A Vortex Contactor for Carbon Dioxide Separations

Kevin T. Raterman (ratekt@inel.gov; 208-526-5444)
Michael McKellar (mgq@inel.gov; 208-526-1346)
Anna Podgorney (poloak@inel.gov; 208-526-0064)
Douglas Stacey (stacde@inel.gov; 208-526-3938)
Terry Turner (tdt@inel.gov; 208-526-8623)
Idaho National Engineering and Environmental Laboratory
P.O. Box 1625
Idaho Falls, Idaho 83415-2110

Brian Stokes (bxs9@pge.com; 415-972-5591)
John Vranicar (jjv2@pge.com; 415-972-5591)
Pacific Gas & Electric Company
123 Mission Street
San Francisco, CA 94105

Introduction

Many analysts [1,2,3] identify carbon dioxide (CO_2) capture and separation as a major roadblock in efforts to cost effectively mitigate greenhouse gas emissions via sequestration. An assessment [4] conducted by the International Energy Agency (IEA) Greenhouse Gas Research and Development Programme cited separation costs from $35 to $264 per tonne of CO_2 avoided for a conventional coal fired power plant utilizing existing capture technologies. Because these costs equate to a greater than 40% increase in current power generation rates, it appears obvious that a significant improvement in CO_2 separation technology is required if a negative impact on the world economy is to be avoided.

The improvement of current separation technologies is one possible solution to this dilemma. According to the IEA study, chemical or physical absorption technologies possess the highest near term potential for the low-cost and effective separation of dilute CO_2 from mixed gases. In practice, this technology utilizes a basic two step process design; first, multi-tray gas-liquid scrubbers affect CO_2 removal via absorption to a liquid phase or solvent; and second, liquid absorbent is regenerated by heating, pressure reduction or both. Capture efficiency is predicated largely on liquid circulation rate and gas residence time.[5] Under the best of conditions, conventional towers operate at 80% of the equilibrium absorbent loading capacity. This means that at least 20% of the absorbent is needlessly regenerated at a significant cost. (Nearly 90% of the process energy requirement is associated with solvent regeneration.) Additionally, conventional towers cannot be operated below 60% of their design capacity. This limits their utility for power generation applications in which peak and minimum demands may exceed this operating range. In the context of dilute CO_2 removal from large volume gas flows (> 100 million standard cubic feet per day (MMscfd)), it is also apparent that very large conventional scrubbers and regenerators will be required. Consequently, anticipated capital and operating expenses will be high and new technologies that decrease the size of these units, increase their operational flexibility, and improve their capture efficiency will be preferred.

Given the proposed scale for CO_2 capture to mitigate global warming, a high efficiency, compact, and operationally flexible absorber is required. Namely, improved contactor designs to process high volume flue gas would eliminate the need for physically large scrubbers that require high liquid absorbent throughputs, incur high operating costs to regenerate absorbent, and have limited turndown capabilities. In this regard, the potential for operational and capital savings are enormous.

Objective

Development and demonstration of a unique gas-liquid contactor design for the separation of carbon dioxide from natural gas and flue gas is being researched. The objective is to achieve significant improvements in performance, operational flexibility and cost over conventional gas absorption technology for the separation of CO_2 from dilute CO_2 -gas mixtures (<15%). This work will specifically address process and design optimization of a vortex tube CO_2-liquid absorber.

Background / Approach

Absorption by aqueous alkanolamine solutions has proven to be the practice of choice for large-scale CO_2 separations from gas mixtures. Carbon Dioxide absorption into alkanolamine solutions (for instance, diethanolamine (DEA)) consists of two major steps, diffusion followed by reaction. For CO_2 - DEA the reaction may be written as:

$$CO_2 + 2\ R_2NH = R_2NCOO^- + R_2NH_2^+ \quad (1)$$

where R stands for $–C_2H_4$-OH.

