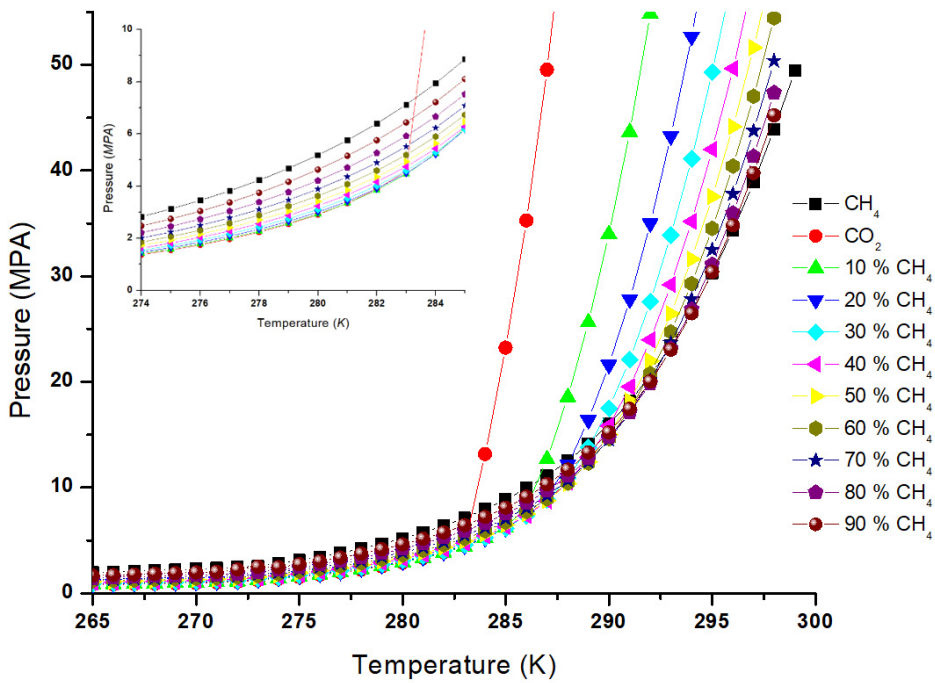


Figure 7. Predicted hydrate phase equilibria for CH_4 + CO_2 mixture. Inset shows expanded view. Reproduced with permission from ref. [9]. 2015 M.N. Khan, Ph.D. Thesis.

Figure 8 presents the changes in fractional cage occupancies of CO_2 and CH_4 in the small (5^{12}) and large cavities ($5^{12}6^2$) as a function of CO_2 mole fraction at 10 MPa at 274 K and 276 K, respectively. The variation in fractional cage occupancy demonstrates the selectivity of CO_2 vs. CH_4 in each cavity as a function of the CO_2 mole fraction.

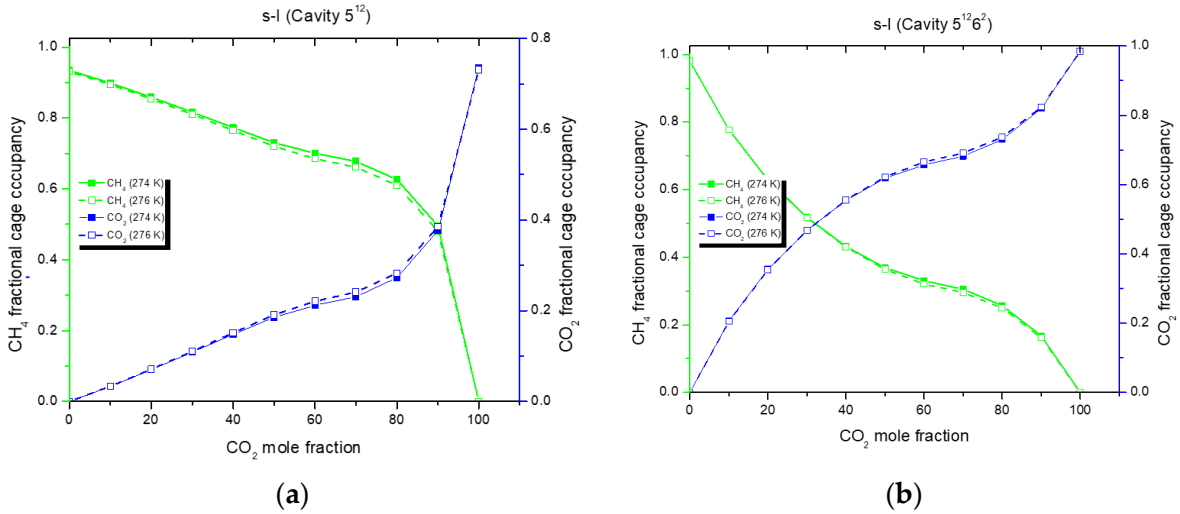


Figure 8. Fractional cage occupancy of hydrate formers in CO_2 + CH_4 binary gas mixture for (**a**) Small Cavity and (**b**) Large Cavity at 10 MPa.

Figure 9 shows the gas separation process design for CH_4 + CO_2 mixture, where the feed gas stream was subjected to hydrate stability conditions followed by dissociation. Due to the complexity in the hydrate phase diagram for this mixture, eight stages were required to achieve a stream comprising 99 mol% CO_2. Rigorous GEM calculations (Figure 10) coupled with mass balance for CH_4 + CO_2 binary systems over a CH_4/CO_2 concentration range also reveal the necessity of multiple stages for CO_2 separation from CH_4.

