The Effective Parameters of Hydrate Formation in the Presence of Porous Media

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Abstract
Generally, the interest on the utilization of porous media in hydrate formation is mainly due to its natural occurrence in the ocean depths. The hydrate formation is potentially influenced by temperature, pressure, salinity, gas composition and interfacial surface area which can be affected by the presence of porous media. The effects of different types of porous media such as silica, activated carbon, carbon nanotube and silica gel on hydrate formation are considerable depending on the specific area, pore volume and pore size distribution. The presence of porous media in methane hydrate formation could affect the rate of hydrate formation and the amount of gas encaged in the hydrate phase. The mentioned parameters are important in selective gas separation utilizing hydrate technology.

In this study, the effect of the presence of porous media on hydrate formation technology was investigated. The aim was to provide a guide to future development in selecting suitable porous media in hydrate formation for gas purification and gas storage as an energy saving method.

Keywords: Separation, Storage, Gas hydrate, Nano-material.

Research Highlights:
- The effect of the presence of porous media in hydrate formation was investigated.
- The type of porous media, its surface properties and specially the amount of water were reviewed as important parameters during hydrate formation.
- The hydrate formation was investigated as a replacing current commercial separation technology.
1. Introduction
The storage and transportation of natural gas are of great interest with ever-increasing demand as a clean and low cost energy source. Gas hydrate formation is considered as a method with high storage capacity of gas and a method to separate especial gas (like methane or CO₂) from gas mixtures.
Nagata et al. used the lever rule to determine recovery ratio of HFC-134a, a typical Fluorine-gas, from a gas mixture of HFC-134a and nitrogen, in equilibrium condition [1]. They compared this factor in liquefaction and gas hydrate formation methods. They used equilibrium pressure-composition phase diagram, vapor phase line and hydrate phase line, to evaluate the recovery ratio and found that the recovery ratio in hydrate based separation method is higher than the liquefaction method. There are some pilot plants to research about hydrate based gas separation (HBGS) that show this method should be studied in separation or purification of different gases [2, 3].
Recently, separation of carbon dioxide and flourine gases from green house gases and purification of methane as a fuel, have encouraged the researchers to find the low price methods to increase efficiency in recovery of gases. With this aim, there are some researches on the gas separation and gas storage utilizing additives and porous media during hydrate formation. The effects of different types of porous media such as silica, activated carbon, carbon nanotube and silica gel on hydrate formation are considerable depending on the specific area, pore volume, pore size distribution [4, 5].
Kumar et al. studied the kinetics of the hydrate crystallization using fixed glass beads. Systems involving water dispersed in silica sand increased the gas uptake [6]. They observed that depending on how water saturated porous media is, tendency of hydrate formation in pores or on the grain surfaces are different. Moreover, the number of gas molecules in the hydrate phase could change depending on the gas composition, amount of water and the structural properties of porous media.
While using hydrate technology to storage or separate gas is an available topic for researches, studies on the gas separation from gas mixtures especially in the presence of porous media is limited.
In this work, the reports on hydrate based gas separation were reviewed. The effect of adding porous media on the hydrate formation were studied. The aim was to provide a guide to future development in selecting suitable porous media in gas purification and gas storage by hydrate technology.

2. Gas separation by hydrate formation
2.1. HBGS without porous media
Finding economically method to separate valuable gas, some researchers tried to use gas hydrate formation technology. C.Y. Sun et.al. used the specification that hydrogen is thought as hardly existing in hydrate phase while methane and some other light hydrocarbons are capable of forming hydrates more easily [7]. They separated hydrogen and methane by HBGS, in pure water and in THF added with concentration 1 and 6mol%. By adding THF, the separation efficiency increased.
Increasing of the world CO₂ gas production, as a by-product of combustion processes, gas hydrate formation was investigated as an possible solution for carbon dioxide sequestration [8]. Linga et al used clathrate hydrate crystal formation to separate CO₂ in hydrate phase from
CO₂ /H₂ (fuel gas) and CO₂ /N₂ (flue gas) mixtures [9, 10]. They obtained the stream 70%-80% CO₂ during two stage hydrate formation [10]. They used Tetrahydrofuran (THF) and observed that reduces induction time and the rate of hydrate formation and it increases gas uptake in comparison some other additives [9, 11]. Linga et al. determined the recovery ratio to evaluate the performance of the CO₂ capture from (CO₂ /N₂/O₂) flue gas by hydrate formation using THF [10]. But they didn’t consider equilibrium condition as a necessary assumption.

