Production and Storage of HFC-125a/CO_2 Solid Clathrate Hydrates for CO_2 Capture Applications

Introduction

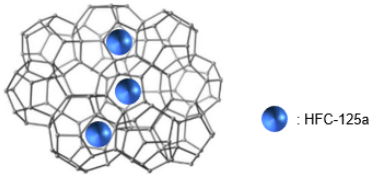
The increasing concentration of carbon dioxide (CO_2) in the atmosphere has intensified concerns rega rding global climate change and has accelerated the development of carbon capture, utilization, and st orage (CCUS) technologies. Among various CO_2 capture and storage methods, clathrate hydrate techn ology has attracted significant attention due to its ability to store large amounts of gas within crystalli ne water cages. Hydrate-based CO_2 capture offers several advantages, including high gas storage capa city, environmental compatibility, and the potential for long-term storage. Despite these advantages, t he practical application of pure CO_2 hydrates remains challenging because hydrate formation generall y requires relatively high pressures and low temperatures. These operating conditions increase energy consumption and limit the economic feasibility of hydrate-based CO_2 capture processes. Therefore, th e use of hydrate promoters has been widely investigated to improve hydrate formation kinetics and re duce hydrate formation pressure. HFC-125a is a hydrate-forming gas that readily forms structure II hy drates and has been reported to promote hydrate formation under milder thermodynamic conditions. T he incorporation of HFC-125a into a CO_2 hydrate system may facilitate hydrate formation and enhanc e CO_2 capture efficiency, particularly under subzero-temperature conditions. In this study, HFC-125a was employed as a hydrate promoter to investigate its potential for enhancing CO_2 capture through cla thrate hydrate formation under subzero-temperature conditions. The effect of the initial HFC-125a pre ssure on hydrate formation behavior and subsequent CO_2 incorporation was examined.

Method

Hydrate formation experiments were conducted to investigate the effect of HFC-125a on CO_2 capture through clathrate hydrate formation under subzero-temperature conditions. Ice powder was used as th e water phase and loaded into a high-pressure reactor. All experiments were performed at 263.15 K. T o evaluate the promoting effect of HFC-125a on hydrate formation, HFC-125a was initially injected i nto the reactor at pressures of 2, 3, 4, and 5 bar. After reaching the target HFC-125a pressure, CO_2 wa s introduced into the reactor to form a mixed-gas hydrate system. The reactor pressure and temperatur e were continuously monitored throughout the hydrate formation process. Hydrate formation behavior was analyzed using pressure reduction profiles and gas consumption characteristics. The influence of t he initial HFC-125a pressure on CO_2 incorporation into the hydrate phase was investigated by compar ing hydrate formation kinetics, gas uptake behavior, and hydrate stability under identical temperature conditions. The experimental results will be used to assess the feasibility of employing HFC-125a as a hydrate promoter for enhancing CO_2 capture and storage performance at subzero temperatures.

Results and Discussion

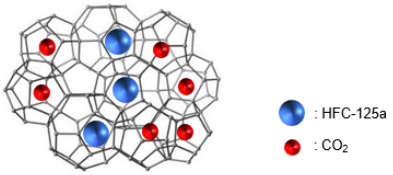
Pure HFC-125 hydrate structure



HFC-125a occupies **only the large cages** of sII hydrate.

Hydrate structure	sII
Water molecules per unit cell	136
Available cages	8L-cage
Small cage occupancy	**Vacant**
Gas storage density	**Lower**

HFC-125 + CO_2 binary hydrate structure



CO_2 **additionally occupies** the vacant **small cages**.

Hydrate structure	sII
Water molecules per unit cell	136
Available cages	8L-cage **+ 16S-cage**
Small cage occupancy	**CO_2 occupied**
Gas storage density	**Higher**

Figure 1 Comparison of cage occupancy in pure HFC-125a hydrates and HFC-125a/CO_2 binary hydrates.

