

A new approach of experimental and modelling study of mixed gas hydrates under non-equilibrium conditions

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Abstract

Although clathrate hydrate formation in the oil and gas industry, from extraction to transportation, is a crucial issue, several applications of clathrate hydrates have been recently investigated, like water treatment, carbon capture and storage, air conditioning, or even planetary science. Moreover, enormous amounts of methane hydrate have been found in the world's oceans and polar regions. The amount of buried methane hydrate is estimated to exceed the volume of all known conventional gas resources (Sloan and Koh, 2007). Hence, it is obvious that studying the thermodynamics and the crystallization mechanisms of clathrate hydrates is really inevitable to investigate gas hydrate phenomena. The determination of the gas composition in hydrate phase, as well as its volume, is also technical challenges due to lack of data in the literature. Therefore, in this work, several experiments were performed to obtain precious experimental data, such as hydrate composition and volume.

Our "GasHyDyn" group has recently found out that the composition of gas hydrate is sensitive to the crystallization conditions (Le Quang et al., 2015). Hence in this work, one of the objectives was to find out the composition of gas in hydrate phase during the crystallization and final state and crystallization rates. Experiments were performed in two batch reactors. Online gas chromatography, connected to the experimental set-up, and an off-line ion-chromatography were used to measure the gas compositions in gas and liquid phases, respectively. By applying mass balance based on these data, the gas compositions in hydrate phase and hydrate volume can be calculated.

During the last decade, our GasHyDyn team has also measured equilibrium data for many gas mixtures (Herri and Chassefière, 2012; Le Quang et al., 2015), and this document adds new data involving propane based on two different experimental procedures; quick crystallization process and slow crystallization process. The aim of the quick crystallization process is to study the gas hydrates formation in usual dynamic conditions and the aim of slow crystallization process is to investigate the impact of the speed of crystallization on the final equilibrium.

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. To evaluate the importance of kinetic effects on hydrate formation, a thermodynamic model, implementing classic van der Waals and Platteuw model, was used. The Kihara parameters for methane were taken from the previous works of our team (Herri and Chassefière, 2012) and the Kihara parameters for propane have been investigated in this work.

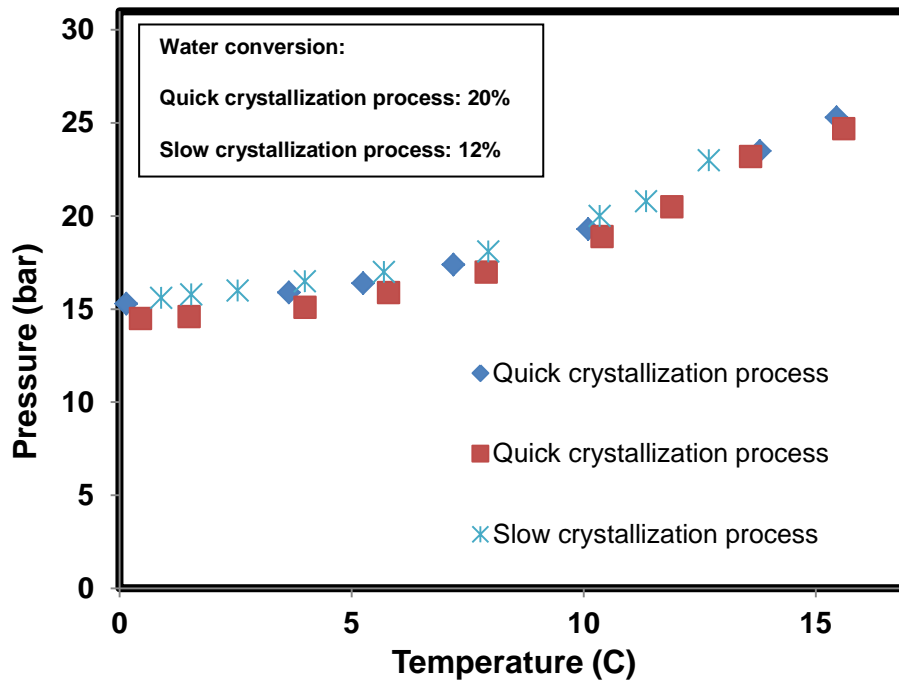


Figure 1. The comparison between the results of equilibrium points for a mixture of methane-propane and two different crystallization rates.

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