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Hybrid membrane-absorption CO_2 capture process

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Abstract

The development of CO_2 capture systems has largely focused on single separation technologies (absorption, adsorption, membranes, cryogenics, etc.). Few studies have examined the merits of combining multiple separation technologies into a hybrid capture system. Membrane Technology & Research, Inc. (MTR) and the University of Texas at Austin (UT Austin) are collaborating to investigate two variations of a hybrid membrane-absorption capture system which combine MTR's air-swept Polaris™ membrane contactor with UT Austin's 5 m piperazine advanced flash stripper (AFS; 5 m PZ-AFS) capture technology with cold and warm-rich bypass. In one embodiment, the systems are arranged in series and in another, in parallel.

In the series configuration, the absorber removes approximately half of the CO_2 in the flue gas, followed by additional separation by the membrane contactor to achieve 90% total removal of CO_2 by the hybrid capture system. In this arrangement, the absorber operates at a higher lean-loading state and also benefits from the ability of the downstream membrane to mitigate fugitive amine emissions. In the parallel configuration, the flue gas leaving the power plant is split and treated by each system in a parallel arrangement. The principal advantage is that the absorber can be roughly half the size it would normally be. In both configurations, the 5 m PZ-AFS system will treat a more concentrated CO_2 stream which is a preferred condition. The project team found that the minimum O_2 content in the combustion air stream (18% for retrofit, 17% for Greenfield) acted to limit the potential of the hybrid-series configuration. In the best case design of the hybrid-parallel arrangement, the 5 m PZ-AFS system treats 53% of the total flue gas volume with a CO_2 concentration in the flue gas greater than 23%.

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Keywords: Membrane; CO_2 Capture; CCS; Hybrid; Amine; Membrane; Piperazine

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1. Introduction

The hybrid capture process is a derivative form of MTR's all-membrane, post-combustion CO_2 capture system developed by MTR with financial assistance from DOE NETL through projects DE-NT0005312, DE-FE0006138 and DE-FE0007553. In those programs, a novel process design that uses incoming combustion air as a sweep stream to generate driving force for CO_2 capture has been designed, and demonstrated in slipstream field tests at a coal-fired power plant. And a low pressure membrane contactor has been developed for use in the high-gas-flow, low-pressure sweep operation (Figure 1) [4].

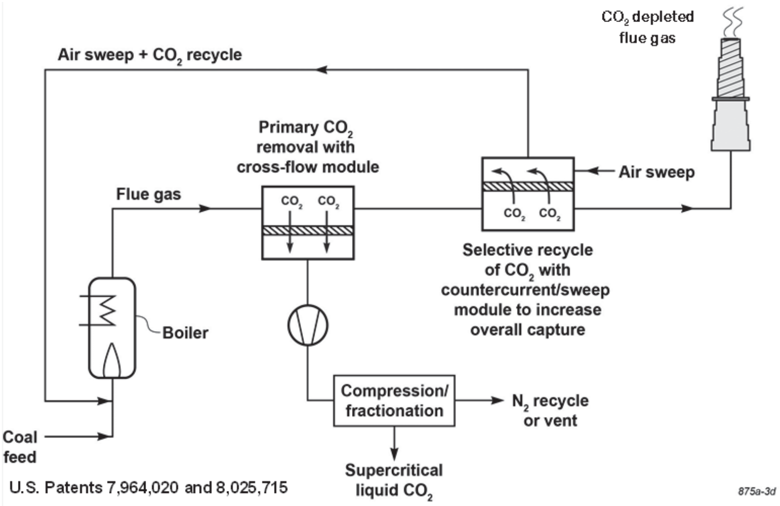

Fig. 1. MTR's all membrane post-combustion CO_2 capture process with selective CO_2 recycle stream [4]

In the hybrid process, the cross-flow membrane module (see Figure 1) which performs the bulk removal of CO_2 from the flue gas, is replaced with another capture technology (*e.g.* absorption, adsorption, cryogenic, etc.). The membrane-based gas contactor uses boiler combustion air as a sweep gas on the membrane permeate side while passing carbon dioxide-rich flue gas at the same pressure across the membrane feed side. In this way, the partial pressure of the carbon dioxide on the permeate side is maintained lower than on the feed side. Carbon dioxide then passes from the flue gas into the sweep air stream that goes to the boiler. The result is to enrich the CO_2 content in the flue gas from a coal fired power plant from 13% to ~23%. If membranes are used that are very permeable to carbon dioxide, but relatively impermeable to oxygen and nitrogen, very little of the nitrogen and oxygen pass from the air sweep into the flue gas. Because the feed and permeate total pressures are the same, the only compression equipment needed are fans to circulate the gases across the membrane at a minimal energy cost.