The forward reaction rate constant has been measured [6] and can be considered rapid with respect to CO_2 diffusion at typical process conditions. Hence, the diffusion process is rate limiting. According to the two film theory of gas-liquid absorption, CO_2 transfer from the bulk gas to the liquid phase is mediated by diffusion through a stagnant gas and liquid film about the interface. [7] It has been noted that the resistance to mass transfer in these films can be significantly reduced if the turbulent mixing between gas and liquid is increased. [8] Likewise, the absorption rate can be enhanced if the interfacial area to mass transfer per unit volume is also increased. An improved contactor design should, therefore, aim to promote higher transfer kinetics by creating turbulence and a greater interfacial area for mass transfer.

Of the various contactor designs currently used, shear jet absorbers exhibit the highest mass transfer fluxes. [9] In these absorbers gas and liquid are simultaneously injected through a nozzle to generate turbulence and large interfacial areas per unit volume. Chakma et. al. [10] achieved near equilibrium CO_2 loadings (defined as the moles of CO_2 absorbed per moles of absorbent) through such a device and observed that the high shear conditions created by the nozzle promoted the formation of fine droplets and the intimate mixing of gas and liquid. The small drop diameters (less than 100 microns) can be attributed to the high differential acceleration and turbulence that drops experience within the nozzle and expansion chamber. Under the flow conditions of the chamber, the critical differential velocity for droplet breakup is exceeded and much smaller drops are produced. Higher mass transfer rates are the practical consequence of smaller drop sizes because mass transfer is inversely proportional to the square of the drop diameter. [11]

The major deficiency of high shear jet absorbers is that high mass transfer efficiencies are attained at the expense of power dissipated through the nozzle. In one study [9] the overall mass transfer coefficient was correlated to the absorbent concentration, the partial pressure of CO_2, and the power dissipated per unit volumetric liquid flow. The latter term is directly related to the gas-liquid flow ratio and is a general measure of turbulence. It was observed that mass transfer efficiency at a fixed gas-liquid ratio improved to a point with power input. Further increases in power, however, had no tangible effect on the transfer efficiency. Thus, it is clear with respect to mass transfer that the nozzle is optimized for a single gas liquid ratio or power input.

The above behavior can be understood by considering the dynamics of the jet. Namely, the ability to atomize liquid and create surface area in a jet is optimized when the mixture velocity is near sonic and the mixture exits the nozzle with an abrupt pressure drop. [12] For mixture velocities below sonic, turbulence production and atomization are limited. Similarly, for a mixture velocity above sonic, power is wasted. Because turbulence production, atomization, and mass transfer are linked, it is clear that a jet absorber should be operated near its critical mixture velocity for a given gas-liquid ratio. Accordingly, it

is recognized that a fixed orifice device is operationally limited and a variable orifice device is required for most gas absorption operations in which input gas-liquid ratios vary.

Based upon the above discussion, this work seeks to design a new absorber that utilizes a variable orifice jet to achieve high mass transfer efficiencies while minimizing energy requirements. This work also seeks to optimize the nozzle type and geometry towards this same goal. The design targets a tenfold improvement in mass transfer efficiency over conventional packed bed technology. Finally, the design aims to package these features into a compact, operationally robust device that is a self-contained gas-liquid contactor and separator. In what follows, the specific features of a vortex tube contactor will be enumerated.

Technology

Ranque-Hilsch vortex tube technology has been used for many years for small cooling applications. The operating principle of a standard tube involves the tangential injection of compressed gas into a tube with exits at either end. The gas undergoes expansion (Joule-Thomson) through the tangential nozzle and a high velocity cyclonic flow is formed. As the gas progresses down the tube, two distinct temperature zones arise – a hot zone near the tube periphery and a cold zone near the tube axis. Although several causes for this temperature segregation have been proposed, none are proven. Nevertheless, at the far end of the tube the center zone is reflected such that hot and cold gases exit the tube at opposite ends. See Figure 1. Due to isoenthalpic expansion, the total gas flow is cooled; but, because of the unique temperature separation within the tube, the cold stream exits the tube at a far lower temperature than the corresponding expansion temperature. It is this aspect that has caused vortex tubes to be utilized for cooling.

