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Modelling of tetrahydrofuran promoted gas hydrate systems for carbon dioxide capture processes

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ABSTRACT

A thermodynamic modelling study of both fluid phase behaviour and hydrate phase behaviour is presented for the quaternary system of water, tetrahydrofuran, carbon dioxide and nitrogen. The applied model incorporates the Cubic-Plus-Association (CPA) equation of state for the fluid phase description and the van der Waals–Platteeuw hydrate model for the solid (hydrate) phase. Six binary pairs are studied for their fluid phase behaviour. CPA descriptions are adjusted when needed by correlation of binary parameters in the applied mixing- and combining rules. Kihara cell potential parameters in the hydrate model are regressed for the three hydrate formers, tetrahydrofuran, carbon dioxide and nitrogen. The developed model provides highly accurate descriptions of both fluid- and hydrate phase equilibria in the studied system and its subsystems.

The developed model is applied to simulate two simplified, gas hydrate-based processes for post-combustion carbon dioxide capture from power station flue gases.

The first process, an unpromoted hydrate process, operates isothermally at a temperature of 280 K. Applying three consecutive hydrate formation/dissociation stages (three-stage capture process), a carbon dioxide-rich product (97 mol%) is finally delivered at a temperature of 280 K and a pressure of 3.65 MPa. The minimum pressure requirement of the first stage is estimated to be 24.9 MPa, corresponding to the incipient hydrate dissociation pressure at 280 K for the considered flue gas.

A second simulated carbon dioxide capture process uses tetrahydrofuran as a thermodynamic promoter to reduce the pressure requirements. By doing so the minimum pressure requirement of the first capture stage is lowered to 0.41 MPa. Selectivity towards carbon dioxide in the hydrate phase is however lower than in the unpromoted process. Therefore the tetrahydrofuran promoted capture process needs four consecutive hydrate formation/dissociation stages to produce a 96 mol% carbon dioxide-rich product stream. This stream is delivered at 280 K and a pressure of 0.17 MPa.

The present modelling study suggests several drawbacks of using tetrahydrofuran as a thermodynamic hydrate promoter, when applied in low-pressure, hydrate-based gas separation processes. Due to the high volatility of this compound, the promoter readily transfers to the vapour phase. Furthermore, tetrahydrofuran lowers the selectivity towards carbon dioxide, and the gas uptake in general, in the hydrate phase compared to the unpromoted system.

1. Introduction

Carbon dioxide is a greenhouse gas. It absorbs and re-emits long-wave (infrared) radiation in the atmosphere of this planet. Part of this re-emitted radiation is send back to the surface of the planet, helping to retain thermal balance.

During the last 200 years, the amount of carbon dioxide present in the atmosphere has increased from 280 ppm to a level of about 390 ppm in 2010 [1,2].

Though ambiguously shown, there is growing consensus that our climate is changing due to anthropogenic emissions of greenhouse gases. Carbon dioxide from anthropogenic sources is considered to be the main contributor to the observed climate change [3].

Much focus has recently been put on reducing carbon dioxide emissions from centralised locations such as, e.g. fossil fuel (coal,

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oil and gas) fired power stations. The International Energy Agency (IEA) estimated the global carbon dioxide emission from fossil fuel fired heat- and energy production to be 8.2 gigaton per year in 2001. This corresponded to approximately 35% of the total carbon dioxide emission related to combustion of fossil fuels that year [4].

Carbon dioxide capture is typically divided into two sections, pre- or post-combustion. In pre-combustion, at fossil fuel is contacted with air or oxygen to form hydrogen and carbon monoxide. The gas is hereafter contacted with steam, whereby the carbon monoxide is further oxidised to form carbon dioxide and more hydrogen. After this stage, the pre-combustion carbon dioxide capture stage is placed to remove carbon dioxide, thereby purifying the fuel (hydrogen) [5]. Post-combustion capture implies removing carbon dioxide from flue gases after combustion, before the flue gas is released to the atmosphere. The post-combustion technology offers the advantage of being easier to retro-fit to existing plants without making significant changes to the combustion technology [6].

A novel gas clathrate hydrate based separation technology forms the basis for the present study. This process has been proposed as an alternative to existing gas separation technologies.

Gas clathrate hydrates, more commonly known as gas hydrates, are solid compounds of sufficiently small molecules and water. These solid compounds form when the constituents come into contact at conditions of low temperature and/or high pressure [7].

Gas hydrates are often referred to as non-stoichiometric solid inclusion bodies, where water (host) form a crystalline lattice by hydrogen bonding [8–10]. The lattice formation generates a number of empty cavities, in which small gas molecules (guests) may be enclathrated. The water lattice itself is a thermodynamically unstable structure, however attractive and repulsive interactions between the water and guest molecules stabilise the lattice [10]. The three most commonly encountered gas clathrate hydrate structures are the sI, the sII and the sH structures. Detailed descriptions of each hydrate structure may be found elsewhere [7].