In October 2013, MTR and UT Austin began a three-year research and development project, sponsored by NETL (DE-FE003118), to investigate a hybrid post-combustion capture system consisting of Membrane Technology & Research, Inc.'s (MTR) cross-flow, air-swept Polaris™ membrane technology with UT Austin's 5 m PZ-AFS absorption-based CO_2 capture system. The primary objective of this work is to investigate and quantify the cost and performance benefits of the hybrid system and to demonstrate the system in integrated tests at UT Austin's 0.1 MWe SRP pilot testing facility.

Two configurations of the hybrid design are considered. In the series configuration, the absorber removes approximately half of the CO_2 in the flue gas, followed by additional separation by the membrane contactor to achieve 90% total removal of CO_2 by the hybrid capture system. In this arrangement, the absorber operates at a higher lean-loading state and also benefits from the ability of the downstream membrane to mitigate fugitive amine emissions. In the parallel configuration, the flue gas leaving the power plant is split and treated by each system in a parallel arrangement. The principal advantage is that the absorber can be roughly half the size it would normally be. In both configurations, the 5 m PZ-AFS system will treat a more concentrated CO_2 stream which is a preferred condition (Figure 2).

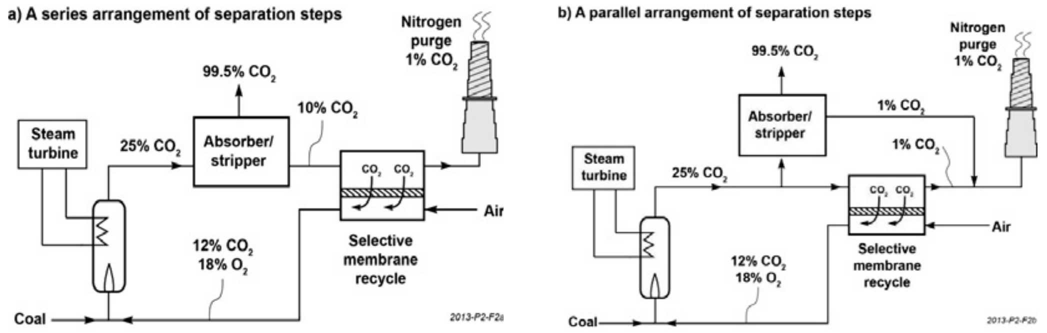

Fig. 2. Two variations on the hybrid design are shown with illustrative stream compositions; (a) Hybrid series arrangement, and (b) Hybrid parallel arrangement.

UT Austin's advanced flash stripper with cold and warm-rich bypass builds upon the technology developed from the two-stage flash and warm-rich bypass configuration tested in previous pilot plant campaigns at UT Austin. The high temperature advanced flash stripping process at 150°C exploits the high thermal stability of piperazine and results in a much higher regeneration pressure (5-10 bar). A heat-exchanger recovers the heat from the overhead vapor and preheats the cold-rich bypass stream. The advanced flash stripping with process offers a smaller footprint, more simple design, and lower capital costs than a conventional packed stripper column (Figure 3) [5].

The higher inlet CO_2 gas concentration of 20% limits the use of concentrated piperazine to 5 m PZ. Use of 5 m PZ will help to increase the solubility window limitations of 8 m PZ and still retain the inherent thermodynamic and thermal stability benefits of concentrated piperazine. The solubility limitation on the rich end is eliminated and lean solubility window is expanded, albeit with a reduction in CO_2 absorption capacity. 5 m PZ has a lower viscosity and will provide approximately the same equivalent work as 8 m PZ. Lower viscosity also results in the faster diffusion of reactants and products, which will help offset the slower reaction rates Adjustments were also made to the design of the absorber intercoolers to account for the higher CO_2 inlet concentrations; the adjustments included changes in the recirculation rates and use of different temperature profiles within each section of the column. UT Austin also optimized the bypass split ratio for the warm-rich and cold-rich solvent flows in the model to solve for minimum regeneration energy configurations. [5].