Although the vortex tube can achieve high centrifugal forces, i.e., on the order of 100,000 g, [13] the tube has not been exploited for gas mixture separations. Early studies with binary gas mixtures showed separation enrichments of nearly 10% when molecular weight differences between components were large. [14] For most commercial gas mixture separations, however, this degree of enrichment is deemed insufficient. Recently, heavier hydrocarbon components have been removed from natural gases by initiating condensation within the tube by way of expansive cooling. Heavier components are efficiently removed, as liquid at the tube wall, prior to exiting at the ends. In this context, vortex tubes have been used to treat natural gas at flowrates approaching 70 MMscfd. [13] The required energy for separation is obtained via compression and the process is best applied to already pressured inlet gases.

The combination of turbulent expansion and mixing, high centrifugal forces, and a modified tube design to separate liquids, affords the vortex tube the necessary attributes to become a high efficiency gas-liquid contactor and separator. See Figure 2. In the context of CO_2 -natural gas or CO_2 -flue gas separations, it is envisioned that liquid phase absorbent be co-injected with gas, mixed, dispersed, and separated via centrifugal action within the same unit operation. Due to the extremely dispersed nature of the liquid (large interfacial area for mass transfer) and the high degree of turbulent mixing at the vortex inlet, the kinetics of CO_2 transfer from the gaseous to liquid phase should be enhanced over that associated with traditional tray or packed column designs by a factor of ten or more. Furthermore, because gas residence times in the vortex tube are on the order of

milliseconds versus several seconds per tray for multi-stage scrubbers, a vortex separation process should incur significantly smaller liquid absorbent fluxes and therefore, regeneration costs. Precedence for the above claims has been established in the literature [13] for commercial natural gas dehydration with triethyleneglycol. In a commercial application, a single fixed aperture vortex tube contactor met dehydration specifications at solvent flowrates less than one half those of conventional glycol absorption gas dehydration units.

It is expected that power dissipation through the nozzle will be the greatest impediment to the cost-effective operation of the device. Consequently, it is imperative that mass transfer efficiency and power dissipation be optimized by maintaining near sonic velocities through the nozzle for all gas-liquid ratios. This will be accomplished by employing a variable aperture design for the nozzle. Mechanically, the nozzle design will be simple. See Figure 3. A fixed position internal housing will be fitted to the existing nozzle. The housing will be slotted such that in the open position the housing slots align with the nozzle channels to allow unrestricted flow. As the nozzle is rotated, however, the channel and housing slots are no longer aligned. Consequently, flow through the nozzles is restricted and the mixture velocity is adjusted to the critical sonic or choke velocity.

In the final analysis, the proposed contactor should be physically small, inexpensive, and easy to maintain due to its near lack of moving parts. For comparison, a commercially available vortex tube (Exair Corporation) with a rated flow of 0.25 MMscfd can be purchased for $750. The tube is approximately 1 inch in diameter and 11 inches long. These characteristics are particular advantageous when compared to other novel gas-liquid contactors, such as “structured packing” and “microchannel reactors”, which are operationally limited by plugging, low throughputs, and high costs.

With regard to high volume CO_2 separations, it is proposed that several vortex tube contactors would be operated in parallel and cascaded if necessary. See Figure 4. This would afford the processing unit a large turndown ratio for variable gas flowrates. It is envisioned that processing rates on the order of several hundred million standard cubic feet per day should be achievable. Conversely, efficient separation for small, dispersed gas sources should also be attainable. In principle, there are no temperature and pressure limitations associated with vortex tube operation. Because of its compact tubular design and lack of moving parts, the contactor can conceivably be fabricated to withstand high pressures and elevated temperatures in a corrosive environment. As always, the most cost-effective operation will be achieved by integration amongst all processes and end uses.