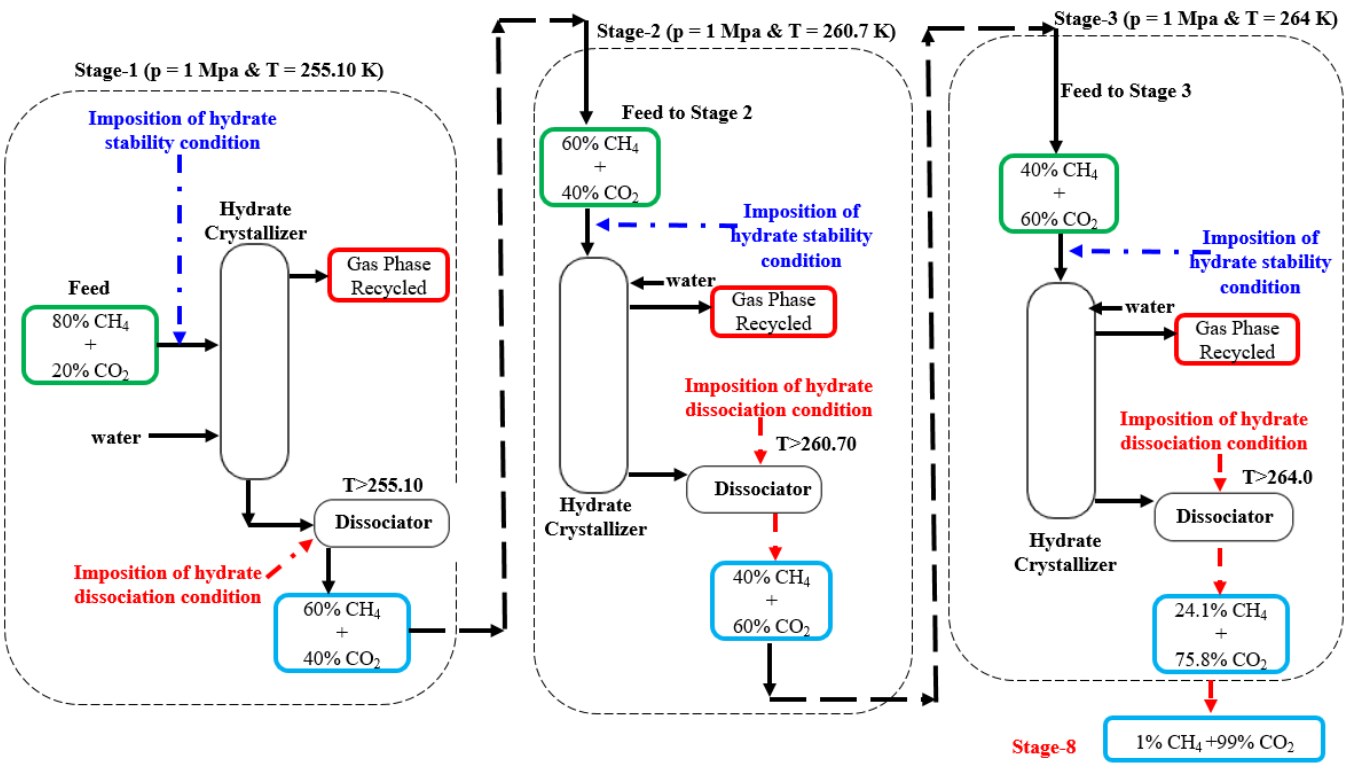


Figure 9. Process design for CO_2 + CH_4 separation. Reproduced with permission from ref. [9]. 2015 M.N. Khan, Ph.D. Thesis.

Additionally, a detailed investigation of the separation stage's dependency on process conditions leads to selecting optimum process conditions to achieve desired separation. Behzad et al. (2019) [35] conducted the experimental investigation to identify the impact

of pressure on the separation of CH_4 from CH_4 + CO_2 gas mixtures. However, their experimental studies on various gas mixture compositions (CH_4/CO_2) with multiple system pressures clearly indicate that there is a non-linear dependency of system pressure to the separation factor. Nevertheless, it was concluded that, in addition to the process parameters (T, P, feed composition), retention time, molecular size, and the presence of promotors (e.g., THF, CP) play an important role in deciding the overall selective separation of the components [35,36]. In addition, the nonlinear dependency may be attributed to the large errors in liquid flow rate and the compositional data collected. A detailed experimental study on the kinetics of CH_4 + CO_2 systems with the simultaneous measurements of compositional data along with fractional cage occupancy measurements may give further insight about the effectiveness of the separation in real time. In addition, a systemic study to analyze the Xe recovery from natural gas in multiple gas hydrate separation was also conducted by Sergeeva et al. (2020) [37]. The efficient recovery of Xe from natural gas mixtures and the number of stages required is dictated by the stability pressure of HF (hydrate former) and is consistent with the current work's conclusion. Figure 11 shows the effect of the process T and P on the number of stages needed for CH_4/CO_2 separation. At low and medium pressures (5–10 MPa), both CH_4 and CO_2 compete for enclathration, which makes it difficult to separate these two gases (pinch point). However, at a high pressure of 80 MPa, one stage is all that is needed for efficient separation.