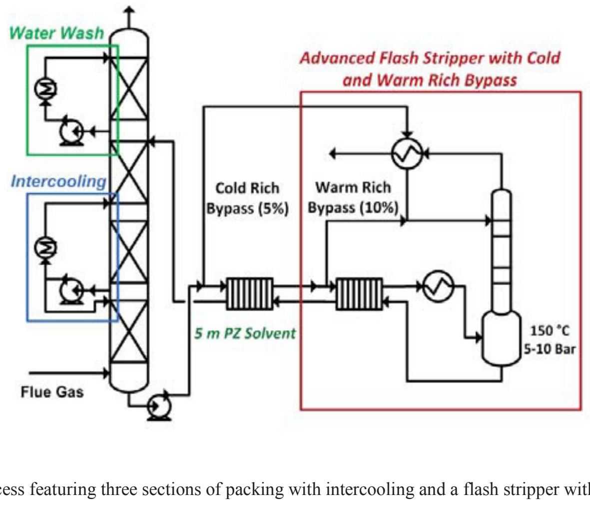

Fig. 3. The 5 m PZ-AFS process featuring three sections of packing with intercooling and a flash stripper with cold and warm rich bypass [1]

2. Methods

A set of existing process simulation models were adapted for hybrid application. MTR developed a new simplified power plant model in ChemCad (v6.3.0, ChemStations, Houston, TX) using the design and operating conditions defined by NETL's Case #11, a 550 MWe supercritical, coal-fired power plant [3]. An existing unit operation for the low-pressure drop, air-swept membrane module, was included in the ChemCad power plant model. A generic unit operation was then added as a proxy for the 5 m PZ-AFS system. This proxy container set the interface points with UT Austin's Aspen Plus® based "Independence" process model (Figure 4). The Independence model consists of separate models for the absorber (rate-based) and the stripper (equilibrium based) portions of the AFS capture system where each can be exercised to produce cost optimized configurations for the system (Figures 5, 6).

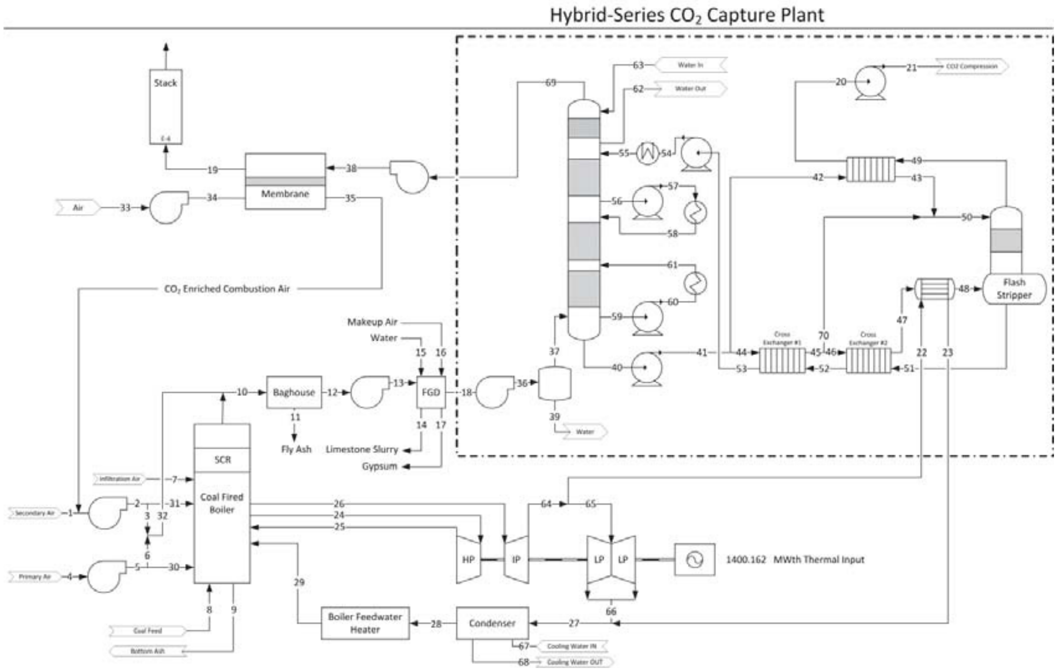

Fig. 4. Major elements of MTR's simulation model showing the interface points with UT Austin's Independence model.