Pure HFC-125a hydrates preferentially occupy the large cages of structure II hydrates, while the incorporation of CO_2 allows additional occupancy of the small cages within the hydrate framework. This dual guest occupancy mechanism is expected to enhance overall gas storage capacity and improve the efficiency of hydrate-based CO_2 capture systems. Therefore, understanding the formation and stability characteristics of pure HFC-125a hydrates is an important prerequisite for the development of HFC-125a/CO_2 mixed hydrate systems. HFC-125a hydrates were successfully formed using ice powder under subzero-temperature conditions. Hydrate formation was confirmed by gas con sumption during the formation stage and subsequent gas release during dissociation. The experimental results demonstrated that HFC-125a can form stable hydrates at temperatures below the freezing point of water, indicating its potential as a hydrate-forming promoter for future CO_2 capture applications. The equilibrium curve shifts toward lower pressures due to the presence of HFC-125a, suggesting that HFC-125a may act as an effective thermodynamic promoter for hydrate-based CO_2 capture and storage processes. The hydrate formation behavior strongly depended on the initial HFC-125a pressur e. For the 4 bar system, hydrate conversion ranged from 46.97% to 75.39%, with an average conversi on of 57.13%. In contrast, the 5 bar system exhibited an average conversion of 45.59%. The highest g as consumption was observed in the 4 bar experiment, where approximately 0.036 mol of HFC-125a was incorporated into the hydrate phase. These results suggest that increasing the initial pressure does not necessarily improve hydrate formation efficiency under subzero conditions. Hydrate stability was further evaluated through controlled dissociation experiments. The stored gas was gradually released a s the temperature increased from approximately 275 K to 288 K. The amount of released gas ranged fr om 0.0319 to 0.0499 mol, confirming that a significant portion of HFC-125a was retained within the h ydrate structure during storage. The highest released gas amount was observed in the 4 bar system, in dicating enhanced gas storage capability compared to the higher-pressure conditions. Overall, the resu lts demonstrate that HFC-125a hydrates can be formed and maintained under subzero conditions with considerable gas storage capacity. The successful hydrate formation and gas retention behavior sugges t that HFC-125a may serve as an effective thermodynamic promoter for future mixed-gas hydrate syst ems targeting CO_2 capture and storage. The successful formation of HFC-125a hydrates under subzer o conditions suggests that HFC-125a may serve as a potential promoter for future CO_2 hydrate capture studies.

Conclusions

HFC-125a hydrates were successfully formed using ice powder under subzero temperature conditions. The hydrate formation performance was influenced by the initial HFC-125a pressure, with the 4 bar condition exhibiting the highest hydrate conversion and gas storage capacity among the investigated conditions. Dissociation experiments confirmed that a significant amount of HFC-125a was retained within the hydrate structure and subsequently released during decomposition, demonstrating the stability of the formed hydrates. These results indicate that HFC-125a can effectively promote hydrate formation under mild subzero conditions and possesses considerable gas storage capability. Therefore, HFC-125a shows strong potential as a thermodynamic promoter for future mixed-gas hydrate systems aimed at CO_2 capture and storage applications.

Acknowledgements

National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (RS2023-00280519)
Korea Basic Science Institute (National research Facilities and Equipment Center) grant funded by the Korea government (MSIT) (RS-2024-00404896)
Korea Planning & Evaluation Institute of Industrial Technology funded by the Korean government (Ministry of Trade, Industry, and Energy, MSIT, Ministry of the Interior and Safety, National Fire

Agency, Project Title: Development of gas hydrate extinguishing agent and fire suppression technology for inaccessible fires, Project Number: 2760000002)
Global - Learning & Academic research institution for Master's·PhD students, and Postdocs (LAMP) Program of the NRFgrant funded by the Ministry of Education (RS-2025-25440216).
This research was supported by the Regional Innovation System & Education(RISE) program through the Institute for Regional Innovation System & Education in Busan Metropolitan City, funded by the Ministry of Education(MOE) and the Busan Metropolitan City, Republic of Korea.(2026-RISE-02-003)

References

Burla, S.K., Seo, S.D. and Lee, J.D. [2026] Structure-dependent formation of HFC-125a/CO_2 mixed hydrates: Raman evidence and implications for fire suppression. *Chem & Bio Engineering*, **3**, 396–405.

Jabeen, M. and Islam, M.S. [2024] A comprehensive review of semi-clathrate hydrates for CO_2 capture: Characterizations, mechanism and role of promoters. *Carbon Capture Science & Technology*, **12**, 100217.

Sabawa, J.P. and Bandarenka, A.S. [2019] Thermodynamic and kinetic influences of NaCl on HFC-125a hydrates and their significance in gas hydrate-based desalination. *Chemical Engineering Journal*, **358**, 598–605.

Lee, J.D. [2024] Exploring the potential of HFC-125a hydrate for innovative fire suppression: A gas hydrate technology approach. *Energy & Fuels*, **38**, 6238–6250.