Chemical Engineering Science 71 (2012) 97–103

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Enhanced cryogenic CO_2 capture using dynamically operated low-cost fiber beds

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ARTICLE INFO

Article history:
Received 27 October 2011
Received in revised form
22 November 2011
Accepted 23 November 2011
Available online 16 December 2011

Keywords:
CO_2 capture
Cryogenics
Packed beds
Phase change
Cellulose acetate
Hollow fibers

ABSTRACT

Recently Tuiniers et al. (2010) proposed a method for CO_2 capture using cryogenically chilled packed beds with spherical packing that served as CO_2 de-sublimation sites. The research presented here extends that work using fibrous packing inside the cryogenic columns, which serve to increase the surface area-to-volume ratio of the column by up to an order of magnitude as well as significantly reducing the sweep gas pressure drop through the column. Two types of fiber were chosen to study the effect of surface area on the total amount of CO_2 captured within the column: hollow cellulose acetate fibers (325 μm OD/125 μm ID) with porous walls and monofilament nylon fibers (200 μm OD). The pre-chilled cellulose acetate fiber columns were able to capture 191.2 kg of CO_2/m^3 of volume at a pressure drop of 3.9 psi/ft (81.0 kPa/m) despite very high superficial velocities of simulated flue gas (10% CO_2 in N_2) through the column (5,700 sccm, or 1.33 m/s). The nylon monofilament fibers were found to capture up to 185 kg of CO_2/m^3 despite lower surface area than the porous cellulose acetate fibers. The total uptake as a function of surface area within the column was found to reach a maximum, which has been tentatively attributed to the limited amount of specific heat held within the column itself. While in actual operation a pure CO_2 sweep may be used to recover the solid CO_2 within the column, a N_2 sweep was used here to unequivocally demonstrate that the process can be used to generate a pure CO_2 product. By performing a two-stage sweep, CO_2 purities between 28 mol% (1.33 m/s sweep) and 99.5 mol% (4.4 cm/s sweep) were obtained. The findings of this study suggest that these low-cost fibrous materials have the opportunity to reduce the capital expenditures of a world-scale cryogenic CO_2 capture system as well as increase the total loading of CO_2 captured per chilling cycle while also reducing gas compression costs.

1. Introduction

As atmospheric CO_2 concentrations approach 400 ppm in 2011, there is concern that anthropogenic CO_2 could induce global climate change (Bungten et al., 2011). While there is still debate over the severity of this anthropogenically induced climate change (Yeager et al., 2011), prudence dictates that engineers and scientists investigate possible methods to reduce or eliminate current and emerging CO_2 emissions. A commonly discussed method for reducing CO_2 emissions is post-combustion CO_2 capture, wherein the CO_2 being emitted by power stations is captured and either sequestered or used to generate a useful product (i.e., gasohol, Luo et al., 2010). The most common target for post-combustion CO_2 capture is coal-fired power stations, as these stations are among the heaviest emitters of CO_2. However, current technologies are too energetically intensive for widespread adoption (Lively et al., 2010), and emerging lower energy options will require more development and demonstration under realistic conditions.

CO_2 capture from liquid natural gas (LNG) plants and CO_2 emitters co-located near LNG re-gasifiers has been proposed as a low-cost method for CO_2 emission reductions due to the available cooling capacity at these stations (Coulson et al., 2010). Typically LNG re-gasifiers are swept with air or seawater to maintain constant temperature during the LNG vaporization step, whereas in a cryogenic capture scenario, a refrigerant could be used, thus transferring the latent heat of vaporization to the refrigerant (Clodic et al., 2005). Ideally, this refrigerant can be re-heated in gas–liquid heat exchangers, where the CO_2-laden flue gas is flushed on the shell side of the heat exchanger, causing the CO_2 to de-sublime on the fins of the heat exchanger, as demonstrated by Clodic et al. (2002). This technique suffers from decreased thermal efficiency as the CO_2 frost layer thickens; moreover, the need for dry flue gas streams for optimum operation adds an additional complication. Recently Assink et al. (2008), Tuiniers

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doi:10.1016/j.ces.2011.11.042

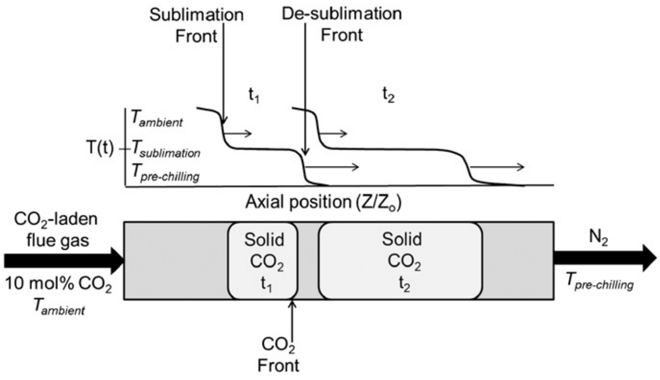

Fig. 1. Overview of thermal (*top*) and concentration (*bottom*) fronts that exist within the cryogenic CO_2 capture column at two different times.

et al. (2010, in press) have proposed and demonstrated a cryogenic CO_2 capture method using dynamically operated packed beds that circumvents both of these issues. Essentially, a packed column is chilled to cryogenic temperatures, and is then exposed to a flowing stream of warm flue gas. The solids chill the CO_2-laden flue gas enough to induce de-sublimation, which will continue to occur until the solids reach the sublimation temperature of CO_2 ($T_{sublimation}$). As the CO_2-laden flue gas progresses through the column, the solid CO_2 will progress through the column as a front, provided the packing stays below $T_{sublimation}$. As warm flue gas continues to wash over the column, the back of the CO_2 frost band will begin to sublime, resulting in a moving sublimation front. Typically, the de-sublimation front progresses at a higher rate through the column than the sublimation front (Tuiniers et al., 2010), which is perhaps due to differences in heat transfer rates between fresh packing and frost-covered packing. As the CO_2 de-sublimation front and temperature front break through the end of the column, the column can be washed in warm (greater than $T_{sublimation}$) CO_2 to sublimate the band of CO_2 that has formed on the available surface area within the bed (Fig. 1). This technique has recently been shown to work in the presence of CO_2 streams saturated with water (Tuinier et al., in press).