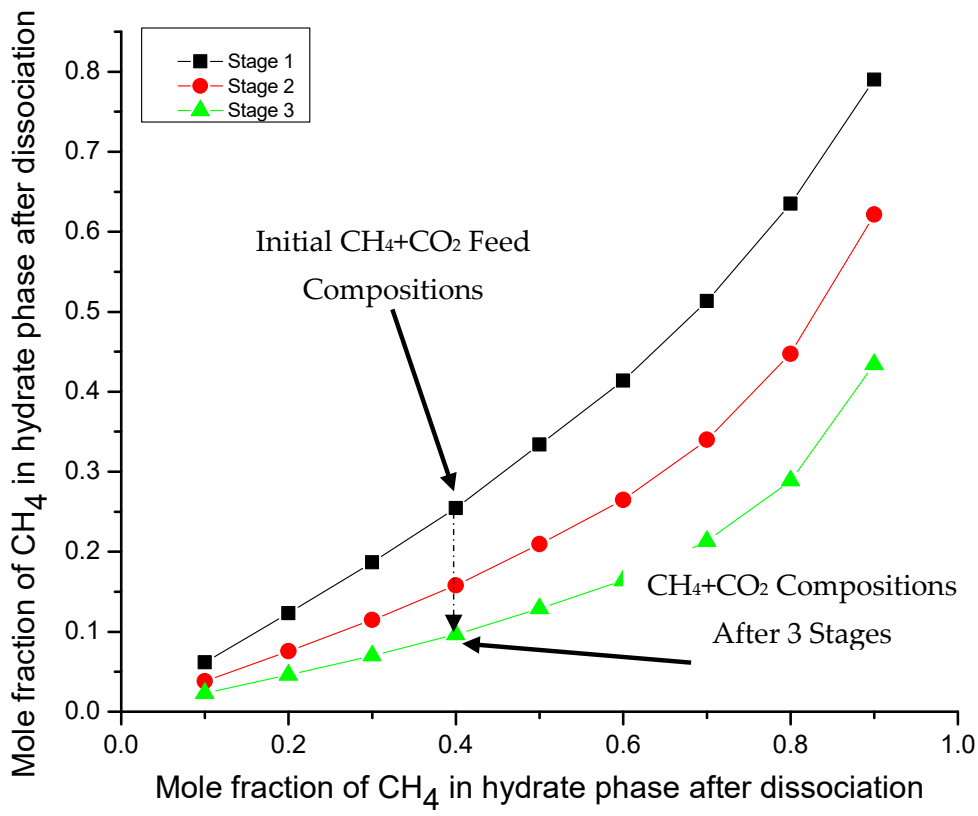


Figure 10. The relationship between mole fraction of CH_4 after dissociation from hydrate phase as a function of feed phase mole fraction for CH_4 + CO_2 binary system.

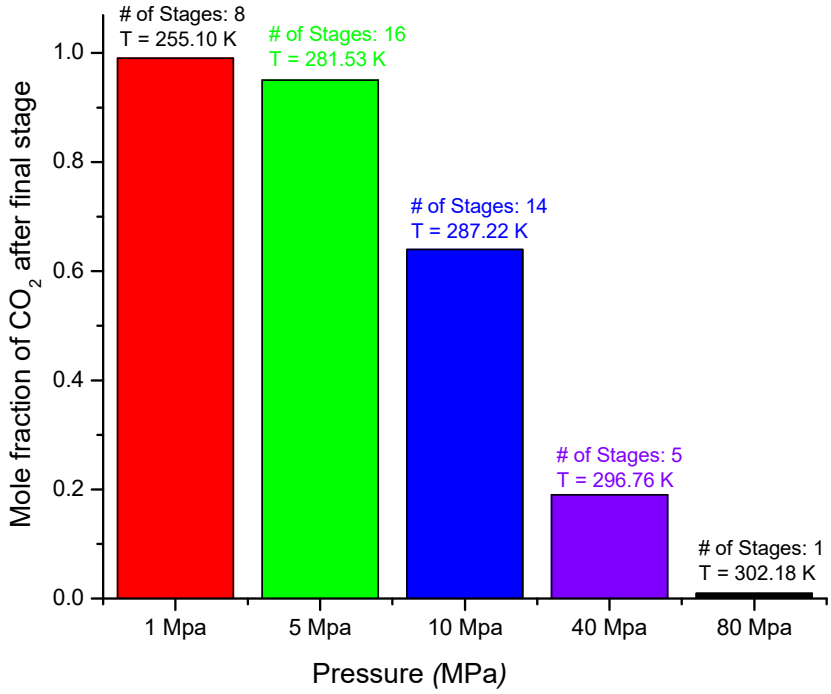


Figure 11. Effect of T, P on the number of separation stages for 80/20 CH_4/CO_2 gas mixture. Reproduced with permission from ref. [9]. 2015 M.N. Khan, Ph.D. Thesis.

3.3. Process Design for N_2 + CO_2 Mixture

To further exhibit the effectiveness of CO_2 capture from the CO_2 + N_2 gas mixture, the phase equilibria calculations were conducted over a range of CO_2 concentrations. The phase equilibria calculations illustrate the range of temperature and pressure conditions over which desired separation can be achieved. Figure 12 shows the hydrate phase equilibria for the CO_2 + N_2 mixture. Increasing N_2 concentration causes the hydrate phase boundary to shift to a higher pressure and lower temperature.

