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Hydrate-based removal of carbon dioxide and hydrogen sulphide from biogas mixtures: Experimental investigation and energy evaluations

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ABSTRACT

This paper presents an experimental study on the application of gas hydrate technology to biogas upgrading. Since CH_4, CO_2 and H_2S form hydrates at quite different thermodynamic conditions, the capture of CO_2 and H_2S by means of gas hydrate crystallization appears to be a viable technological alternative for their removal from biogas streams. Nevertheless, hydrate-based biogas upgrading has been poorly investigated. Works found in literature are mainly at a laboratory scale and concern with thermodynamic and kinetic fundamental studies. The experimental campaign was carried out with an up-scaled apparatus, in which hydrates are produced in a rapid manner, with hydrate formation times of few minutes. Two types of mixtures were used: a CH_4/CO_2 mixture and a $CH_4/CO_2/H_2S$ mixture. The objective of the investigation is to evaluate the selectivity and the separation efficiency of the process and the role of hydrogen sulphide in the hydrate equilibrium. Results show that H_2S can be captured along with CO_2 in the same process. The maximum value of the separation factor, defined as the ratio between the number of moles of CO_2 and the number of moles of CH_4 removed from the gas phase, is 11. In the gas phase, a reduction of CO_2 of 24.5% in volume is achievable in 30 min.

Energy costs of a real 30-min separation process, carried out in the experimental campaign, are evaluated and compared with those obtained from theoretical calculations. Some aspects for technology improvement are discussed.

1. Introduction

Biogas plays an important role among the renewable energy sources, thanks to its versatility of use in gas engines, microturbines and fuel cells for continuous energy production [1–4].

Improvements in biogas technology are achievable through the production of biomethane, an upgrading that

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requires the development of processes aimed at effectively storing and refining biogas.

Biogas is mainly composed of CH_4, ranging from 60%v/v to 70%v/v by volume and CO_2 ranging from 40% v/v to 30% v/v along with small amounts of H_2S generally not greater than 1% v/v.

In order to convert biogas into biomethane, two major steps are performed: a cleaning process to remove the trace components and an upgrading process to adjust the calorific value. Upgrading is generally performed in order to meet the standards for use as vehicle fuel or for injection in the natural gas grid [5]. Typical natural gas pipeline specifications require a CO_2 content of less than 3% [6] whereas vehicle fuel specifications require a combined CO_2/N_2 content of 1.5–4.5% in order to avoid significant changes in the vehicle's fuel economy and emission [7]. Therefore, after transformation, biomethane typically should contain 95–97% CH_4 and 1–3% CO_2.

Different methods for biogas cleaning and upgrading are used and comprise the separation of carbon dioxide, the drying of the gas, the removal of trace substances like oxygen, nitrogen, hydrogen sulphide, ammonia or siloxanes [5]. They differ in functioning, the necessary quality conditions of the incoming gas, efficiency and their operational bottlenecks. Condensation methods (demisters, cyclone separators or moisture traps) and drying methods (adsorption or absorption) are used to remove water in combination with foam and dust [5]. CH_4 is separated from CO_2 using adsorption-based processes, membrane separation, physical or chemical CO_2-absorption [8–10]. After separation, the captured carbon dioxide should be finally stored or used in energy production devices such as fuel cells [11–12].

Although carbon dioxide is the major contaminant in the raw biogas during the production of biomethane, it has been shown that the removal of hydrogen sulphide can be of crucial importance for the technological and economic feasibility of the whole gas upgrading chain. A number of techniques have been developed to remove H_2S from biogas. The most important methods are sulphide precipitation, biological scrubbing, chemical-oxidative scrubbing, adsorption on metal oxides or activated carbon [13].

For CO_2 and H_2S removal, hydrate technology may be considered as a new separation method in addition to those above mentioned.

Gas hydrates are crystalline solids composed of polyhedra of hydrogen bonded water molecules. The polyhedra form cages that contain at most one guest molecule. The cages are stabilized by van der Waals forces between the water molecules and the enclathrated guest molecule [14]. The application of gas hydrates to gas mixtures separation is based on the difference of hydrate formation characteristics of various species. When gas hydrates are formed from a gas mixture, the concentrations of components in the hydrate phase are different than that in the original gas mixtures.

For biogas, which can be assimilated to a CH_4–CO_2–H_2S mixture, the hydrate phase will be richer in CO_2 and H_2S than CH_4 under certain conditions [15] due to the difference in chemical affinity between CO_2, H_2S and CH_4 in the hydrate structure. This selective information is the basis for utilization of gas hydrate formation as a separation process. The hydrate phase is then dissociated and CO_2 can be recovered as a separated gas [16].

Separation and recovery of CO_2 from fuel and flue gas such as mixture of CO_2/H_2 and CO_2/N_2 have been already proposed [17–21]. Moreover, energy analyses for practical applications to CO_2/N_2 mixtures have also been carried out and the energy cost for CO_2 capture through the formation of CO_2 hydrate has been assessed [22]. Most of the energy consumption can be attributed to the compression process, because high pressure conditions are necessary for CO_2 hydrate formation, since concentration of this component in flue gases is very low (about 10–15%) [22]. On this basis, the application of gas hydrates may be much more competitive and suitable for mixtures rich in CO_2 such as biogas.

Nevertheless, the separation of CH_4/CO_2 mixtures has been poorly investigated. Works found in literature are mainly at a laboratory scale and deal with thermodynamic and kinetic fundamental studies [23–27]. It was found that under appropriate pressure and temperature conditions hydrates formed from a CO_2–CH_4 mixture contain more than 90 mol% CO_2 when the equilibrium vapor phase composition is in the range of 40 mol% CO_2 [24,25]. In addition, CO_2 uptake by gas hydrate formation proceeds more quickly than the methane uptake [26,27].

One of the possibilities to enhance hydrate formation is the use of chemical additives (water-soluble organic compounds or surfactants). Previous studies reported that addition of surfactant to liquid water causes a drastic promotion on the rate of formation and occupancy of gas hydrates, and decreases the induction time, even in unstirred reactors [28–33]. In particular, a recent investigation about a great number of surfactants (both commercial and not) of various charge type, various hydrophobic/hydrophilic balance, various chemical nature of the polar head group showed how negatively charged compounds are strong hydrate promoters [34]. Sodium dodecyl sulfate (SDS) is an anionic surfactant which has been widely studied and used as a kinetic hydrate promoter [34]. In fact, several investigations reported that SDS increases hydrate formation rate and storage capacity [28–33], although it also decreases hydrate stability [35].

Among the compounds normally found in biogas, hydrogen sulfide forms hydrates at the lowest pressures and highest temperatures. In fact, H_2S is a very powerful hydrate former. At 2 °C pure it forms SI structure hydrates at only 0.13 MPa [36]. The addition of 30 mol% H_2S causes the hydrate equilibrium temperature to increase by 12 °C from the pure methane system [36]. Therefore, in a hydrate-based process, it is possible to use the capability of the H_2S to form hydrates. This is an important feature since H_2S can be captured along with CO_2 in one stage: there is no need for a H_2S removal and sulfur recovery system in this process resulting in further energy saving.

Results of theoretical feasibility studies show that biogas can be upgraded to biomethane via gas hydrates namely with a SEC (specific energy consumption) of 3.9–3.8%, thus resulting in a cost effective process [37]. In addition, energy cost of a hydrate-based process is theoretically quite competitive when compared to other existing technologies for biomethane production [37].