Previous work (Tuiniers et al., 2010, in press) has demonstrated the energetic viability of the above-mentioned technique using spherical glass beads as packing within the cryogenic column. Ideally, the amount of CO_2 that de-sublimates within the column scales linearly with the surface area present in the column (Eqs. (1) and (2)), implying that it is advantageous to use small particles in order to increase the total surface area available within a set column volume. Typical industrial flue gases, however, usually exhibit very high volumetric flowrates and are usually at near-ambient pressure, resulting in a situation that is not favorable for a tightly packed column due to the pressure drop across such a column. As a result, packed beds are usually made with ~4.0 mm spheres which exhibit a surface area-to-volume ratio of approximately 1,000–1,500 m^2/m^3, depending on the column filling fraction.

The overall gas phase mass balance is described by Tuiniers et al. (2010):

$$\varepsilon_{bed}\frac{\partial(m_g)}{\partial t} = \frac{-\partial N_{gas}}{dz} - N_{CO_2,sub}\hat{A}_{surface} \tag{1}$$

The overall solid phase mass balance is:

$$\frac{\partial(m_{CO_2})}{\partial t} = N_{CO_2,sub}\hat{A}_{surface} \tag{2}$$

This paper extends the previous work by replacing the spherical beads with either simple monofilament lines or porous hollow fibers. In this way, much higher *specific* surface area-to-volume ratios (m^2 of available surface area per m^3 of empty module volume) can be obtained at substantially lower pressure drops. The porous substructure of the hollow fibers allows for significantly increased surface areas when compared to the geometric surface area of a non-porous fiber. Furthermore, fiber systems have the potential to be much more scalable than spherical packing due to the relative ease of processing, resulting in lower capital expenditures. Typically, even consumer quantities of monofilament are inexpensive, costing less than $5/$m^2$, whereas equivalent consumer quantities of Pyrex® packed bed packing typically cost approximately $600/$m^2$. Cellulose acetate hollow fibers for membrane separations cost about $20/$m^2$ (Vu et al., 2003). Fibers also offer the advantage of being quite tunable in terms of morphology; fiber outer diameter, inner diameter, porosity and fiber shape can all be readily changed. The fibers are formed using the dry-jet, wet-quench non-solvent induced phase separation spinning technique (McKelvey et al., 1997). In this technique, a polymer solution consisting of several solvents and non-solvents is extruded into a non-solvent bath. As the nascent fiber proceeds through the non-solvent bath, an influx of non-solvent into the fiber walls will induce phase separation, effectively creating a porous polymer-rich phase and a polymer-lean phase, which is washed out. The porous polymer-rich phase can develop by either a nucleation and growth mechanism, a spinodal decomposition mechanism, or a combination of the two, depending on how the parent polymer solution is made up. This paper first describes the experimental set-up used for spinning hollow fibers and the cryogenic CO_2 capture system. Subsequently, the paper will discuss the fiber properties and their performance in the cryogenic CO_2 capture system in terms of flue gas pressure drop, the CO_2 capacity of the column, the CO_2 breakthrough time in the column, the velocities of the concentration and thermal fronts, and the purity of the recovered product using a N_2 sweep recovery method.

2. Materials and methods

2.1. Fiber spinning

Porous hollow fibers were spun using the well-known dry-jet, wet-quench non-solvent-induced phase inversion technique (McKelvey et al., 1997). Cellulose acetate (MW 50,000, Sigma-Aldrich) was chosen as the polymer material due to its low cost, availability, and spinning data available for the polymer. A dual layer spinning approach was taken in order to ensure that no outer skin layer was formed on the fibers during the spinning process; the sheath layer dope was fabricated in such a way that a skin layer should not form. Furthermore, the core dope was fabricated in such a way that very rapid phase separation would occur, ideally leading to a spinodal decomposition pore-formation mechanism. This dual-layer approach allows CO_2 unfettered access to the porous, high-surface area substructure of the fiber wall. Though not the focus of this work, optimization of the spinning solutions could result in similar fibers being spun in a single-layer. N-methylpyrrolidone (NMP, *ReagentPlus*^{TM} *99%*, Sigma-Aldrich, Milwuakee, WI), dimethyl sulfoxide (DMSO, ACS reagent grade, Sigma-Aldrich), and acetone were used as spinning solvents. Water was used as spinning non-solvent, and lithium nitrate ($LiNO_3$, *ReagentPlus*^{TM} *99%*, Sigma-Aldrich) was used as a pore former. A wide range of polymer solutions were made in 20 mL scintillation vials and were visually inspected to determine the ternary phase behavior of the cellulose acetate solutions. A solution that was both sufficiently viscous (30,000 cP–100,000 cP, determined by Brookfield® Viscometer) and sufficiently close to