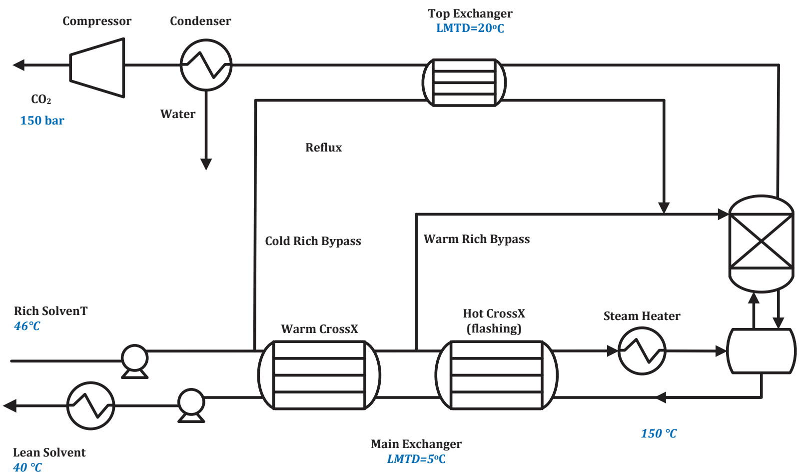

Fig. 5. Major elements of UT Austin's 5 m PZ-AFS absorber model [2]

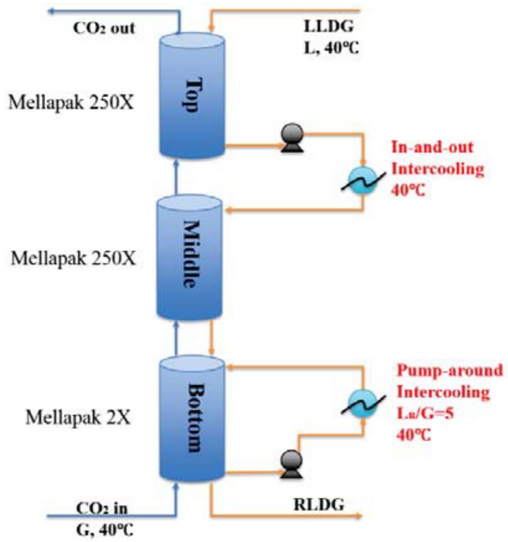

Fig. 6. Major elements of UT Austin's 5 m PZ-AFS stripper model [1]

The objective of the modeling was to evaluate the performance over a range of possible operating and design conditions for the integrated membrane and absorption systems (*e.g.*, different split flows, removal rates) and consider optimal design within each system (*e.g.*, intercooling design, solvent flow rates, rich and lean solvent loadings) and to determine the superior hybrid configuration.

For the series configuration, the main design variable is the fraction of CO_2 removed by the absorber. In the hybrid parallel-configuration, there are two primary variables; the fraction of CO_2 removed by the absorber, and the fraction of flue gas sent to the absorber (vs. the membrane contactor).

Another design constraint is the oxygen content in the combustion air directed to the boiler. As part of the MTR project DE-FE0005795 with NETL, Babcock and Wilcox, Inc. (B&W) modeled and tested combustion effects over a range of CO_2 concentrations in the combustion air. In the hybrid system designs, the CO_2 permeating the membrane dilutes the air sweep stream, effectively reducing the concentration of oxygen. In testing, stable and attached flames were observed at oxygen concentrations down to 16.5%. The conclusions from these tests (which are documented in the Project DE-FE0005795 report, "Effect of CO_2-Enriched Air on Combustion Performance: Pilot Scale Evaluation") were that for retrofit applications, 18% O_2 should be considered a minimum content in the combustion air. For new power plants, where modest changes to the boiler can be made to optimize for changing combustion conditions, then 17% O_2 could be an appropriate minimum. In the hybrid system models, these minimums are used as design constraints [4].

In all simulations, the thermal input (coal flow rate) was held constant at 1400.2 kWth and the total CO_2 removal rate by the hybrid system was held constant at 90%. Using these constraints and assumptions, a test matrix was developed.

3. Results and discussion

Four cases were selected to represent the hybrid-series and hybrid-parallel configurations. In the Tables below, Case #13 and Case #14 represent the series design and Case #18 and #19 represent the parallel design. All cases assume flue gas with 20% CO_2 concentration. The series case has a 60% CO_2 removal requirements for the absorber, Case #18 assumes 99% removal, and Case #19 assumes 95% removal (Tables 1, 2). UT Austin then optimized their system using the Independence model for these conditions.