Specifically, the following process improvements are claimed for a vortex tube contactor for dilute CO_2 mixture separations. These claims are made in comparison to conventional gas absorption technology. Namely,

- Lower capital costs due to a high-efficiency, compact, and simple design;
- Higher CO_2 capture efficiencies;
- Lower maintenance expenses due to a simple design;
- High process turn-down and scale-up capability when operated in parallel;
- Reduced absorbent and absorbent regeneration requirements because of high mass transfer and liquid separation efficiencies; and,

- Lower solution losses due to efficient liquid separation.

Results

Design and fabrication of a prototype vortex contactor began in the third quarter of 2000. The initial design was predicated on an existing one for a commercial cooling device. The contactor is depicted in Figure 2. Specific design requirements were based on the anticipated gas-liquid loading for a gas containing up to 15% CO_2 using DEA as the absorbent. Significant modifications to the tube were made to facilitate the injection and removal of liquid. Notably, the contactor has separate liquid and gas inlets. This design feature should allow for an even disbursement of liquid with minimal liquid slugging because the liquid and gas are mixed immediately within the regulator nozzle. The regulator nozzle, itself, has six fixed aperture tangential orifices through which the gas - liquid mixture is simultaneously fed. The separation chamber or tube follows the nozzle. Due to the centrifugal force imparted to the fluids by the tangential nozzle, liquid is thrown to the separator wall upon exiting the nozzle. The separator tube is tapered in a stepwise fashion. Thus expelled liquid will migrate down the tube and accumulate at the steps. Located at each step are a series of orifices that will serve to conduct liquid to an outer annulus where solvent is collected for regeneration. As with standard vortex tubes, two primary gas exits are provided. The flow split between these exits is adjusted with a throttling valve. At this time, the utility of these last features in the context of gas absorption are not well understood. Fabrication of a 2 SCFM prototype is complete. The prototype has a working pressure of 500 psia.

The flow test apparatus depicted in Figure 5 is also complete. Major components of the test apparatus are two mass flow controllers (Brooks Instruments, Model 5851E) for mixing compressed CO_2 and N_2 gases in any proportion from 0 to 15% CO_2; a high pressure positive displacement pump (Lewa, Inc. Model EKM7-2-16MM); high efficiency coalescing filters (Reading Technologies, Inc, Model 3P-061-M04-DCP-HP); flow, temperature and pressure sensors; and a gas chromatograph (Scentex Systems, Inc., Model Scentograph Plus II) for real time gas analysis.

A total systems analysis will be conducted to evaluate the vortex tube contactor. Contactor performance will be defined and quantified within the context of separation and energy efficiencies. Issues pertaining to performance, reliability, flexibility, and scalability will be addressed. Process benefits and liabilities will be assessed in the context of CO_2 removal from natural gas and flue gas; both of which represent a significant target for greenhouse gas capture and sequestration. Initially, the ability to separate gas and liquid in a vortex tube will be demonstrated. The proposed work will evaluate the efficacy of the proposed design over a broad range of liquid to gas ratios. Design improvements, if necessary, will be affected by adjusting the length of the tube, the number and location of the separator orifices, and the method of liquid introduction. Gas-liquid loading tests will be conducted with air and water.

The interim prototype contactor will next be evaluated for its ability to efficiently remove CO_2 from a carrier gas. These tests will utilize a fixed aperture nozzle and a CO_2 - nitrogen mixture. The absorbent will be an aqueous solution of diethanolamine (DEA). CO_2 capture efficiency will be measured as a function of liquid loading, pressure ratio (P_{inlet}/P_{exit}), DEA concentration, and CO_2 content. A kinetic expression for CO_2 capture

will be developed from the data. This expression will be compared to similar expressions reported in the literature for other contacting devices [9]. Obvious improvements in the contactor design will be noted and incorporated into the prototype.

Concurrent with experimental studies, a Computational Fluid Dynamics (CFD) model of the vortex nozzle will be developed. Shape optimization software (Arbitrary Shape Optimization) will be used in conjunction with the CFD model to select a nozzle geometry and variable aperture design. The design will seek an optimal compromise between turbulence intensity and power dissipation through the nozzle. The intent is to improve gas-liquid mixing while minimizing energy consumption. Again, design improvements will be incorporated into the contactor, as necessary.