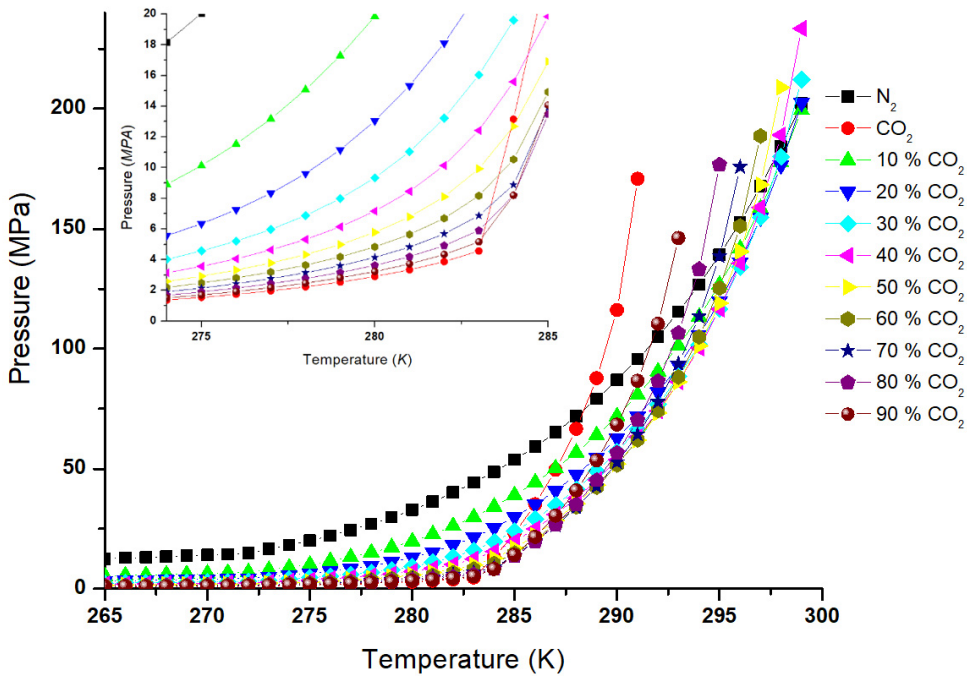
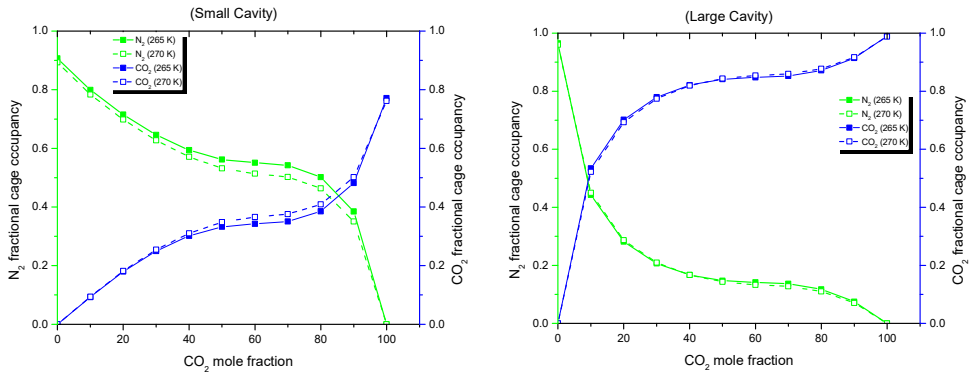


Figure 12. Predicted hydrate phase equilibria for N_2 + CO_2 mixture. Inset shows the expanded view. Reproduced with permission from ref. [9]. 2015 M.N. Khan, Ph.D. Thesis.

Fractional cage occupancies of CO_2 and N_2 in the small and large cage are shown in Figure 13. It can be observed that the N_2 cage occupancy in the small (5^{12}) and large ($5^{12}6^2/5^{12}6^4$) cavities decreases with increasing CO_2 content. The decrease in N_2 cage occupancy with the increase in temperature is associated with the decrease in the Langmuir constant.



(**a**) (**b**)

Figure 13. Fractional cage occupancy of hydrate formers in CO_2 + N_2 binary gas mixture for (**a**) Small Cavity and (**b**) Large Cavity at 15 MPa.

Figure 14 shows the process design diagrams for N_2 + CO_2 mixture. Upon subsequent hydrate formation and dissociation, 99 mol% of CO_2 can be removed with a total of at least two stages from the feed stream at 1 MPa.

