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CO_2 removal from biogas with supported amine sorbents: First technical evaluation based on experimental data

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ABSTRACT

Biogas from fermentation of manure and organic residues produces a gas stream that can be fed into the natural gas grid, provided impurities (CO_2, H_2S and H_2O) are removed according to specifications prior to grid injection. Compared to conventional technologies, supported amine sorbents (SAS) seem attractive for their high working capacity and fast uptake rate. In this study a technical evaluation for the conceptual design of a system for CO_2 capture from biogas with SAS is carried out and the performance is compared with liquid amine scrubbing. As the basis of this study, 1000 Nm^3/h of raw biogas with 45%-v of CO_2 is to be upgraded to gas product containing max. 10%-v of CO_2, according to low calorific gas specifications. For the selected SAS (Lewatit VP OC 1065 and PEI/SiO_2) capacity measurements were carried out and results were correlated by Toth sorption isotherms. The heat of adsorption was calculated from the isotherms using the Clausius-Clapeyron equation and validated by measurements at different temperatures using calorimetry. Using the isotherms, a process analysis study with Aspen Plus software was carried out to obtain the best operating conditions for temperature swing between adsorption and desorption conditions, and subsequently the contactor size was determined. System integration studies show that the heat released during the adsorption can be integrated with the heat required in the digester (~60 °C), resulting in a primary energy use of 20–22% for SAS, while for conventional amine scrubbing this is 38%. This study shows that SAS is an attractive technology option for CO_2 removal from biogas.

1. Introduction

Renewable biogas from anaerobic fermentation is an energy source that is receiving increasing interest. Biogas is formed via anaerobic fermentation of manure and organic residue streams in a digester. The raw biogas contains significant amounts of sour components such as CO_2 and H_2S. Before biogas can be utilized or injected in local gas grids, these contaminants must be removed from the gas stream to prevent corrosion and to increase the heating value of the gas. The removal of CO_2 is of primary interest, this being the primary constituent next to methane.

The market for biogas digester systems is young, fast growing and characterised by a large number of suppliers, each offering their own technology for gas upgrading. Several technologies compete on costs and performance. The main commercial technologies are water scrubbing, membranes, pressure swing adsorption (PSA), and chemical scrubbing using amines, according to an extensive overview [1]. These processes can be characterised on the basis of methane emissions, electricity use, heat use and waste produced, as presented in Table 1.

Membranes have a low thermal energy use, but require power for compression of feed and/or permeate gas. Limited selectivity of membranes towards CO_2 leads to methane being emitted along with the CO_2. This can largely be overcome using a line-up with two or more stages, but this comes with additional costs for permeate recompression. Water scrubbing has the advantage of being a relatively simple technology requiring heat to release the CO_2 from the water stream. Methane will, however, be co-absorbed in the water and released with the CO_2. PSA processes use mostly carbon-based sorbents at ambient temperature. The simplicity of

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Abbreviations: SAS, supported amine sorbents; PEI, polyethyleneimine; SiO_2, silicon oxide; SRPEU, system relative primary energy use; PSA, pressure swing adsorption; TGA, thermal gravimetric analyzer; DSC, differential scanning calorimetry; DTA, differential thermal analysis; SiC, silicon carbide; TSA, temperature swing adsorption; MEA, monoethanolamine; MDEA, methyldiethanolamine; L/R HX, lean/rich heat exchanger.

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Table 1
Qualitative assessment of biogas processing technologies.

Technology	CH_4 emissions	Electricity use	Heat use	Consumables/waste
Membranes	–	O	–	+
Water scrubbing	–	O	+	–
PSA	–	–	+	+
Chemical scrubbing	+	O	–[a]	–
Supported amine Sorbents (SAS)[b]	+	+	O	+

[a] Use of rejected heat perhaps possible.
[b] Projected performance.

operation and high CO_2 partial pressure make (partial) PSA popular options. Compression power for running the pressure cycle is required, and co-adsorption of methane on the sorbent leads to significant methane losses and emissions. To avoid emissions of the methane, which is a much stronger greenhouse gas than CO_2, a more selective removal technology is desired.

Chemical solvent scrubbing using amines has the advantage of having a very high selectivity towards CO_2, as it is based on a specific chemical affinity for CO_2 and has no affinity to methane. In this way methane emissions can be minimized. Regeneration of the amine solution requires thermal energy. It is known that amines have a limited stability, so periodic replacement is required. Also metal corrosion is an issue frequently reported in amine systems [2].