Upon completion of testing, an engineering and economic analysis of the vortex contactor will be conducted. A HYSYS (AEA Technology) process model will be constructed based on kinetic data supplied from the testing protocol. The process model will include a full cycle analysis of CO_2 capture by amine solvent and solvent regeneration. The process model and conditions will be predicated on those for an actual natural gas processing plant (BPAmoco's Florida Mesa Gas Plant, San Juan Basin, CO). Estimated capital and operating costs will be compared to those for the conventional technologies already employed.

Benefits

This work is significant in light of its potential applications for the multi-billion dollar gas processing industry and for future industrial concerns related to the capture and sequestration of harmful greenhouse gas emissions. Moreover, this project directly supports the Department of Energy's (DOE) effort to develop innovative technologies to substantially reduce the costs associated with CO_2 capture from greenhouse gas sources. The cost of CO_2 capture and separation from these sources is estimated to comprise over 70% of the total cost of mitigation by sequestration.

Summary

Carbon Dioxide removal from natural and flue gases is a costly endeavor in light of current technology and capabilities. The vortex tube contactor may provide an inexpensive means to achieve CO_2 separations with relatively known technology in a short developmental time frame. The separation is performed by forcing an expanding gas and dispersed liquid absorbent into a turbulent rotational flow field wherein CO_2 transfer to the absorbent phase is greatly facilitated. Subsequent liquid separation from CO_2 -free gas is achieved within the same device fitted with a liquid collector. This aspect of the separation is strictly analogous to centrifugal or cyclonic separation. The clean gas is discharged for end use while the liquid absorbent is regenerated and recycled. Relatively pure CO_2 is captured from the regeneration process for sequestration. The process is potentially cost competitive as a consequence of significantly reduced absorbent fluxes and the attendant regeneration requirements. Both reduced capital and operating expenses are expected with respect to current absorber technologies. Although the process requires gas compression, this cost can be minimized with a variable aperture nozzle design. Broad application to natural gas upgrading and greenhouse gas capture from large to small point sources is envisioned.

Acknowledgements

Support by the U.S. Department of Energy under Contract Number DE-AC07-99ID13727 is gratefully acknowledged.

References

1. Herzog, H. J. 1998. “The Economics of CO_2 Capture,” presented at the Fourth International Conference on Greenhouse Gas Control Technologies, Interlaken,Switzerland, August 30 – September 2.
2. US Department of Energy 1999. Carbon Sequestration State of the Science, A Working Paper on Carbon Sequestration and Science, February. (Draft)
3. Socolow, R., ed. 1997. Fuels Decarbonization and Carbon Sequestration: Report of a Workshop, Report 302, Princeton University Center for Energy and Environmental Studies, September.
4. International Energy Agency 1998. Carbon Dioxide Capture From Power Stations, ISBN 1 898373 15 9.
5. Bullin, J. A., Polasek, J. C., and Donnelly, S. T. 1990. “The Use of MDEA and Mixtures of Amines for Bulk CO_2 Removal,” Proceedings of the Sixty-Ninth GPA Annual Convention, Tulsa, OK, 135-139.
6. Dankwerts, P. V., Sharma, M. M. 1966. “The Absorption of Carbon Dioxide into Solutions of Alkalis and Amines,” The Chem. Eng., CE244-CE280.
7. Whitman, W. G. 1923. “The Two Film Theory of Gas Absorption,” Chem. Met. Eng., 29, 146-148.
8. Eckert, j. S., Foote, E., Rollison, L., and Walter, F. 1967. “Absorption Processes Using Packed Towers,” Ind. Eng. Chem., 59, 41-47.
9. Chakma, A. and Islam, R. 1989. “A Compact High-Performance Absorber for Small-Size Remote Field Gas Processing,” presented at the SPE Gas Technology Symposium, Dallas, TX, June 7-9.
10. Chakma, A., Chornet, J., Overend, R., and Dawson, W., "Absorption of CO_2 by Aqueous Diethanolamine (DEA) Solutions in a High Shear Jet Absorber," The Canadian Journal of Chemical Engineering, 68: 592-598.
11. Chemical Engineers’ Handbook, Perry, R. H. and Chilton, C. C. eds, 1973. McGraw-Hill Book Company, New York.
12. United States Patent 5045245, “Device for Atomizing Liquid or for Comminuting Gas into Small Bubbles,” Chawla, J. M., September 3, 1991.
13. Lorey, M., Steinle, J., Thomas, K. 1998. “Industrial Application of Vortex Tube Separation Technology Utilizing the Ranque-Hilsch Effect,” presented at the 1998 SPE European Petroleum Conference, The Hague, Netherlands, October 20-22.
14. Marshall, J. 1977. “Effect of Operating Conditions, Physical Size and Fluid Characteristics on the Gas Separation Performance of a Linderstrom-Lang Vortex Tube,” International J. Heat and Mass Transfer, 20:227-231.