Utilization of multi-step CO₂ hydrate formation was shown to be capable of capturing 68% CO₂ from syngas at a single pass in the presence of hydrogen sulfide and pure water [2]. Surovtseva et al. used a combination of two low temperature processes, condensation at -55°C and the hydrate formation using hydrate promoters at 1°C for CO₂ capture from gas stream. Their process produced hydrogen gas with purity more than 90%. Using hydrate technology the purity of CO₂ increased to 95-97 mole%. This system was found lower cost and energy demand comparing to another systems in one step to separate carbon dioxide.

Generally, gas hydrate technology was introduced as a sustainable technology to separate greenhouse gases, separation of CO₂ and methane from emitted industrial gas steams, separation of H₂ and N₂ [12].

2.2. HBGS using porous media

Using hydrate formation by water dispersed in pores of silica gel particles, to CO₂ recovery from fuel gas (the mixture of CO₂ and H₂) could separate 95mol% of CO₂ in hydrate phase that was considerable comparing in case of bulk water hydrates, which shows just 70 mol% of CO₂ separation [13]. The efficiency of methane separation from natural gas could increase in the presence of silica based porous media[14].

3. The effect of porosity on hydrate formation

The hydrate formation is potentially influenced by pore size distribution and surface area of porous media. Liu et al. studied the effect of the ordered mesoporous carbon consisted of silica nanoroads with pore size distribution centered 2-5nm on hydrate formation [15]. According to their work, the time needed to reach equilibrium depends strongly on the water amount in the sample. They could store 41,2wt% of methane per unit mass of carbon. This was about 31% higher than the adsorption on the activated carbon.

Li Zhou et. al. observed that the uptake of CH₄ in water-loaded carbon nanotubes is five times more than dry porous media, due to the formation of methane hydrates [16]. The gas storage increased about 410% in the wet nanotube carbon comparing with the increase of 63% methane storage in the wet activated carbon. The maximal gas storage observed at RW=1. It is considerable that the amount of adsorbed gas is about zero at pressures lower than 3.9MPa which is lower than adsorption on the dry porous media. Because the maximum storage capacity of multiwall carbon nanotube (MWNT) for methane is less than the other available storage methods, this novel material is unlikely to be used as methane carrier either. The formation of hydrate in the pore space as well as in the space between solid particles on water-loaded carbon nanotubes could store five times higher gas than dry porous media [16].

Y.Zhou et al. explained that the pore size distribution of carbon can effect on the storage capacity [17]. Because, the side length of clathrate type SI is 1.2 nm and the diameter of the methane molecule is 0.381 nm, Therefore, the space allows for at least one layer of clathrate
and two layers of of methane adsorbed in a slit pore, if the slit width is larger than 2 nm. Thus the pore size and the size of gas molecules could be considered in selection of the porous media. Y.Wang et al. compared the CO₂ and CH₄ sorption on activated carbon [18]. They presented that CO₂ is a subcritical gas, that is condensable and partially soluble in water whereas CH₄ is a supercritical gas and neither condense nor dissolve in water, thus CO₂ hydrate can form at much lower pressure and reached much higher sorption capacity than methane. The rate of hydrate formation in higher pressure is increases sharply for CO₂. Kumar et al. studied the kinetics of the hydrate crystallization using fixed glass beads [6]. They concluded that systems involving water dispersed in silica sand increased the gas uptake. While the gas storage capacity can improve in the presence of different water-loaded porous material, the high cost of some of these materials makes the process uneconomical. Thus, the low dose porous material hydrate formation could be recommended in the case.