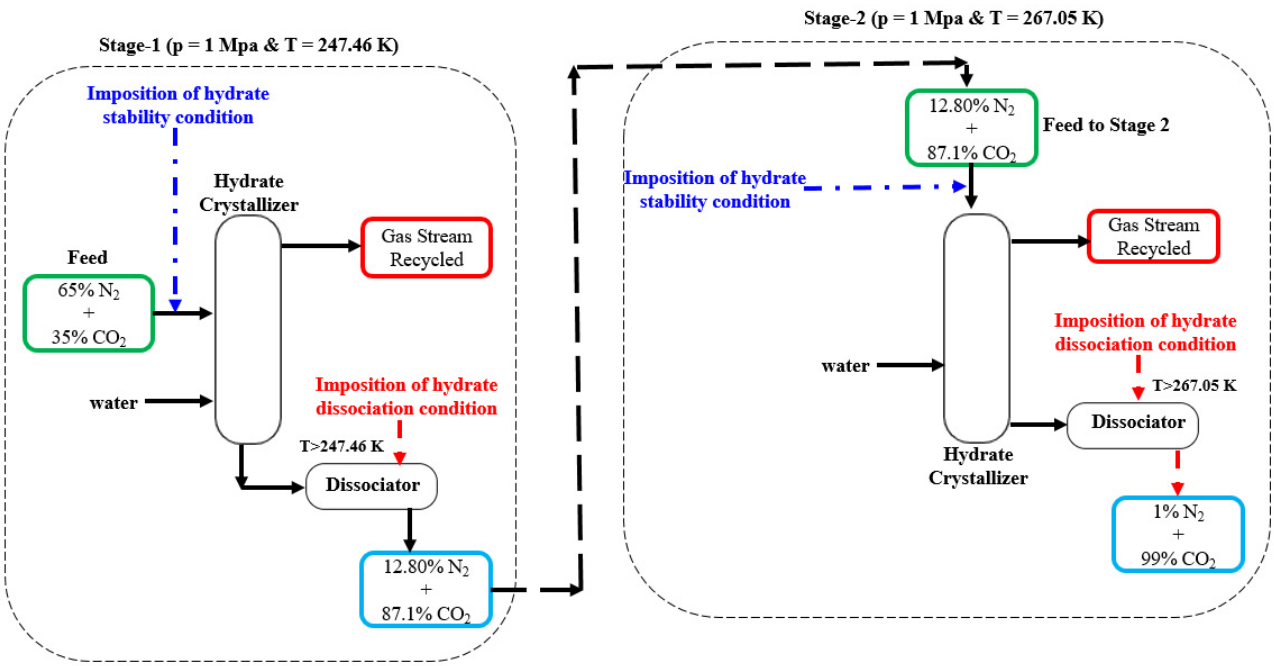


Figure 14. Process design for CO_2 + N_2 separation. Reproduced with permission from ref. [9]. 2015 M.N. Khan, Ph.D. Thesis.

Figure 15 illustrates the effect of process T and P on the number of separation stages needed for N_2/CO_2 separation. The calculations reveal that, for CO_2 + N_2 separation, two stages are sufficient to have the desired separation, even at lower pressures (<1 MPa), as N_2 is a high-pressure hydrate former. However, at high pressures, N_2 and CO_2 show comparable fractional cage occupancies in small and large cages, which may lead to a pinch point.

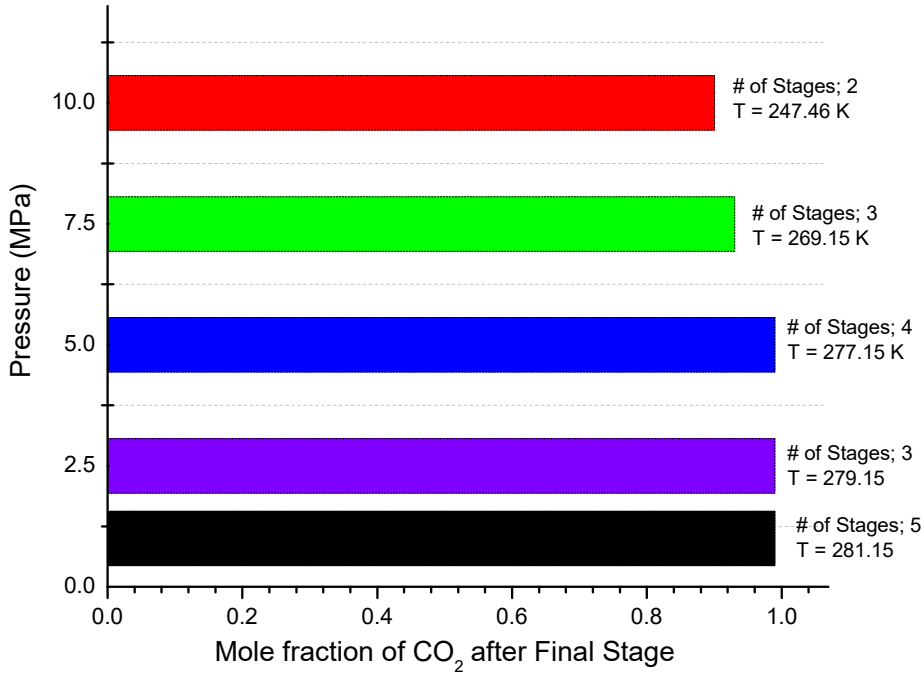


Figure 15. Effect of process T and P on the number of separation stages for N_2/CO_2 (65/35 mol.%). Reproduced with permission from ref. [9]. 2015 M.N. Khan, Ph.D. Thesis.

Moreover, it can be observed from Figure 16 that, for N_2 + CO_2 binary systems, a minimum of at least three stages are necessary for the clear and efficient removal of N_2 from the binary gas mixture. With increasing CO_2 concentration in the feed gas, nitrogen molecules were replaced by CO_2 in the hydrate phase, which is relatively more stable at critical process conditions.

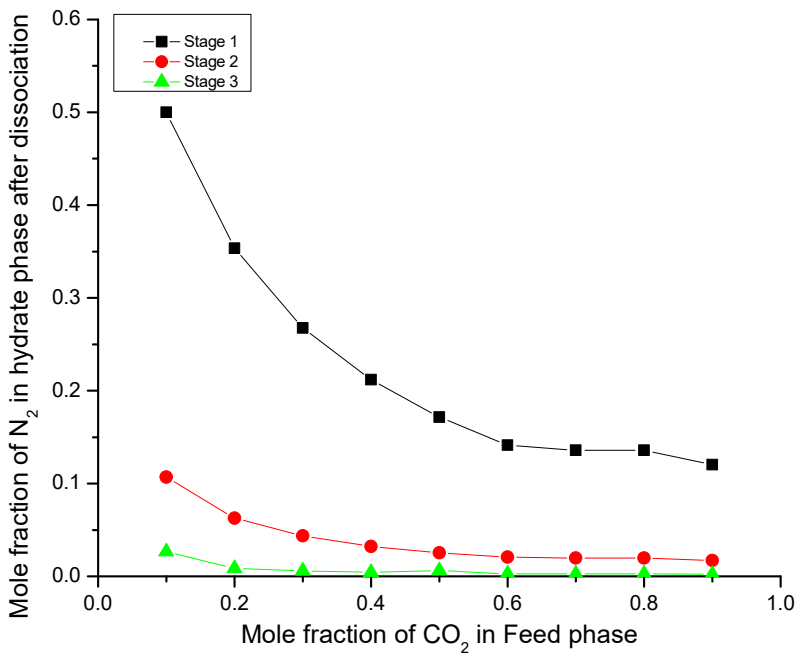


Figure 16. The relationship between mole fraction of N_2 after dissociation from hydrate phase as a function of CO_2 feed phase mole fraction for N_2 + CO_2 mixture.

