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Full Length Article

Hydroquinone clathrate based gas separation (HCBGS): Application to the CO_2/CH_4 gas mixture

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ABSTRACT

Hydroquinone (HQ) clathrates have recently been identified as promising candidates for selective gas capture and storage processes. This study evaluates the effectiveness of HQ clathrates in the separation of CO_2 from CO_2/CH_4 gas mixtures, through direct gas/solid reactions in a fixed-bed reactor. The influence of the process operating parameters (i.e. reaction time, pressure, temperature and feed gas composition) on the CO_2 capture kinetics, selectivity towards CO_2, and transient storage capacity were investigated. The experiments were performed using either pure HQ or HQ-based composite materials, with temperatures ranging from about 283 to 343 K, pressures from 3.0 to 9.0 MPa, and CO_2 mole fraction in the gas mixture ranging from 0.2 to 1. The experimental results show that over the range of gas composition investigated, the enclathration reaction is selective to CO_2. This preferential CO_2 capture is enhanced at high CO_2 mole fractions, low temperatures and high pressures. Regarding gas capture kinetics, it was confirmed that the composite material is much more efficient than pure HQ crystals. The CO_2 enclathration rate increases with temperature, pressure and CO_2 fraction in the feed gas. For the first time, the feasibility of such gas separation techniques using HQ clathrates was demonstrated at bench scale.

1. Introduction

Natural gas is the 3rd energy source after coal and oil, according to the International Energy Agency [1]. It is mainly composed of CH_4, but it can also contain other compounds including low molecular-weight hydrocarbons (such as ethane, propane, butane, pentane), acid gases (such as CO_2 and H_2S), incondensable gases (N_2 and O_2), and traces of rare gases, mercury and water [2]. Light hydrocarbons (especially CH_4) are the main valuable compounds in natural gases. The other constituents are defined as impurities because of the complications they induce, such as decreasing the gas calorific value, and their operating constraints (e.g. condensation, corrosion and plugging). To respect the required specifications for valorization and commercialization of the natural gas, the removal of these impurities is of paramount importance. As acid gases are generally the most constraining (due to their toxic and corrosive properties) and most abundant, in terms of impurities, a gas-sweetening treatment (i.e. removal of CO_2 and H_2S) is required. CO_2 in particular – one of main gases contributing to greenhouse effects [3] – must be captured and stored (e.g. by injection into an underground reservoir) to curb its concentration from increasing in the atmosphere [4]. Actually, several processes are available for removing CO_2 from natural gas (e.g. chemical absorption using amines, adsorption on porous materials, permeation through membranes, condensation, and cryogenic separation) [4,5] for which the CO_2 recovery rate is high, reaching values > 80%. However, these processes are limited by economic criteria related to energy consumption [5,6]. In this way, alternative techniques for CO_2 gas capture – clathrate-based technologies being one of them – are subjects of great interest.

Gas clathrates are solid state host – guest compounds consisting of a network of self-associating molecules forming cavities (called “hosts”) in which gas species (called “guests”) can be encaged [7,8]. The combination of host and guest molecules to form clathrates is only possible in appropriate thermodynamic conditions. These inclusion compounds are known to store large amounts of gases such as CO_2, H_2S, CO, SO_2, CH_4 [9], and to be potentially selective to a specific gas present in a mixture [8]. This latter property has motivated many researchers to investigate the potential of clathrates in gas separation. The principle of this concept is based on the simple fact that when a gas clathrate is formed from a gas mixture, one of the constituents (e.g. CO_2 in a CO_2/CH_4 mixture) may be selectively engaged in the solid structure. A clathrate-based separation process would thus comprise a clathrate-formation step followed by a dissociation step: (i) the formation step leads to a residual vapor and a solid clathrate under equilibrium, both having different gas compositions (e.g. the gas containing a lower CO_2

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concentration than the initial gas mixture, and the clathrate a higher one); (ii) the dissociation step: by changing only the thermodynamic conditions (e.g. an increase of temperature, a decrease of pressure, or both), the gaseous molecules contained in the clathrate are released (e.g. producing a CO_2-rich gas mixture). Theoretically, this concept is very attractive, especially when the gas to be treated is already pressurized, such as for production gas. Actually, additional work is truly necessary to demonstrate the feasibility of such separations at larger scale (e.g. using bench and pilot scale apparatuses).