4. The effect of type of the porous media

The effects of different types of porous media such as silica, activated carbon, carbon nanotube and silicagel on hydrate formation are considerable depending on the specific area, pore volume, pore size distribution [4, 5]. Li Zhou et. al. observed that the uptake of CH₄ in water-loaded carbon nanotubes is five times more than dry porous media, due to the formation of methane hydrates [16]. The gas storage increased about 410% in the wet nanotube carbon comparing with the increase of 63% methane storage in the wet activated carbon. The pressure of a sudden increase in gas storage in the wet nanotube carbon is about 0.7 MPa less than wet activated carbon. Zhou et al. studied the methane hydrate formation on silica gel [19]. They observed the change of silica gel pore size structure in different time intervals and suggested it as an influencing factor on storage capacity. They related it to the hydrolysis of the silicon-hydroxyl groups of silicon surface. Alumina has a low mechanical strenght and its structure could change to soft material in acidic media [20]. Thus it shouldn’t be suitable for hydrate formation of acidic gases, CO₂ and H₂S. Y.Wang et al. investigated the formation of methane hydrate on the syntesized carbon material [18]. Comparing the gas storage at 275K on this porous media (2.5nm pore diameter) with activated carbon (2-5nm pore diameter) consisted of silica nanoroads (C/Si=1.25), [15] shows more gas adsorption in the presence of silica. Figure 1 shows the sorption isotherm of CH₄ on the mentioned media at 275K with the water ratio 2.13. It can be observed that the gas sorption on the C/Si at pressure higher than 5MPa is more than that on the activated carbon [15, 18].
The effect of adding silica on the surface of activated carbon can suggest that chemically modification of the surface of porous media may change the polarity and surface tension. Thus it can affect on the mass transport to the inside of pores.

5. The effect of the water content

Liu et al. studied the effect of the ordered mesoporous carbon consisted of silica nanoroads with pore size distribution centered 2-5nm on hydrate formation [15]. According to their work, the time needed to reach equilibrium depends strongly on the water amount in the sample. They emphasised on the critical value of water ratio, \(R_{WC}\), due to two things. The first, if the water content is below the critical value, the rate of mass and heat transfer is fast, otherwise it takes long time to reach equilibrium. The second, more water is preadsorbed, higher sorption capacity is reached. They increased the sorption capacity of the material by a factor of 3.7, in wet ratio of 3.86 water/porous media. They could store 41.2wt% of methane per unit mass of carbon. This was about 31% higher than the adsorption on the pre-adsorbed water at activated carbon.

Zhou et al. studied the effect of the amount of water on the sorption/desorption equilibrium of methane on silica gel [19]. The isotherm curves was similar to wet carbon active, the inflection pressure in the isotherm curves was a little higher than the formation pressure of methane hydrate in pure water (3.23 MPa) and the sorption capacity of the wet samples was less than that of dry silica gel for lower content of water. The highest adsorption happened at above 4MPa for \(R_W = 1.17\). It is interesting that water content more than this critical amount, make fall down the sorption isotherm. They assumed that both interior and exterior space between the sorbent particles have totally been occupied by water that prevent methane from getting into the pore space to form hydrate.

