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Post-combustion CO_2 capture using super-hydrophobic, polyether ether ketone, hollow fiber membrane contactors

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ABSTRACT

The feasibility of utilizing a super-hydrophobic polyether ether ketone (PEEK) hollow fiber membrane contactor in combination with chemical solvents to separate and capture CO_2 from simulated flue gases was investigated. Greater than 90% CO_2 capture with greater than 95% CO_2 purity has been achieved in one stage with both activated methyldiethanolamine (aMDEA) and activated K_2CO_3 solvents. The measured volumetric mass transfer coefficient was as high as 1.7 s^{-1}, which is more than 20 times greater than the mass transfer coefficient of a packed column. Preliminary tests indicated that the CO_2 capture performance was not affected by flue gas contaminants, including O_2, NO_2, and SO_2, with aMDEA solvent. The PEEK membrane module showed good mechanical properties and stable permeation properties at process design conditions for duration of the test (120 h). The process economics were evaluated assuming direct substitution of the conventional absorber by the membrane contactor, while using a conventional packed column in the regeneration step. Relative to the cost estimation with no CO_2 capture, the evaluation indicates a 56% increase in the levelized cost of electricity (LCOE) for the PEEK membrane contactor technology, which is 29% lower than DOE's benchmark amine absorption technology (85% increase in LCOE).

1. Introduction

The greatest concern to climate change is the emission of greenhouse gases, especially CO_2 from a range of sources. According to the Environmental Protection Agency, the US emitted 6.1 billion metric tons of CO_2 to the atmosphere in 2007 [1]. About 40% of this CO_2 was produced by electric generating power plants, of which ~50% are fueled by coal. Existing coal-fired power plants emit ~85% of the total CO_2 of all power plants' generating CO_2. Therefore, to address concerns about global climate change and to reduce US greenhouse gas emissions of 17% by 2020 and 83% by 2050 from a 2005 baseline [2], Federal legislation targeting coal-fired power plants is likely.

The US Department of Energy (DOE) has a 2020 Carbon Capture Program post-combustion capture goal of achieving 90% capture in existing plants with less than a 35% increase in the levelized cost of energy (LCOE). To achieve this goal by any technological means is very difficult, because flue gas is hot, dilute in CO_2 content, near atmospheric pressure, high in volume, and often contaminated with other impurities (O_2, SO_x, NO_x, and ash). Amine absorption is the current industry and DOE benchmark technology for capture of CO_2 from power plant flue gas. Residual oxygen in the flue gas is especially troublesome for conventional amine plants because of oxidative degradation of the amine. These factors result in enormous amine circulation rates, large equipment, and large energy requirements. In addition, the heat duty of the stripper places a substantial burden on the steam supply. It is estimated that for every pound of CO_2 captured 2 to 3 pounds of steam is required [3,4]. DOE/NETL systems analysis studies estimated that using aqueous monoethanolamine absorption process to capture 90% of the CO_2 from flue gas in existing plants will result in an increase in LCOE services by 75–85% [5]. These values are well above the 2020 DOE NETL Carbon Capture Program post-combustion capture cost goal (35% increase in LCOE). Therefore, it is important to develop new advanced CO_2 capture technologies in order to maintain the cost-effectiveness of U.S. coal-fired power generation.

Recently published system analysis and feasibility studies demonstrate that gas separation membranes are a technically and economically viable option for CO_2 capture from the flue gas exhaust in pulverized coal-fired (PC) power plants [6]. Furthermore, membranes are compact and can be retrofitted onto the tail end of a power-plant flue gas stream without complicated integration schemes. Conventional gas separation membrane process operates by a solution/diffusion mechanism, and the separation driving force is provided by the partial pressure difference of each component across the membrane. This process requires either flue gas compression, permeate sweep, application of permeate side vacuum, or a combination of these steps to provide the separation driving

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force required. Elaborate process design and optimization become prerequisite for conventional membrane processes in CO_2 capture from flue gases [7].

The main limitation of conventional membrane processes is the process pressure ratio (feed gas pressure/permeate gas pressure) limitation [8]. A flow of component m across the membrane can only occur if the partial pressure of m on the feed side is greater than that on the permeate side. That is:

$$y_{m,f}p_f \geq y_{m,p}p_p \tag{1}$$

Thus, the maximum separation achieved by the membrane can be expressed as:

$$\frac{p_f}{p_p} \geq \frac{y_{m,p}}{y_{m,f}} \tag{2}$$

where, p_f and p_p are the feed and permeate side pressures, $y_{m,f}$ and $y_{m,p}$ are mole fractions of component m in the feed and permeate sides, respectively. Eq. (2) simply illustrates that the enrichment achievable in the permeate relative to the feed ($y_{m,p}/y_{m,f}$) is always less than the feed-to-permeate pressure ratio (p_f/p_p), no matter how selective the membrane. In practical gas separation applications, the pressure ratio across the membrane is usually between 5 and 15 [9]. When the membrane separation process is pressure ratio limited, the product CO_2 concentration will be limited even when the membrane selectivity is much larger than the pressure ratio. Thus, multiple membrane stages are required to generate greater than 95% pure CO_2 product (DOE's target) from flue gases using the conventional membrane process.