Among the clathrate-based processes, the most studied involves gas clathrate hydrates (often simply called gas hydrates), where the host molecules are water molecules associating by hydrogen bonds, generally formed at high pressure (several MPa) and moderately low temperature (close to 273 K) [10]. Accordingly, the hydrate-based gas separation (HBGS) process has already attracted widespread interest [11–20]. Nevertheless, although the HBGS process may be economically competitive (as the enclathration precursor is water, and the process can work under pressure), the deployment of the proof-of-concept to industrial scale is still limited by numerous critical disadvantages: (i) the additional cost of maintaining a relatively low temperature, required in the reactor to form the hydrates; (ii) the slow crystallization rate; (iii) the insufficient capture selectivity, particularly for the CO_2/CH_4 gas mixture; (iv) the necessity to add chemical promoters to overcome the thermodynamic and kinetic limitations [19], some of which can be toxic (e.g. tetrahydrofuran) or cause foaming problems during hydrate dissociation (e.g. sodium dodecyl sulfate); and (v) the operating and technological constraints related to the handling and transport of the multiphase mixture under pressure (i.e. slurry composed by solid hydrates, liquid water, and gases). There are plenty of examples in literature of studies carried out to address these challenges, many of them based on semiclathrates (e.g. TBAB, TBAF, etc.). The main advantage of using these substances is that the HGBS process can be operated at near-ambient pressure and/or temperature conditions [20].

Alternatively, hydroquinone (α-HQ) is an organic compound from the phenol family, well known to form gas clathrates. Although organic clathrates were discovered over a century ago [21], they were mainly fascinating scientific curiosities, but very few practical applications were proposed to date. A very limited number of studies involving organic clathrates is available in literature, in comparison to common gas hydrates. For example, the precise molecular structure of the simple CO_2-HQ clathrate was reported only recently by Torré et al. [22] showing that much remains to be done even at the fundamental level to increase our understanding of such compounds. The stoichiometry of the HQ clathrate (β-HQ) is 3:1 (i.e. 3 molecules of HQ per guest molecule), leading to a maximum storage capacity of $3.03\,mol^{Guest}/kg^{HQ}$ [23]. Recently, Coupan et al. showed that HQ clathrates can be formed with CO_2, CH_4 and CO_2/CH_4 mixtures over a wide range of temperatures (up to about 354 K) and at moderate pressure (< 1 MPa) [24,25]. Moreover, HQ clathrates can form by direct gas-solid reaction (i.e. a solvent is not required) by simply contacting solid HQ with the gas in appropriate pressure and temperature conditions [26–28]. As the kinetics of this solid-solid transition (i.e. from α- to β-HQ) is rather slow, an innovative HQ-based composite material had already been developed by the authors to primarily improve the enclathration kinetics, as well as to also overcome some process limitations. With the composite: (i) a gas-solid enclathration reaction is achieved, for which the induction time (i.e. the waiting period before the α-HQ starts to transform into α-HQ) is cancelled and the global kinetics is significantly improved; (ii) it permits both enclathration formation and additional adsorption phenomena; (iii) it is compatible with industrial gas-solid contactors such as fixed bed reactors; (iv) this composite can be re-used over several capture/regeneration cycles; and (v) it avoids the handling of HQ powder, the fine particles to be blown in the process unit, and high pressure drop in the gas/solid contactors [27]. Interestingly, various authors have reported that the HQ clathrates could be used for the selective capture of CO_2 from various CO_2-containing gas mixtures (such as CO_2/H_2, CO_2/N_2 and CO_2/CH_4 gas mixtures) [29–33]. Particularly, Coupan et al. and Lee et al. gave clear evidence on the capability of HQ clathrates in the selective trapping of CO_2 from an equimolar CO_2/CH_4 mixture [32–33]. However, only one quantitative selectivity of $29\,mol^{CO2}/mol^{CH4}$ from the equimolar CO_2/CH_4 mixture has been reported in literature to date, without any precision on the pressure and temperature condition associated to this result [33].