Celzard and Mareche reported that increasing water amount to saturate pore volumes of active carbons can decrease the hydrate formation pressure correspondingly that observed in bulk water [4]. It can decrease the gas storage and slows down the formation kinetics. The maximum gas storage will be observed in the optimal wetting ratio. They reported that for \(R < R_{max}\) more hydrate can formed by adding more water inside the pore volumes, i.e. by increasing \(R\). But above \(R_{max}\) diffusion of gaseous methane is more and more difficult because diffusion pathways become increasingly scarce throughout the pore network. Since methane
has a very low solubility in water, hydrates cannot form inside the material, because the accessibility decreases, and hence only a few of them may occur at the periphery of grains [4]. Li Zhou et al. observed that the uptake of CH₄ in water-loaded carbon nanotubes is five times more than dry porous media, due to the formation of methane hydrates [16]. The gas storage increased about 410% in the wet nanotube carbon comparing with the increase of 63% methane storage in the wet activated carbon. The maximal gas storage observed at Rw=1. Y. Zhou et al. studied the charging and discharging methane from the water pre-loaded activated carbon [17]. They found that the optimal packing density of this wet porous media is about 0.6gcm⁻³. The storage capacity didn’t change significantly by thermal change of the bed carbon. Depending on extent of water saturation of porous media, tendency of hydrate formation in pores or on the grain surfaces are different. Kumar et al. reported that systems involving water dispersed in silica sand increased the gas uptake [6]. Perrin et al. studied the possibility of natural gas storage within wet active carbons [21]. They used four carbonous material from different origins. Three of them was microporous and the fourth was mesoporous. The adsorption behaviour in the same wet ratio R=1, compared with the saturated samples showed that the rate of equilibrium decreases by saturation of porous media and the process of filling-emptying the storage tank is not fully reversible in this condition. Ju Dong Lee et al. studied the morphology of gas hydrate formation and dissociation on water droplet [22]. They reported that the measured induction time for methane-ethane and methane-propane hydrate crystals. The droplet size and shape had no noticeable effect on induction time and crystal growth but water having memory could decrease nucleation significantly, thus they recommended to use water memory to overcome the long induction time. The amount of hydrate formation could control by the amount of water due to the change on the number of large or small hydrate cavities formed. Also, it can affect on the accessibility to pore’s inside.

6. The effect of homogeneous additives

There are different additives that uses in hydrate technology such as hydrate formers (such as THF, EO,…), non-hydrate former (such as SDS, DTAB, CTAB,…) and semihydrate formers (that can use to control the size of hydrate pores for separation of larger molecules by hydrate formation). In this investigation, the results of the use of some of them were reported. Adding sodium dodecyl sulphate, SDS, (well known kinetic promoters of methane) to the carbon active can decrease the hydrate formation pressure and the amount of gas storage [4]. However making large amount of foam forming in line during pumping make the use of this surfactant less attractive [2]. Adding Tetra-butylammonium bromid (TBAB) increases the efficiency of CO₂ capture from the feed gas mixture (60.8mol% hydrogen/39.2 mol% carbon dioxide). 54% capture of CO₂ was reported by using TBAB [23]. Kang and Lee reported the capability of capturing 99mol% CO₂ from the flue stream using tetrahydrofuran(THF) [13]. The overall CO₂ capture rate can be increased to 90% using ammonium salt additives as promoters [3]. The para-toluene sulfonic acid (PTSA) decrease CO₂ capture in hydrate phase, by increasing CO₂ solubility in water, but using a small amount of commercial detergent additive, Triton
X-100 (mixture of alkylpolyglucosides, essentially octylpolyglucoside) was found to facilitate CO₂ hydrate formation [2].

7. Conclusion

This paper reviewed the reports on the gas separation and purification utilizing hydrate based gas separation (HBGS). Also, the effect of porous media in split fractionation was investigated. The influencing structural parameters including the specific area, pore volume, pore size distribution and the type of porous media were reviewed.

HBGS has shown a good efficiency in selective gas separation, especially in CO₂ removal field by continuous stepwise gas hydrate formation. This system was found lower cost and energy demand comparing to another systems in one step to separate carbon dioxide. According to the articles, using porous media decreases the time of nucleation. These colloidal material increases the gas storage capacity of the formed hydrate. The hydrophobic and hydrophilic properties of the pore could control by the modifier reagents. By using suitable functional modifiers it may be possible to enhance the selective separation as well as the preferential adsorption of impurities into the enhanced hydrate structure formed inside the pores.

Using silica in porous media has shown more gas uptake in the hydrate phase than carbon active.

Porosity and other structural parameters including the specific area, pore volume, pore size distribution and the type of porous media could change the gas diffusion in hydrate phase. The weight ratio of water to porous media is an important factor in hydrate formation. By control this ratio, the final gas composition can change. While the gas storage capacity can improve in the presence of different water-loaded porous material, the high cost of some of these materials makes the process uneconomical. Thus, the low dose porous material hydrate formation could be recommended.

The type and pore size distribution and water content of porous media should be selected according to the feed gas composition and the desirable selectivity.

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