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# Membrane process optimization for carbon capture

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ABSTRACT

The utilization of membrane technology in post-combustion applications is hindered by low $CO_2$ feed partial pressure in the flue gas stream. In order to meet the separation targets of 90% $CO_2$ recovery, 95% or higher $CO_2$ purity, and a Levelized Cost of Electricity (LCOE) increase of less than 35%, Membrane Technology and Research, Inc. (MTR) (Merkel et al., 2010) has proposed the use of the boiler air feed as a sweep stream to increase the $CO_2$ concentration in the flue gas and partial pressure driving force for permeation without additional compression or vacuum. Such a design significantly reduces capture cost but leads to a detrimental reduction in the $O_2$ concentration of the feed air to the boiler. The transport properties and operating pressures of the membrane stages are optimized in this study. Membrane $CO_2/N_2$ selectivity is varied over a broad range encompassing the values considered by MTR. Membrane $CO_2$ permeability is varied with selectivity according to the variation anticipated by the upper bound of the Robeson plot for $CO_2$ and $N_2$. Membrane $CO_2$ permeance is calculated assuming membranes can be fabricated with an effective thickness of 0.1 μm. Additionally, the two stages may utilize different membrane materials. The feed and permeate pressures also are varied over ranges encompassing the values proposed by MTR. The optimization space of membrane properties and operating conditions is scanned globally to determine the process design that minimizes LCOE. The $O_2$ concentration to the boiler is evaluated during the optimization process and can be used to constrain viable alternatives. The results indicate a fairly broad range of membrane properties can yield comparable LCOE near the minimum. The optimal operating pressure range is somewhat narrower. The minimum allowable $O_2$ concentration constrains viable designs significantly and is critical to process economics.

## 1. Introduction

In comparison with pre-combustion and oxy-fuel combustion capture processes, post-combustion carbon dioxide ($CO_2$) capture processes must handle the lowest $CO_2$ content in the flue gas stream due to the presence of nitrogen ($N_2$) in air. Because of the low $CO_2$ feed partial pressure driving force, this technology suffers from a severe energy efficiency penalty. Therefore, the key to achieve the stringent 90% recovery and 95% purity targets, without increasing the Levelized Cost of Electricity (LCOE) by more than 35% (Matuszewski et al., 2012), is to generate an affordable $CO_2$ feed partial pressure driving force. Membrane processes are one option under development that offer unique advantages in terms of energy consumption and physical size (Mat et al., 2014).

Several factors hinder the effective use of membrane processes in post-combustion applications. The first is the availability of a membrane material that will allow synthesis of a process that satisfies capture criteria. Increasing $CO_2$ permeability reduces the required membrane area and associated capital cost while increasing $CO_2/N_2$ selectivity reduces the process energy requirements and associated operating cost. Unfortunately, the literature suggests that material changes which increase $CO_2$ permeability will lead to a concomitant decrease in $CO_2/N_2$ selectivity. In the context of carbon capture applications, such a tradeoff also reflects a tradeoff between total module area and energy requirement. This relationship commonly is referred to as the Robeson plot (Robeson, 2008) and arises from the physics of the solution-diffusion process that governs transport in polymeric materials. Therefore, to move above the upper bound line, most of the reported $CO_2$ membrane material development work has sought to improve both $CO_2$ permeability and $CO_2/N_2$ selectivity by using non-polymeric membranes or mixed matrix membranes that are polymer-inorganic composites (Rezakazemi et al., 2014). Recently, Roussanaly et al. (2016) used a cost-based comparative numerical model to identify optimal membrane properties that includes the impact of membrane technology maturity level and membrane price sensitivity. While optimal membrane properties may vary with technol-

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ogy maturity level, membrane price, and process configurations, the ability to manufacture high performance, high permeance membranes is the crucial factor when evaluating the economic competitiveness of membrane processes with other technologies.

In addition to development of novel membrane materials with improved separation properties, improvement of existing process designs is essential to minimize LCOE. Because of the low $CO_2$ feed partial pressure driving force in flue gas, it is impossible for a single stage-membrane process to achieve the prescribed $CO_2$ recovery and purity targets even for high $CO_2/N_2$ selectivity materials due to pressure ratio limitations (Merkel et al., 2010). However, the targets can be realized in multi-stage configurations (Zhao et al., 2008). Thus, implementing multi-stage designs is required to increase the $CO_2$ feed partial pressure by creating an internal gas recycle loop. Zhao et al. (2010) describes two stage configurations with and without permeate vacuum as well as stage cycle. Results are presented for $CO_2$ recoveries up to 90%. While the results show the promise of carbon capture with staged membrane processes, the target of 90% and 95% purity were not achieved for the process conditions considered. Several other authors have addressed the analysis of multi-stage membrane configurations and performed economic feasibility studies for post-combustion applications (Hussain and Hägg, 2010; Swisher and Bhown, 2014). Most of the reported multi-stage process configurations for membrane systems have sought to generate affordable $CO_2$ partial pressure driving forces for permeation by a combination of feed compression, vacuum permeation and feed-air sweep system (Ho et al., 2008; Merkel et al., 2010; Ramasubramanian et al., 2012). Combining membranes with other separation techniques, such as cryogenic flash and absorption, also can potentially minimize $CO_2$ capture cost (Chowdhury 2011; Belaissaoui et al., 2012).