The present work aims at providing a technical performance evaluation of a HQ clathrate-based gas separation (denoted as HCBGS in the following) process applied to a CO_2/CH_4 gas mixture. The CO_2/CH_4 gas mixture and the experimental conditions of this study were chosen to approach the industrial case study of the gas sweetening applications [2,34]. The experiments were performed with CO_2/CH_4 gas mixtures with CO_2 mole fraction from 0.2 to 1 in the ~283–343 K and pressure from 3.0 to 9.0 MPa. The CO_2 capture selectivity, the transient gas storage capacity (i.e. the quantity of gas captured at a given time), and the capture kinetics were assessed. The first part of the study was devoted to the use of pure native HQ. Although we believe that the direct use of such crystals is not suitable for industrial purposes, this configuration represents a case-study in which the gas capture is due only to enclathration. Therefore, this medium was used to investigate and understand the influence of the process parameters on the separation efficiency. In the second part, an HQ-based composite was used for the separation. This conditioning has shown to give better results in terms of kinetics than native HQ crystals, but the phenomena involved in the CO_2 capture are more complex as they involve both adsorption (on the porous medium) and enclathration (with HQ). With this composite, the influence of the process parameters was also analyzed and compared against the native HQ crystals.

2. Experimental section

2.1. materials

HQ (purity of 99.5 mol%) was purchased from Acros Organics. Helium, CO_2 and CO_2/CH_4 gas mixtures (minimum mole fraction purity of 99.995%) were purchased from Linde Gas SA. The CO_2 mole fractions of the CO_2/CH_4 mixtures were measured by chromatography at 0.204, 0.399, 0.501, 0.601, 0.733 and 0.795. These values are in agreement with those given by the supplier specified within a relative uncertainty of ± 2%. The mixtures will be referenced in the following by the nominal values, as 0.20, 0.40, 0.50, 0.60, 0.75 and 0.80.

For the experiments, either native HQ or HQ-based composite were used. Native HQ was put in contact with pure CO_2 gas at 3.0 MPa and ambient temperature for 1 month to form CO_2-HQ clathrates, followed by a dissociation step at 1 kPa and 343 K until all the stored gas was released. This process generates a preformed form of HQ with a highly-reduced induction time [32]. The structure of the preformed HQ was investigated by Raman spectroscopy just before contacting the CO_2/CH_4 gas mixture (by taking a sample inside the reactor). The analysis revealed the presence of a mixture of α-HQ and guest-free β-HQ, with the α-HQ structure in majority (the two HQ forms cannot be dosed precisely with such Raman analysis). Moreover, several other Raman spectroscopic analyses achieved on the cross-section of preformed HQ crystals revealed that (in these conditions) the crystals present a core shell-structure: the guest-free β-HQ structure forms the external shell while the crystal core is composed of α-HQ.

The HQ-based composite used in this work is the one synthesized by Coupan et al. with a dry-impregnation process [27]. It consists of Siliasphere® silica particles (size 200–500 µm, pore size of 100 nm, specific area of $57\,m^2/g$, and porous volume of $0.83\,cm^3/g$) impregnated with HQ. The HQ content is $0.44\,g^{HQ}/g^{Silica}$. The composite material was also pre-formed with the pure CO_2 in the same conditions as those used for preforming native HQ. As the HQ crystallites are mainly deposited inside the pores of the silica particles, the internal structure of