PHASE BEHAVIOUR STUDY OF GAS HYDRATES: POTENTIAL OPPORTUNITIES FOR CO_2 SEPARATION

by

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ABSTRACT

The presence of high CO_2 in certain natural gas reservoirs has posted huge challenges in the natural gas purification. Although there are several separation technologies like amine absorption and cryogenic process, their separation capability is limited to low CO_2 in natural gas. An alternative approach to separate high CO_2 from CO_2-CH_4 mixtures by formation of CO_2 hydrate is being explored in this work. The objectives were to study the phase behaviour of various gas hydrates and to investigate the effect of pressure, temperature, water and CO_2 compositions towards the separation of CO_2 from CO_2-CH_4 mixtures via formation of CO_2 hydrates. The research work was carried out by using an established thermodynamics hydrate program, CSMGem. This work was successfully predicted the equilibrium pressures of hydrate-liquid water-vapor (H-L_W-V) line for single hydrates (CH_4, C_2H_6, C_3H_8, CO_2 and N_2) with calculated AAD% less than 5%. The formation of single hydrates was found to be more favourable by increasing operating pressure and decreasing temperature. The AAD% was further improved by introducing pressure correction factor known as cavity constant, λ. It was found that the calculated AAD% for CO_2 and C_3H_8 hydrates were improved by 20% and 27%, respectively. The formations of binary hydrates (CH_4-C_2H_6, CH_4-C_3H_8, CH_4-CO_2 and CH_4-N_2) were found to depend on the type and compositions of gases present. The equilibrium lines of mixed hydrates were located in between those of single hydrates. Introduction of cavity constant of mixture, λ_{mix} has generally improved the predicted data for all binary hydrates. The highest improvement obtained was 69% for CH_4-C_3H_8 hydrate with CH_4 composition of 36.2%. The separation factor on separation of CO_2 from CO_2-CH_4 mixture was found in the range of 1.0 to 2.4 in the operating conditions studied. The separation factor was increasing with decreasing of pressures, temperatures and CO_2 compositions and vice-versa with water compositions. Introduction of multistage separation has further improved the separation factor from 2.3 to 22.5 for gas mixture with 30% of CO_2. However, it is not recommended for high CO_2 concentration as the number of moles in vapour phase at each stage decreases with increasing number of stages. It can be

concluded that the formation of CO_2 hydrate has a great potential to be further explored since it can be used to address separation of CO_2 from CO_2-CH_4 mixtures.