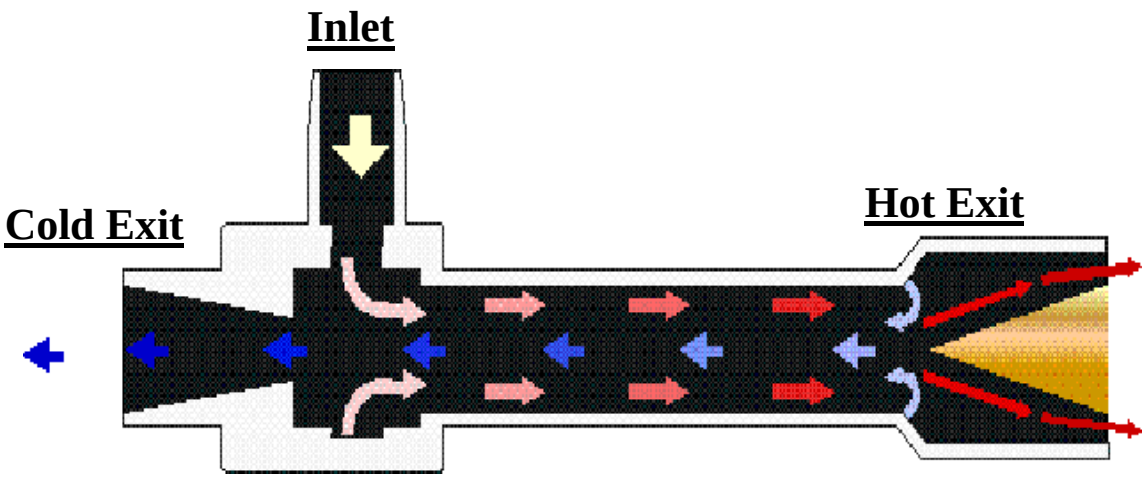

FIGURE 1: Ranque-Hilsch Tube

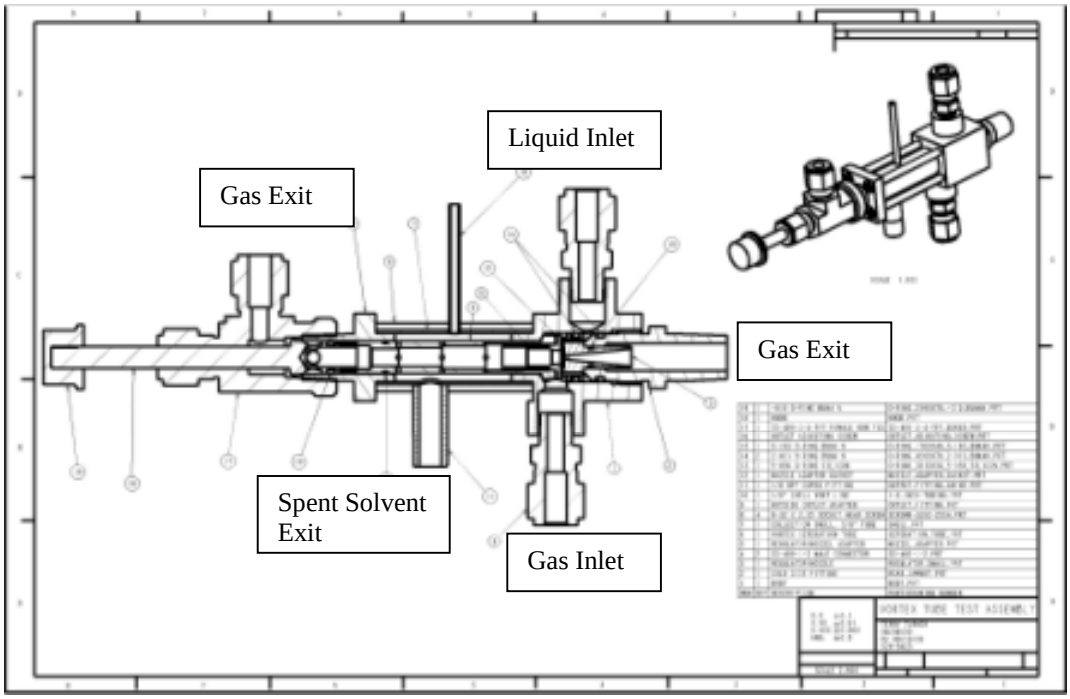