Membrane contactor process (also known as hybrid membrane/absorption process) combines advantageous features of both absorption and membrane processes to provide a cost-effective solution for CO_2 capture from flue gases. Hollow fiber membrane contactors for CO_2 capture, especially the absorption process, have been reported [10–14]. In this process, CO_2-containing gas passes through small-diameter membrane tubes (hollow fibers with porous walls) while a CO_2 selective solvent (typically an amine solution) flows on the shell side of the membrane. CO_2 permeates through the membrane and is absorbed in the solvent. The CO_2 rich solvent can be regenerated in a second membrane module operated in a reverse process.

The specific surface area per volume for hollow fiber membrane contactors can be as high as $\sim$1000–9000 m^2/m^3, which is up to two orders of magnitude greater than conventional contactors (free dispersion columns: $\sim$3.0–35 m^2/m^3, packed and tray columns: 30–300 m^2/m^3, mechanically agitated columns: $\sim$160–500 m^2/m^3) [15,16]. Thus, the use of a membrane contactor instead of a conventional amine scrubber leads to a much smaller space requirement. This technology is well suited for new and existing PC power plants due to the reduced footprint requirement and a much lower visual impact as well as providing more options for placement in the confines of existing plants.

In the hybrid membrane/absorption process, the permeate side partial pressure of CO_2 can be considered close to zero due to the chemical reaction of CO_2 with the absorption solvent, and thus overcomes the pressure ratio problem encountered by the conventional gas membrane process. Feed compression or permeate vacuum is not required to create the separation driving force for gas molecules to be transported through the membrane. The process selectivity for the hybrid membrane/absorption process is determined by the chemical affinity of the absorption solvent to CO_2. Therefore, high purity CO_2 product can be realized in a single stage hybrid membrane/absorption process.

The objective of the current study was to develop and demonstrate a practical and cost effective hybrid membrane/absorption process for CO_2 separation and capture. The membrane contactor is based on chemically and thermally resistant commercially engineered plastic PEEK [17], which is virtually non-destructible under the operating conditions encountered in typical flue gas applications. It can withstand contact with all common treating solvents or advanced absorption solvents under development. Specifically, a "real-world" assessment of the necessary and desirable features including the following elements has been undertaken:

- **Membrane module**: membrane modules with their performance essentially capable of being linearly scaled to commercial size were used.
- **Solvent**: solvents used in our membrane contactor technology are commercially available. Four types of solvents were investigated.
- **Feed**: simulated flue gas compositions were used for existing pulverized coal power plants. The effects of flue gas contaminants, such as O_2, NO_x, and SO_x on membrane contactor performance were investigated.
- **Stability**: membrane contactor stability at process design conditions was investigated by continuously performing CO_2 capture for 120 h.
- **Techno-economic analysis**: experimental results were combined with process design to determine the technical performance for a variety of process scenarios and economic costs associated with each scenario.

2. Experimental methods

2.1. Hollow fiber membrane fabrication and surface modification

The hollow fiber membranes are manufactured from the best in class commercial engineered plastic, PEEK. Porous PEEK hollow fibers used in preparation of super-hydrophobic membranes are manufactured by a high temperature melt extrusion process. In this process, a mixture containing PEEK and PEI (polyether imide), is melt extruded to form a hollow fiber, which is then cooled in air and sent to reagent bath, where PEI is removed. The resulting product is porous PEEK fiber. The details of the process were described previously [18].

The super-hydrophobicity of the porous PEEK membrane was generated by surface modification with a functional perfluoro oligomer. Prior to grafting with the perfluoro oligomer the surface of the porous PEEK was functionalized with –OH groups by reacting ketone groups in the PEEK polymer backbone with monoethanolamine. The functionalized porous PEEK was prepared in a single step Reactive Porogen Removal process during porous PEEK fiber preparation according to US Patent 7,176,273 [19]. The process is illustrated schematically in Fig. 1.

2.2. Membrane module preparation

Module design and construction have significant impact on the overall gas mass transfer coefficient by minimizing liquid side resistance and maximizing the driving force. The hollow fiber membrane modules were of the four-port, counter-current flow design, which took into account gas side and liquid side pressure drops. The hollow fiber cartridges were formed by computer-controlled helical winding hollow fibers around a mandrel. The cartridges (Fig. 2) were nominally 2-inch- (5-cm-) diameter and 12-inch- (30.5-cm-) long. The effective membrane surface areas were about 0.12–1 m^2. The cartridge was sealed with o-rings and housed in a stainless steel pressure vessel.

2.3. Membrane module characterization

The non-wetting characteristics of membrane modules were determined by pressurizing a feed liquid in the shell side of the module and observing collection of liquid in the tube side if any.