The use of SAS to remove CO_2, H_2S and H_2O from sour, methane-rich gases (such as biogas and sour natural gas) as well as from flue gas (post-combustion CO_2 capture) is a relatively new development. In comparison with more conventional liquid phase processing, the application of these sorbents is attractive for different reasons: (i) It may reduce the energy requirement for sensible heat when switching between adsorption and desorption conditions, since the heat capacity of solids is lower than that of liquids and evaporation of water can be avoided [3]. (ii) It will potentially lower emissions of degradation products and minimize corrosion issues because of the immobilization of the amines. (iii) For small scale systems it may be easier to operate, if a simple gas-solid fixed bed can be used instead of a process with gas/liquid circulation. (iv) SAS can also be tuned thanks to the availability of various supports and active materials as discussed in several reviews [4,5]. The projected relative performance of SAS has been added to the overview in Table 1.

In the assessment of a novel technology, a design study provides the first insight of technical feasibility of the process. Hence in this paper, the design strategy for a supported amine-based adsorption system for CO_2 removal from biogas is discussed, using an integral approach addressing the interaction of sorbent characteristics, cycle design, heat management and system integration. Energy requirements and productivity of this process are compared with an amine-based solvent process as the most common technology for industrial CO_2 removal. A direct comparison between two technologies is not possible given the simplifications made in the SAS system and the higher uncertainty range for such a novel technology. Nevertheless, important insights in the potential and specific advantages and challenges of SAS technologies can be obtained. One specific potential advantage explored in this paper is that these sorbents can operate at relatively high temperatures and have a very large heat effect during adsorption because of the absence of evaporating water in the adsorber. This potentially allows heat integration with the fermenter.

2. Materials and methods

2.1. Materials

The first used sorbent is a commercial sorbent Lewatit VP OC 1065 from Lanxess. The sorbent has a support of spherical polystyrene beads with primary benzyl amine units [6]. Another sorbent is prepared in-house by impregnation of 35% w/w of polyethyleneimines (PEI), with a mixture of primary, secondary and tertiary amine groups and an average molar mass of 600 g/mol, on a silicon oxide (SiO_2) support. PEI based sorbents are chosen because they have been successfully utilized for CO_2 removal from air [7] or flue gas [8] in other studies.

2.2. Equipment

Capacities of the sorbents used at temperatures and partial pressures relevant to biogas upgrading were measured using Netszch STA 449 F1 Jupiter thermal gravimetric analyzer (TGA) with CO_2 concentration limited to 80%-v CO_2 at 1 atm. High purity (grade 5.0) N_2 and CO_2 gasses were used in the experiments. The procedure has been presented in a previous study [6].

The heat of adsorption is measured calorimetrically using a Mettler-Toledo TGA-DSC1 (Differential Scanning Calorimetry) with DTA (Differential Thermal Analysis) sensor, following a similar procedure as described in the previous section. For a certain amount of sorbent, the total quantity of heat produced during the adsorption process is obtained by integrating the calibrated sensor output (voltage over time), which can be recalculated to the heat of adsorption in J/mol CO_2.

Adsorption studies on ternary mixtures with all the major components found in biogas (CH_4, CO_2, H_2O, H_2S) were carried out in a packed bed reactor with 2.5 g PEI/SiO_2 (PEI/SiO_2:Silicon Carbide (SiC) = 1:11; inertness of SiC verified) at 40 °C (and a limited set of experiments at 60 °C), desorption at 110 °C, 80 mL/min in atmospheric pressure. The adsorbent was first pre-conditioned in 5% H_2O-N_2 at 110 °C. It was then exposed to the gaseous mixture fed for the selected experiment at 40 °C for 30 min. The temperature was then increased to 110 °C in N_2 with 5%-v H_2O for 30 min of regeneration. The sorbent was then cooled down in dry N_2 to the adsorption conditions. Each setting was repeated for 5 cycles and all reported capacities are breakthrough capacities.

2.3. System modeling

2.3.1. Digester

The formation of biogas in the digester is not considered in detail, but the heat demand that is relevant for system integration is taken into account in the model. Methane production by anaerobic digestion can be done at different temperature levels. Mesophilic digesters operate at 35–40 °C and are generally robust [9]. Thermophilic digesters operate at a somewhat higher temperature level of 45–55 °C, are less stable, but can achieve a higher throughput. Larger scale systems are generally fed with relatively stable feed streams, and thermophilic digesters are preferred because of their higher throughput. These digesters are generally well insulated, and heating of the feed streams is a main requirement. Heating is generally done through the walls or floor of the digester and a temperature difference with the heating medium of 5–10 °C is sufficient. In the digester itself, heat is also generated depending on the energy content of the digester feed. Thus, the net amount