3.4. Ternary Gas Mixture

A similar methodology was employed for ternary gas mixtures to further check the effectiveness of hydrate-based gas separation. The Gibbs energy minimization calculations were conducted for CH_4 + H_2S + CO_2 gas mixtures over a range of x_{H2S}/x_{CO2} ratios, as shown in Figure 17a–d. It is evident from Figure 17 that the percentage of H_2S recovered after hydrate dissociation increases over consecutive stage operations. A clear hydrate-based separation was achieved over a range of CH_4 mole fractions for various x_{H2S}/x_{CO2} ratios.

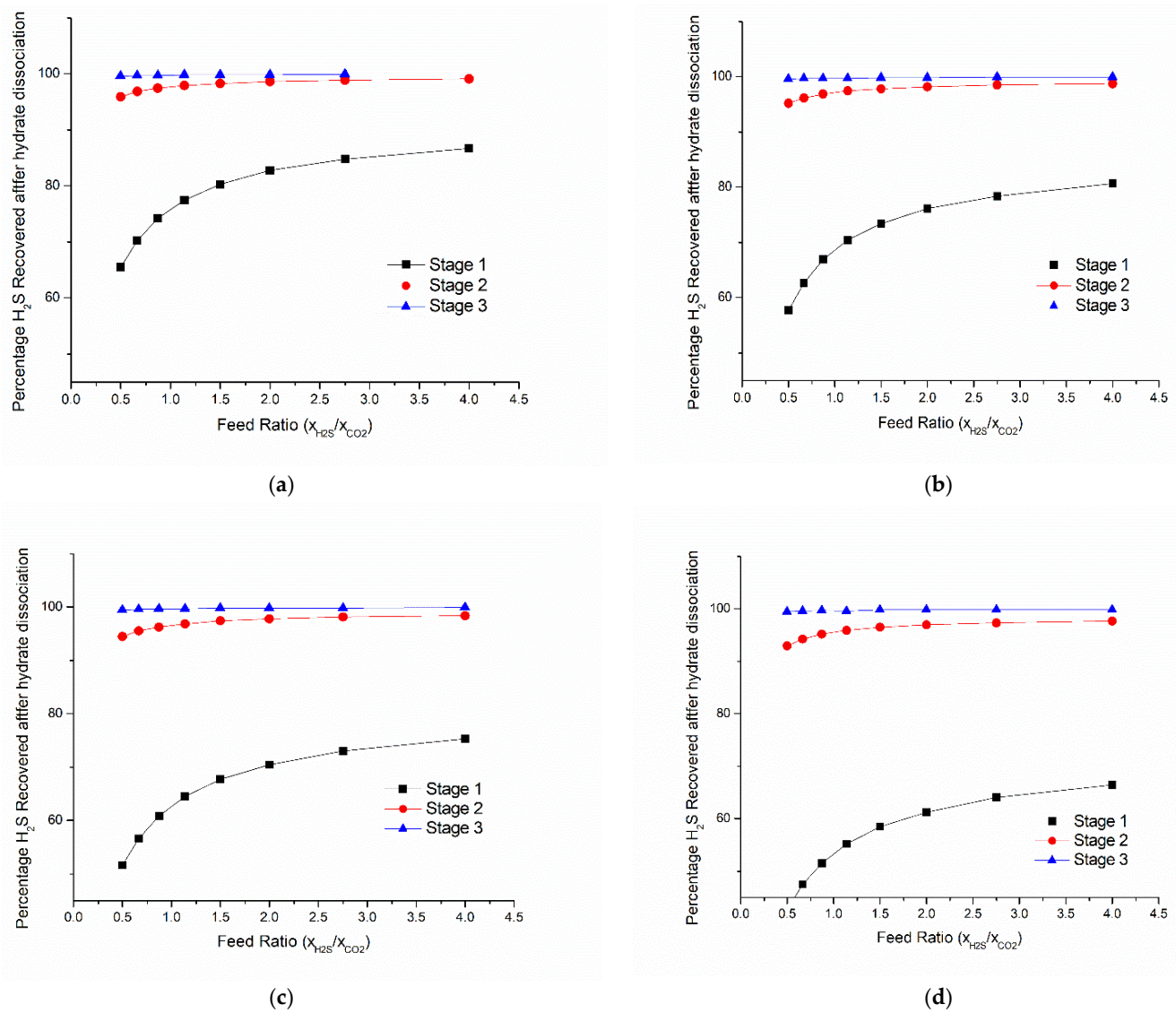
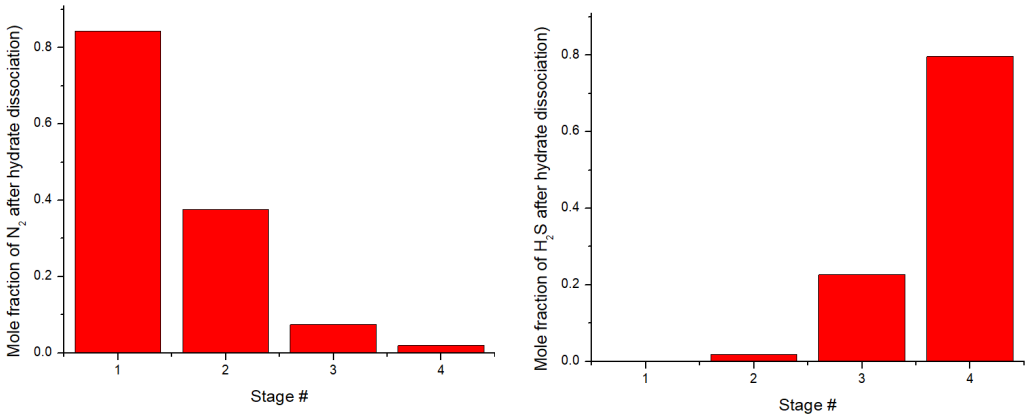


Figure 17. Effect of feed ratio (x_{H2S}/x_{CO2}) on percentage of H_2S recovered after hydrate dissociation: (**a**) 70 mol.% CH_4 in feed, (**b**) 80 mol.% CH_4 in feed, (**c**) 85% mol.% CH_4 in feed (**d**) 90 mol.% CH_4 in the feed.