Membrane Technology and Research, Inc. (MTR) (Merkel et al., 2010) proposed a new scheme to increase $CO_2$ partial pressure driving force in an affordable manner by incorporating an air-feed sweep in a staged membrane system. The proposed design is a hybrid configuration which utilizes a cryogenic liquefaction and flash step to yield a liquid $CO_2$ product in the desired purity and recovery (Fig. 1). This process utilizes MTR's Polaris membrane which possesses a high $CO_2$ permeance of 1000 GPU and a $CO_2/N_2$ selectivity of 50. The high $CO_2/N_2$ selectivity allows production of a $CO_2$ permeate with the purity required to meet the final purity target after a cryogenic flash. The high $CO_2$ permeance reduces the required membrane area to achieve the $CO_2$ recovery target. As shown in Fig. 1, the majority of $CO_2$ re-circulation arises from the $CO_2$-enriched permeate stream produced by sweeping the second counter-current stripping stage (module II) with the boiler feed air. Although this scheme has been successfully demonstrated to reduce capture cost, it produces an oxygen ($O_2$) deficient feed air stream to the boiler (the $O_2$ concentration is reduced from 21% to 18%) that could potentially reduce the boiler adiabatic temperature efficiency (Franz et al., 2013; Scholes et al., 2013). The impact of this reduction in $O_2$ concentration on LCOE remains unclear.

Recent work on optimization of membrane separation applications has utilized both stochastic algorithms (Corriou et al., 2008; Yuan et al., 2014) as well as gradient based methods such as Nonlinear Programming (NLP) and Mixed Integer Non Linear Programming (MINLP) (Qi and Henson, 2000; Kookos, 2002; Chowdhury, 2011; Scholz et al., 2015). While past work with gradient based optimization has included membrane $CO_2/N_2$ selectivity and permeability as decision variables and the effect of multicomponent permeation, the case studies considered were not representative of utility scale power plants. Moreover, the past work neglected the initialization strategies in both MINLP and NLP models. The convergence processes in gradient based methods are extremely sensitive to the initial points in the model. Thus, a poor initial guess may lead to suboptimal configurations and process parameters (Safdarnejad et al., 2015).

Optimization of multi-stage hybrid membrane processes for post combustion $CO_2$ capture requires systematic evaluation of several design variables on LCOE. While increasing $CO_2$ membrane permeability results in significant savings in capital cost, it comes with the tradeoff of lower $CO_2/N_2$ selectivity which eventually results in larger plant parasitic loads. Cost reductions in membrane manufacturing also may reduce capital cost and reduce LCOE (Roussanaly et al., 2016). Therefore, to determine the optimum operating conditions and membrane separation properties for post-combustion application, one should not only consider the balance between required feed to permeate operating pressure ratio and $CO_2/N_2$ selectivity (Huang et al., 2014), but also the trade-off relationship between $CO_2/N_2$ selectivity and $CO_2$ permeability embodied in the Robeson plot.

Here the multistage hybrid membrane-cryogenic air-feed sweep

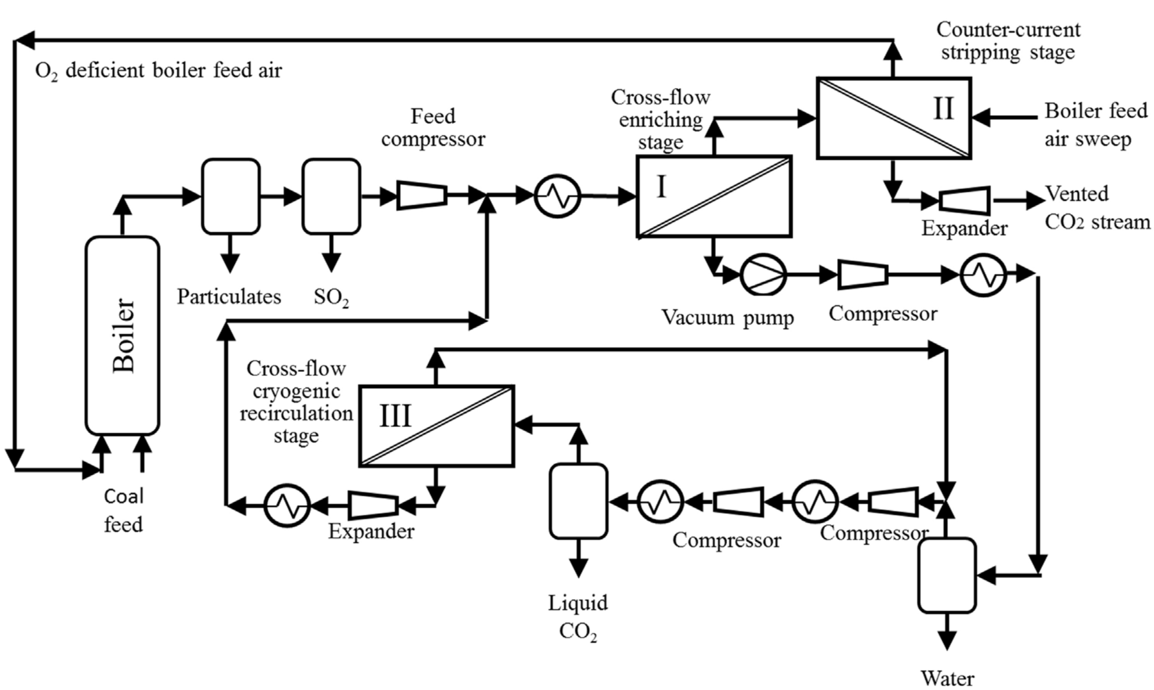


**Fig. 1.** Membrane-cryogenic hybrid configuration proposed by Merkel et al. (2010).