**Novel Hydrate-Based Gas Separation: A Process Design and Phase Equilibria Calculations**

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**Highlights**

* A Novel design for separation of high CO2 and H2S contents from sour gas mixture
* Implementation of GEM algorithm for gas separation process design
* # of stages required for desired separation dependent on process conditions

**1. Introduction**

Removal of acidic gases from natural gas mixtures is one of the prime objectives of industry. Depending upon the nature of separation and contaminants present in gas mixtures, there are various separation techniques available, e.g.: cryogenic fractionation, polymeric membranes, metal organic frameworks. Among them adsorption and absorption processes are the most common. Removal of high *H2S* and *CO2* contents require adequate methods to isolate them from natural gas (*NG*) mixtures. However, economic factors, high energy consumption and effective removal from the *NG* mixture is a restraining step [2-8].To achieve an efficient separation, several attempts were made to find a reliable and energy efficient alternative compared to conventional separation methodologies [9]. The use of hydrate formation for acidic gases removal can be a promising technique over a range of *T*, *P* and acidic gas contents. The separation of H2S & CO2 gases from acid gaseous mixture can be achieved via gas hydrate formation and as represented by the simplified scheme shown in Figure 1 [1].



Figure 2. Gibbs free energy minimization algorithm.

Figure 1. Conceptual picture for gas separation using hydrate formation [1].

**2. Methods**

Phase equilibria calculations were carried out using the modified vdWP model + Gibbs energy minimization algorithm over a range of temperature, pressure and CO2/H2S concentrations. Simplified algorithm for the Gibbs energy minimization algorithm was demonstrated in Figure 2 [1].

**3. Results and discussion**

The enclathration of carbon dioxide, hydrogen and natural gas are key applications for gas hydrates, since clathrates can adsorb gases in high concentrations. Hence, gas hydrates can provide an effective removal of acidic gases from natural gas mixtures. In this work gas separation via hydrate formation was proposed and a statistical thermodynamic model was used for hydrate phase equilibria calculations to validate the performance of a hydrate-based separation process. During hydrate-based separation, gas mixtures with various acidic gas contents were brought in direct contact with brine or pure water under low temperature and high-pressure conditions to attain stable conditions for hydrate crystals nucleation. Multiphase equilibria calculations were also performed for various gas mixtures (*CH4 + CO2, CH4 + H2S, CO2 + CH4 + H2S and CO2 + CH4+C2H6 + H2S + N2*) over a range of compositions and T, P conditions to establish the suitable region for separation. In addition, the fractional cage occupancy and the compositions of gases in each phase were also calculated to support the optimal selection of separation temperature and pressure conditions. Recovery and selectivity for gaseous mixtures were found to be significantly dependent on the hydrate former polarity and process conditions. Furthermore, a novel process design diagram (*PDD*) was also proposed for various gas mixtures to be separated and process conditions.

**4. Conclusions**

A process design has been proposed for removal of acidic gases from natural gas mixtures to achieve desired selectivity in gas mixtures, where removal of H2S & CO2 is carried out based on a component’s ability to form hydrate crystals. Moreover, hydrate phase equilibria calculations for hydrates of CO2, H2S with various hydrocarbons compositions are calculated to locate optimum separation conditions. Fractional cage occupancy and acidic gas fractions were calculated in all the possible phases present to determine separation *T* and *P* conditions. Recovery and separation factor for various acidic gas mixtures were found to be strongly dependent on process conditions and feed gas compositions. A detailed analysis of the hydrate-based separation leads to the fact that the number of stages required to attain a desired separation efficiency was dependent on the nature of the gas mixture and the hydrate stability.

**5. References**

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