Phase equilibria calculations were also carried out for ternary gas mixtures (Figure 18; 84.2% N_2 + 0.05% H_2S + 15.7% CO_2). Multiple stages are necessary to capture H_2S from the ternary gas mixture. A detailed analysis of the hydrate-based separation shows that the number of stages required to attain the desired separation efficiency depends on the nature of the gas mixture and on hydrate stability.



(**a**) (**b**)

Figure 18. The enclathration of (**a**) change in N_2 mole fraction for subsequent stages and (**b**) change in H_2S mole fraction for subsequent stagesfrom ternary gas mixture as a function of separation stage #.

In addition, calculations were performed for multiple other ternary gas mixture compositions (for N_2 + H_2S+ CO_2 ternary systems), and the decrease in mole fraction of nitrogen for each stage is presented in Figure S1 (Supplementary Materials).

4. Conclusions

A clathrate hydrate-based process has been presented for separating different components of industrial waste gas mixtures. The fundamental principle behind this separation is the thermodynamics of the formation of the hydrate phase by different molecules. Hydrate phase equilibria for various binary and ternary gas mixtures were computed to determine the feasibility of hydrate-based gas separation. The fractional cage occupancies and component mole fraction were also estimated to determine optimum process parameters to achieve the desired separation. Process designs have also been proposed for separation of some industrially relevant gas mixtures, including CH_4 + CO_2, N_2 + CO_2, CH_4 + H_2S, CH_4 + H_2S + CO_2, and N_2 + H_2S + CO_2 mixtures. Recovery and selectivity for gaseous mixtures were significantly dependent on the hydrate former polarity and process conditions.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/en15030966/s1. Table S1. Phase Stability criteria for GEM algorithm. 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). Figure S2. Predicted Recoveries of CH_4 and H_2S in binary hydrate systems for a range of H_2S concentrations.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Linga, P.; Kumar, R.; Lee, J.D.; Ripmeester, J.; Englezos, P. A new apparatus to enhance the rate of gas hydrate formation: Application to capture of carbon dioxide. *Int. J. Greenh. Gas Control* **2010**, *4*, 630–637. [CrossRef]
2. Matsuda, S.; Tsuda, H.; Mori, Y.H. Hydrate formation using water spraying onto a cooled solid surface in a guest gas. *AIChE J.* **2006**, *52*, 2978–2987. [CrossRef]
3. Chatti, I.; Delahaye, A.; Fournaison, L.; Petitet, J.P. Benefits and drawbacks of clathrate hydrates: A review of their areas of interest. *Energy Convers. Manag.* **2005**, *46*, 1333–1343. [CrossRef]
4. Gudmundsson, J.S.; Andersson, V.; Levik, O.I.; Mork, M. Hydrate Technology for Capturing Stranded Gas. *Ann. N. Y. Acad. Sci.* **2000**, *912*, 403–410. [CrossRef]
5. Englezos, P. Clathrate hydrates. *Ind. Eng. Chem. Res.* **2002**, *32*, 1251–1274. [CrossRef]
6. Makogon, I. *Hydrates of Natural Gas*; PennwWell Books: Tulsa, OK, USA, 1981.
7. Thomas, S.; Dawe, R.A. Review of ways to transport natural gas energy from countries which do not need the gas for domestic use. *Energy* **2003**, *28*, 1461–1477. [CrossRef]
8. Adeyemo, A.; Kumar, R.; Linga, P.; Ripmeester, J.; Englezos, P. Capture of carbon dioxide from flue or fuel gas mixtures by clathrate crystallization in a silica gel column. *Int. J. Greenh. Gas Control* **2010**, *4*, 478–485. [CrossRef]
9. Khan, M. *Phase Equilibria Modeling of Inhibited Gas Hydrate Systems Including Salts: Applications in Flow Assurance, Seawater Desalination and Gas Separation*; Colorado School of Mines: Golden, CO, USA, 2016.
10. Trautz, R.; Swisher, J.; Chiaramonte, L.; Hollis, R.; Perron, J.; Pronske, K.; Myhre, R.; Stone, M.; Saini, D.; Jordan, P.; et al. *California CO_2 Storage Assurance Facility Enterprise (C2SAFE): Final Technical Report*; Pittsburgh, PA, USA; Morganrown, WV, USA, 2018. [CrossRef]
11. Bergerson, J.A.; Lave, L.B. Baseload coal investment decisions under uncertain carbon legislation. *Environ. Sci. Technol.* **2007**, *41*, 3431–3436. [CrossRef] [PubMed]
12. U.S. Energy Administration, Office of Integratedand International Energy Analysis. *Annual Energy Outlook 2013 with Projections to 2040*; 2013. [CrossRef]
13. Carbon Capture and Storage: An Effective Way to Mitigate Global Warming on JSTOR. Available online: https://www.jstor.org/stable/24098511 (accessed on 29 September 2021).
14. Abbasi, T.; Tauseef, S.M.; Abbasi, S.A. Anaerobic digestion for global warming control and energy generation—An overview. *Renew. Sustain. Energy Rev.* **2012**, *16*, 3228–3242. [CrossRef]
15. Yu, C.-H.; Huang, C.-H.; Tan, C.-S. A Review of CO_2 Capture by Absorption and Adsorption. *Aerosol Air Qual. Res.* **2012**, *12*, 745–769. [CrossRef]
16. Lott, D.E. Improvements in noble gas separation methodology: A nude cryogenic trap. *Geochem. Geophys. Geosystems* **2001**, *2*, 2001GC000202. [CrossRef]
17. Bernardo, P.; Drioli, E.; Golemme, G. Membrane Gas Separation: A Review/State of the Art. *Ind. Eng. Chem. Res.* **2009**, *48*, 4638–4663. [CrossRef]
18. Kang, S.-P.; Lee, H.L. Recovery of CO_2 from Flue Gas Using Gas Hydrate: Thermodynamic Verification through Phase Equilibrium Measurements. *Environ. Sci. Technol.* **2000**, *34*, 4397–4400. [CrossRef]
19. Aaron, D. Separation of CO_2 from Flue Gas: A Review. *Taylor Fr.* **2005**, *40*, 321–348. [CrossRef]
20. Klara, S.M.; Srivastava, R.D. U.S. DOE integrated collaborative technology development program for CO_2 separation and capture. *Environ. Prog.* **2002**, *21*, 247–253. [CrossRef]
21. Linga, P.; Kumar, R.; Englezos, P. Gas hydrate formation from hydrogen/carbon dioxide and nitrogen/carbon dioxide gas mixtures. *Chem. Eng. Sci.* **2007**, *62*, 4268–4276. [CrossRef]
22. Linga, P.; Kumar, R.; Englezos, P. The clathrate hydrate process for post and pre-combustion capture of carbon dioxide. *J. Hazard. Mater.* **2007**, *149*, 625–629. [CrossRef]
23. Linga, P. Separation of Carbon Dioxide from Flue Gas (Post-Combustion Capture) via Gas Hydrate Crystallization. Ph.D. Thesis, University of British Columbia, Vancouver, BC, Canada, 2009. [CrossRef]
24. Azari, A.; Atashrouz, S.; Mirshekar, H.; González, A.; Okumura, K.; Ten Elshof, J.E. Prediction the Vapor-Liquid Equilibria of CO_2-Containing Binary Refrigerant Mixtures Using Artificial Neural Networks. *ISRN Chem. Eng.* **2013**, *2013*, 930484. [CrossRef]
25. Platteeuw, J.C.; van der Waals, J.H. Thermodynamic properties of gas hydrates. *Mol. Phys.* **1958**, *1*, 91–96. [CrossRef]
26. Ward, Z.T. *Phase Equilibria of Gas Hydrates Containing Hydrogen Sulfide and Carbon Dioxide*; Colorado School of Mines: Golden, CO, USA, 2015.
27. Khan, M.N.; Warrier, P.; Peters, C.J.; Koh, C.A. Advancements in hydrate phase equilibria and modeling of gas hydrates systems. *Fluid Phase Equilib.* **2018**, *463*, 48–61. [CrossRef]
28. Khan, M.N.; Warrier, P.; Creek, J.L.; Peters, C.J.; Koh, C.A. Vapour-liquid equilibria (VLE) and gas hydrate phase equilibria predictions using the cubic-plus association equation of state: CSMGem extension to association EoS model. *J. Nat. Gas Sci. Eng.* **2021**, *94*, 104083. [CrossRef]
29. Shock, E.L.; Helgeson, H.C. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic species. *Geochim. Cosmochim. Acta* **1990**, *54*, 915–945. [CrossRef]
30. 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.