FIGURE 2: Prototype Vortex Contactor

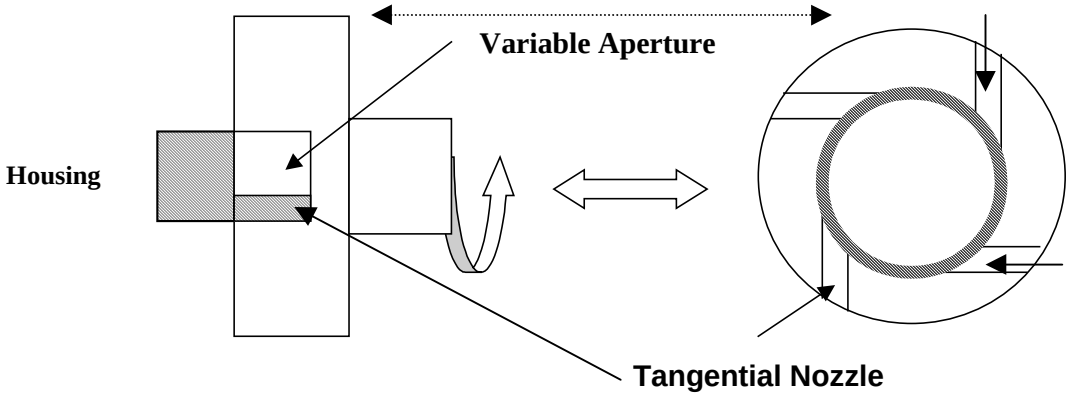

FIGURE 3: Variable Aperture Nozzle

