

A new experimental and modelling study on non-equilibrium crystallization of mixed gas hydrates involving hydrate volume and composition

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Abstract

The importance of studying clathrate hydrate is not only the issues in the oil and gas extraction and transportation, but also several new applications, like water treatment, carbon capture and storage, air conditioning, or even planetary science [1]–[3]. The enormous amounts of methane hydrate which have been found in the world's oceans and Polar Regions, is also a vital importance [4]. Hence, it is obvious that studying the thermodynamics and the crystallization mechanisms of clathrate hydrates is really inevitable to investigate gas hydrate phenomena.

However gas hydrates from hydrocarbon gas mixtures have been widely studied, but few data involving propane and butane are available. Moreover, these studies do not provide the hydrate volume and water consumption. The determination of the gas composition in hydrate phase, as well as its volume, is also technical challenges and few data is available in the literature. During the last decade, our "GasHyDyn" team has measured equilibrium data for many gas mixtures [5], [6], and this document adds new data involving propane. Based on a new approach in our laboratory, the molar composition of each phase (Gas, liquid and hydrate phases) as well as hydrate volume and water conversion has been also investigated. This document also adds the impact of the crystallization rate on the composition of gas in hydrate phase during the crystallization and final state, based on two different experimental procedures; quick crystallization process and slow crystallization process. To evaluate the importance of kinetic effects on hydrate formation, a thermodynamic model, implementing classic van der Waals and Platteuw model, were used.

The results show that from the same initial conditions, the final pressure and water conversion are slightly different for two different crystallization processes (Figure 1). Furthermore, it was noticed that the enclathration of the heavier molecule (here propane) is more important at slow than quick crystallization rate and composition of propane in hydrate phase at final state in slow crystallization is more than quick crystallization. The Volume of hydrate and also water conversion in quick crystallization process is larger than slow crystallization rate. Moreover, the thermodynamic simulation of hydrate phase has a better accordance with the results of slow crystallization rate. Hence, it might be concluded that mixed hydrate equilibrium could not be at thermodynamic equilibrium.

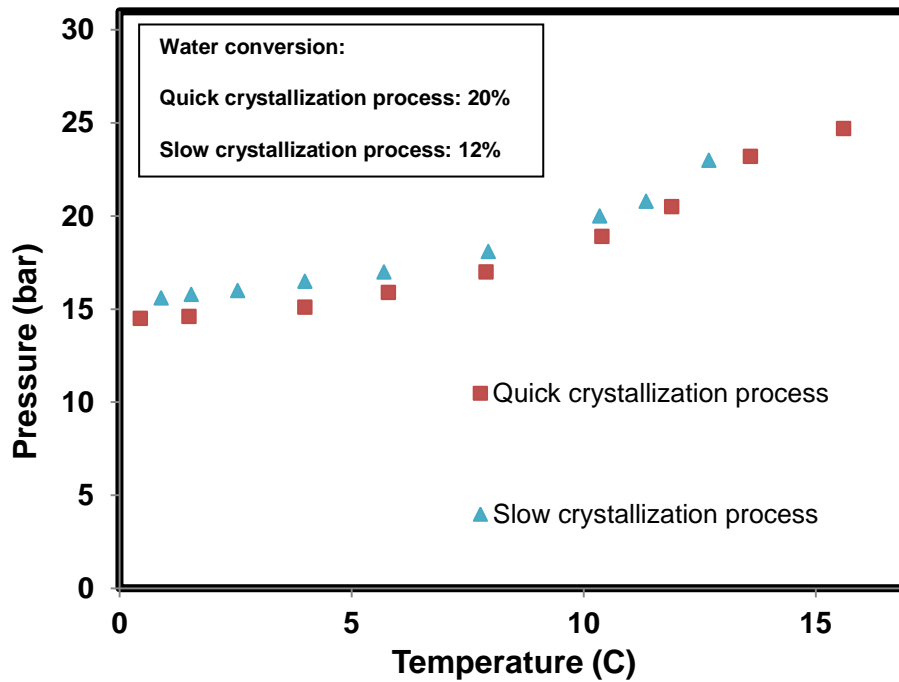


Figure 1. The comparison between the results of equilibrium points for a mixture of methane-propane and two different crystallization rates.

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