31. Sloan, E.D., Jr.; Koh, C.A. *Clathrate Hydrates of Natural Gases*; CRC Press: Golden, CO, USA, 2007.
32. Ballard, A.L.; Sloan, E.D. The next generation of hydrate prediction: Part III. Gibbs energy minimization formalism. *Fluid Phase Equilib.* **2004**, *218*, 15–31. [CrossRef]
33. Jager, M.D.; Ballard, A.L.; Sloan, E.D. The next generation of hydrate prediction: II. Dedicated aqueous phase fugacity model for hydrate prediction. *Fluid Phase Equilib.* **2003**, *211*, 85–107. [CrossRef]
34. Ballard, A.L.; Sloan, J.D. The Next Generation of Hydrate Prediction: An Overview. *J. Supramol. Chem.* **2002**, *2*, 385–392. [CrossRef]
35. Partoon, B.; Sabil, K.M.; Lau, K.K.; Nasrifar, K.; Shariff, A.M. Selective Separation of Methane from Carbon Dioxide through sII Hydrates Formation in a Semibatch Process. *Ind. Eng. Chem. Res.* **2019**, *58*, 16834–16842. [CrossRef]
36. Partoon, B.; Sabil, K.M.; Lau, K.K.; Lal, B.; Nasrifar, K. Production of gas hydrate in a semi-batch spray reactor process as a means for separation of carbon dioxide from methane. *Chem. Eng. Res. Des.* **2018**, *138*, 168–175. [CrossRef]
37. Sergeeva, M.; Petukhov, A.; Shablykin, D.; Trubyanov, M.; Atlaskin, A.; Malyshev, V.; Vorotyntsev, V. Xenon recovery from natural gas by multiple gas hydrate crystallization: A theory and simulation. *Sep. Sci. Technol.* **2020**, *55*, 144–154. [CrossRef]