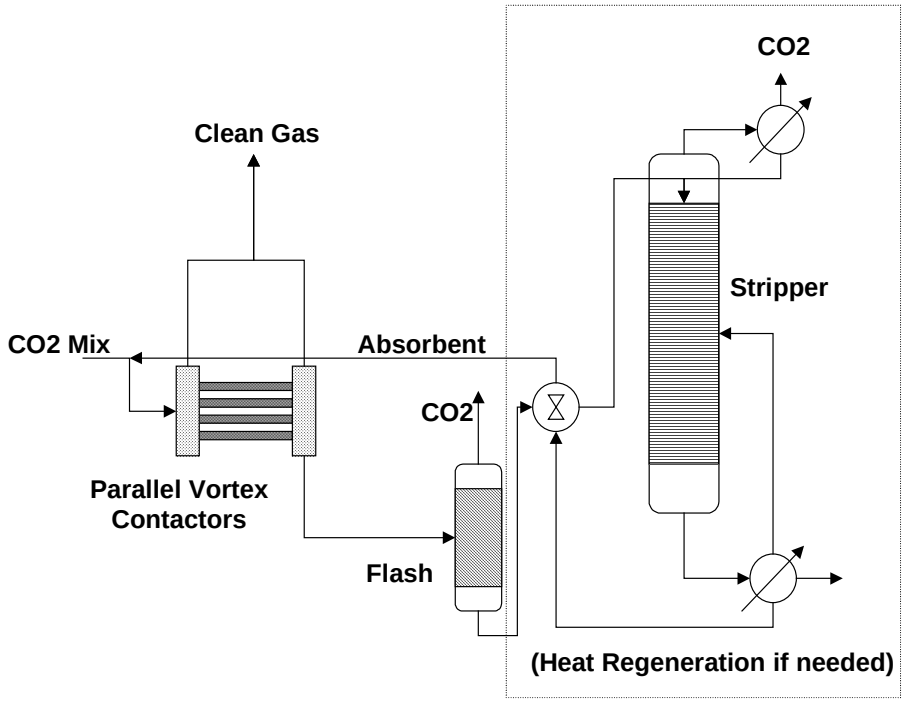

FIGURE 4: Scaled Vortex Contactor

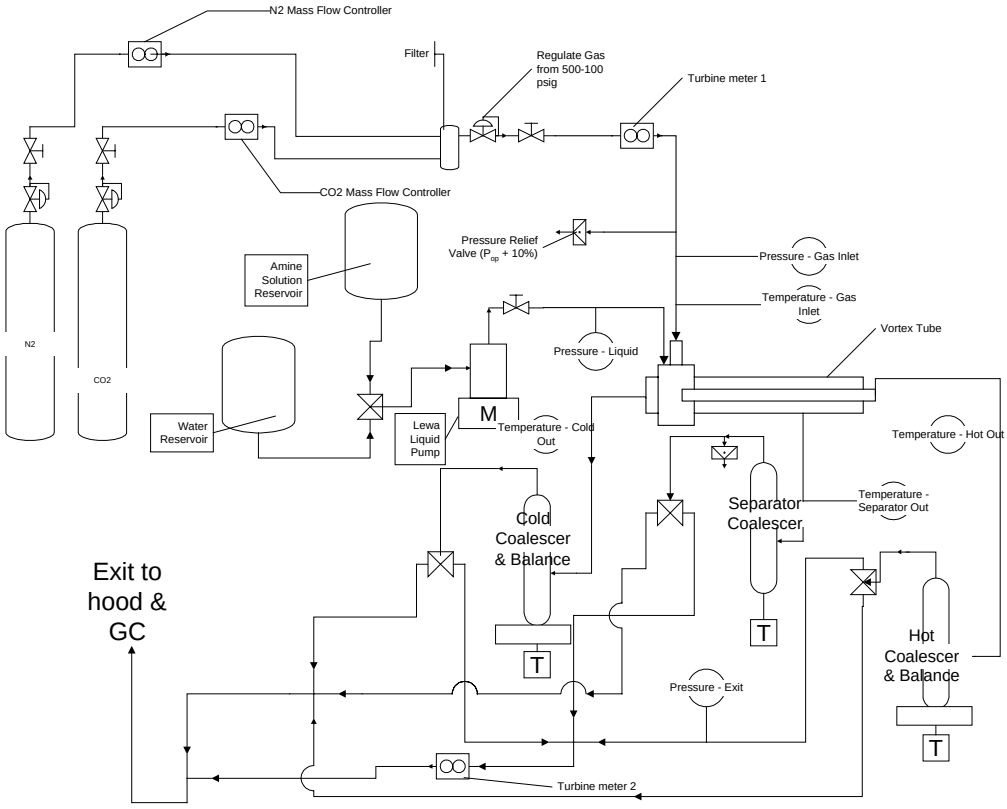

FIGURE 5: Test Apparatus