In the absorber model, a solvent flow rate of 1.1*L_{min} was used. The model has three degrees of freedom: CO_2 concentration coming into the absorber, absorber CO_2 removal percentage and solvent lean loading (the solvent lean/rich loading terms describe a CO_2 molar loading relative to the amine, and are expressed as moles of CO_2: moles of alkalinity). To better understand and further estimate the absorber performance in this range, a factorial design has been used to define the model inputs. To improve the mass transfer rate, both in-and-out intercooling and pump-around intercooling have been simulated for the absorber. The model calculates the solvent flow rate, packing height, rich loading, and optimized position of intercooling for each case. The absorber performance with intercooling can be seen from the liquid/gas temperature profile and CO_2 composition profile in Aspen Plus, and the intercooling loops of the absorber model can be further modified to minimize energy use. Empirical correlations for normalized packing and rich loading have been derived. Normalized packing and rich loading can be predicted from CO_2 concentration, removal, and lean loading [2].

A comprehensive accounting of the absorber modeling effort and expanded results are presented to GHGH-12 in a companion paper [2]. A similar GHGT-12 companion paper on the stripper modeling and results is also available [1].

Table 1. Model inputs and absorber conditions for hybrid series an parallel design (packing area for Case #19 was not determined). [2]

Case	CO_2 (%)	CO_2 capture (%)	Lean loading (mole CO_2/mole alk)	Rich loading (mole CO_2/mole alk)	L/G (mol/mol)	Total packing area (1000 m^2)
13 (Series)	20	60	0.29	0.41	6.2	342
14 (Series)	20	60	0.38	0.42	19.0	996
18 (Parallel)	20	99	0.23	0.40	7.1	520
19 (Parallel)	20	95	0.25	0.43	9.2	--

Table 2. Regeneration energy performance for the two hybrid designs.[1]

Case	CO_2 (%)	CO_2 capture (%)	Total equivalent work (kJ/mole CO_2)	Heat duty (kJ/mole CO_2)	Stripping pressure (kPa)	Cold rich bypass (%)	Warm rich bypass (%)
13 (Series)	20	60	30.7	93.2	701	6	21
14 (Series)	20	60	30.9	94.7	784	5	15
18 (Parallel)	20	99	34.4	84.6	613	7	29
19 (Parallel)	20	95	34.0	83.7	668	6	22

For Case #14, the higher lean loading (0.38 mole CO_2/mole alkalinity) allows for higher stripper pressure (784 kPa) which reduces the compressor duty, but the decreased carrying capacity of the solvent dramatically increases the recirculation rate (19.0 L/G) which increases packing area requirements (996,000 m^2) compared to a lower lean rate in Case #13. The hybrid parallel cases have somewhat higher total equivalent work (34 kJ/mole CO_2), but the area for the membrane is reduced.

In MTR's simulation model, in the low-pressure membrane contactor, CO_2, N_2 and H_2O in the membrane feed (partially decarbonated flue gas) permeate the membrane and become part of the sweep gas (air), thus diluting the O_2 content of the sweep. At the same time, O_2 permeates from the air sweep to the flue gas stream, resulting in additional O_2 loss via the CO_2-enriched combustion air stream. As such, permeating an increasing quantity of CO_2 reduces the O_2 content in the combustion air.

For the hybrid-parallel case, O_2 content in the combustion air is plotted for two CO_2 absorber removal rates (95% and 99%) over a range of flue gas split percentages (the division of flue gas between the absorber and membrane contactor) to determine the minimum ratios which meet the minimum O_2 content levels for new and retrofit applications. For retrofit applications (18% O_2), 65% of the flue gas flows to the absorber when 95% of the CO_2 is removed, and a 60.5% split ratio is used for the 99% CO_2 removal case. For new build applications (17% O_2), the percentage of flue gas flow to the absorber is reduced to 53% for the 99% CO_2 capture rate case, and 57.5% for the 95% CO_2 capture rate case (Figure 7). The CO_2 concentration in the flue gas is nearly 24%, which is higher than what was used in the original test matrix which used 20%.

