# Effect of the Reactor Configuration and Operational Parameters on Formation, Growth and Dissociation of Carbon Dioxide Hydrate – A Combined Experimental and Computational Study

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## ABSTRACT

Clathrate hydrate-based technologies have been considered as promising alternatives for the mitigation of the climate change caused by emissions of carbon dioxide produced by combustion of fossil fuels by industrial facilities, and other human activities. Clathrate hydrates (also called gas hydrates) are nonstoichiometric crystalline ice-like substances, consisting of a hydrogen-bonded lattice formed by water molecules (host) and entrapped gas molecules (guest), which are not bonded with the lattice [1]. These ice-like inclusion compounds are formed under particular conditions of temperature and pressure. Their main advantage is the drastic reduction of the volume of the enclathrated gas compared with that in the gaseous phase. The environmentally friendly profile of the clathrate hydrate-based processes, their low energy costs and simplicity, constitute some of their evident benefits, comparing to conventional methods for capturing $CO_2$. Under standard temperature and pressure, the maximum volume of gas stored in 1 $m^3$ of $CO_2$ hydrate is about 170 $m^3$. The large uptake of $CO_2$ in clathrate hydrates renders them a promising option for carbon capture and storage [3], flow assurance and safe $CO_2$ pipeline transportations [4], $CO_2$ disposing and sequestration [5], as well as for $CO_2$-rich natural gas upgrade [6].

This work presents a combined experimental and computational investigation of the effects of the operational procedures and experimental configuration characteristics, on the phase diagrams of $CO_2$-$H_2O$ systems and $CO_2$ hydrates formation, growth and dissociation conditions. The operational modes involved (i) incremental (step-wise) temperature cycling and (ii) continuous temperature cycling processes, in the framework of an Isochoric Pressure-Search method. Also, two different high pressure PVT configurations were used, of which one encompassed a stirred tank reactor with mechanical agitation of the liquid phase, and the other incorporated an autoclave of constant volume with magnetic stirring. The experimental results implied a dependence of the subcooling degree, (P, T) conditions for hydrate formation and dissociation, and thermal stability of the hydrate phase on the applied temperature cycling modes, and the technical features of the utilized PVT configurations. The experimental findings were complemented by a thermodynamic simulation model, with the aim to resolve the phase diagrams including the $CO_2$ dissolution over the entire range of the applied (P, T) conditions.

## REFERENCES

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