Carbon dioxide may form gas hydrates with water at a pressure of approximately 1.2 MPa and temperature of 273 K [7]. The crystalline structure formed by the hydrogen bonded water molecules creates a total of 8 cavities for each 46 water molecules. Assuming single occupancy of carbon dioxide in each of these cavities allows for a maximum carbon dioxide mole fraction of 0.15 in the solid phase. This corresponds to a mass fraction of carbon dioxide in the solid hydrate phase of approximately 0.31. Since gas hydrates are non-stoichiometric phases, full occupancy of carbon dioxide in the hydrate structure is however rarely achievable at moderate conditions of temperature and pressure.

Nitrogen and oxygen, like carbon dioxide, may form gas hydrates. However, these compounds form hydrates at significantly higher pressures. The formation pressure of the nitrogen hydrate at 273 K is approximately 16 MPa [7]. Gas mixtures of nitrogen, oxygen and carbon dioxide will form hydrates at conditions in between those of the pure gases. The hydrates formed from these mixtures will enclathrate all gas phase components with appropriate sizes. Since carbon dioxide forms hydrates at the lowest pressures of the three main constituents of the flue gas, the mixed hydrates are expected to be rich in carbon dioxide.

Assuming liquid carbon dioxide is the desired end-product, the hydrate based carbon dioxide capture process, like the chemical absorption process, will contain two sections, capture and release. In the capture part, the flue gas is compressed, cooled and mixed with water, whereby hydrates may form by crystallisation. A carbon dioxide-rich hydrate slurry is hereafter transferred to the release section, where the solid particles are dissociated (melted) by either heating or pressure release. The captured gas is released at conditions of moderate to high pressures and low temperature. The aqueous liquid phase may be re-cycled to the capture section.

Fig. 1 illustrates a simplified schematic of a suggested process configuration.

One of the main advantages of the hydrate based separation technology is that it operates at temperatures, where low-quality heat can be used in the release section of the process. Also, a smaller amount of excess liquid is heated in the release part, since the hydrate slurry may be concentrated before being heated. Finally, the captured gas is delivered at high pressure and low temperature, reducing costs for liquefaction of the final carbon dioxide product.

The main drawback of this process is the high pressure/low temperature requirement in the capture part. Large amounts of flue gas must be compressed in large multi-stage compressor trains. A significant amount of nitrogen is basically compressed just to be let down in pressure after the capture stage. By introducing a turbine generator downstream of the capture stage, some energy may be recovered from the carbon dioxide lean flue gas before emission to the atmosphere. This will however further increase the capital cost of the capture plant. Other challenges with this process are low kinetics of the hydrate crystallisation, low water conversion as well as handling of the particle suspension. With solid particles in the system, a high risk of plugging of process equipment is expected due to agglomeration of particles.

Recent attempts of improving this technology have looked into ways of lowering the pressure requirement in the capture stage. It has been found that the addition of low pressure/high temperature gas hydrate stabilisers, so-called thermodynamic gas hydrate promoters, may significantly lower the pressure requirement of this process. A thermodynamic gas hydrate promoter is a gas hydrate former that stabilises the hydrate structure at low pressures/high temperatures, thereby allowing for gas phase components to enter the hydrate phase at milder conditions. The result is a hydrate phase that enclathrates both the promoter and the gas phase constituents. If the additive is soluble in water at the operating conditions of the process, it does not pollute the final gas product since it will remain with the liquid phase when the hydrates are dissociated. One disadvantage of adding thermodynamic hydrate promoters is that they lower the gas storage capacity of the solid phase. Thus, much research has gone into finding the ideal gas hydrate promoter that allows for hydrate formation at near-atmospheric pressure with high gas uptake capacity.

Tetrahydrofuran, a five-sided cyclic ether, has been suggested as a potential thermodynamic gas hydrate promoter for the hydrate based carbon dioxide capture process.

Kang and Lee [11] investigated hydrate dissociation pressures and compositions for the ternary system water–N_2–CO_2 and the quaternary system water–THF–N_2–CO_2.

A simulated flue gas vapour phase containing initially 17 mol% CO_2 was shown to form hydrates at pressures of 0.475 MPa (275 K), if 1 mol% THF was added to the aqueous liquid phase. The hydrate equilibrium pressure for this system without the addition of THF was 8.35 MPa (275 K).

It was found that CO_2 selectivity in the hydrate phase was lowered by the addition of THF, compared to the un-promoted system. Moreover, CO_2 selectivity was lowered with increasing temperature. A simulated flue gas phase initially containing 17 mol% CO_2 could form hydrates containing approximately 35 mol% CO_2 on a THF- and water-free basis.

From their results, Kang and Lee proposed a capture process in three hydrate formation/dissociation stages. In the first step, 1 mol% THF should be used as a thermodynamic hydrate promoter. In the second and third step, no promoter should be added, in order to increase CO_2 selectivity.

Kang et al. [12] measured three-phase hydrate–liquid–vapour (H–L–V) equilibria in the ternary system of water, carbon dioxide (CO_2) and nitrogen (N_2), as well as in the quaternary system of water, tetrahydrofuran (THF), CO_2 and N_2.