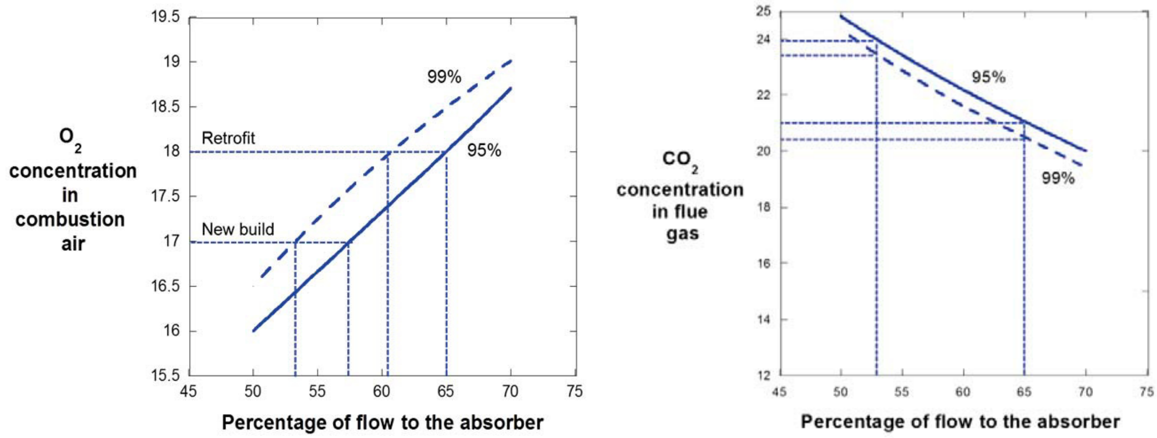

Fig. 7. Hybrid-parallel: The O_2 concentration limits in the combustion air (left) determine the split of flue gas to the absorber and the maximum CO_2 concentration in the flue gas (right).

The hybrid-series configuration has lower CO_2 concentration in the combustion air compared to the hybrid-parallel configuration and, by virtue of treating the entire flue gas volume instead of only a portion of it, the membrane operates at a lower sweep ratio. This results in stronger dilution effects, and requires a higher CO_2 removal rate by the 5 m PZ AFS capture plant. For a retrofit power plant (18% O_2), the absorber must remove 77% of the CO_2 in the flue gas (Figure 8). This improves (~63%) for a new build power plants, but only marginally. These are worse conditions compared to the assumptions in the original test matrix.

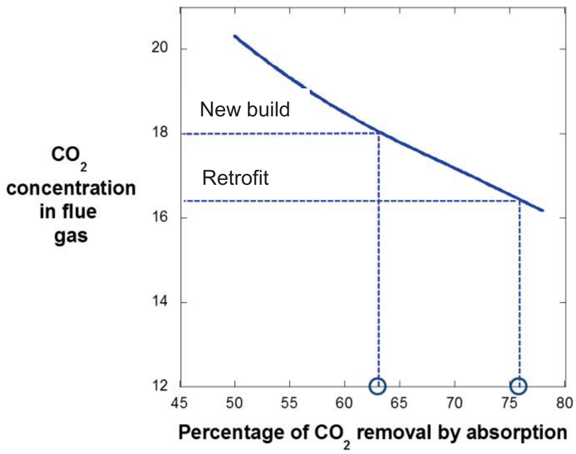

Fig. 8. Hybrid-Series: Maximum possible CO_2 concentration in the flue gas and minimum CO_2 removal requirements.

While the 5 m PZ-AFS applied to the hybrid-parallel system is more compact and will be less expensive relative to a 5 m PZ-AFS applied conventionally, the capacity of the solvent limits additional performance gains afforded by the elevated CO_2 concentration in the flue gas. In response, in addition to 5m PZ, the project team is investigating solvent blends with higher CO_2 capacity (to take advantage of the high CO_2 concentration provided by the membrane) is also being modeled. The solvent blend of 5 m MDEA/5 molal m PZ offers higher CO_2 capacity and the VLE curve of the solvent blend is flatter at the rich end than the curve for the PZ solvent. It is expected to result in greater delta loading and lower energy cost. Different intercooling configurations have also been tested to get better absorber performance and minimize energy use.

4. Conclusions

- It is always preferred to have the highest possible CO_2 concentration in the flue gas stream being treated by the absorption system.
- The hybrid process offers the potential for two modes of cost savings; a reduction in regeneration energy in the series case and a reduction in capital costs in the parallel case.
- While high lean loadings allows for high stripper pressures, the implications of high solvent flow rates diminish any gains.
- The hybrid-parallel configuration provides for superior condition for the air-swept membrane contactor.
- The potential of the hybrid-series case is limited by the O_2 dilution effects in the membrane which act to limit the CO_2 concentration potential in the flue gas which in turn increase the CO_2 removal requirements by the 5 m PZ-AFS system.
- Higher capacity solvents should show have better performance treating flue gas with high CO_2 concentrations.

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