Prospectus

Texas Carbon Management Program

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Please consider participating in the Texas Carbon Management Program at the University of Texas at Austin. The research program is focused on the technical obstacles to the deployment of CO_2 capture from flue gas by amine absorption/stripping. The primary objective is to develop and demonstrate evolutionary improvements to monoethanolamine (MEA) scrubbing for CO_2 capture from coal- and gas-fired flue gas, including power plants and other sources. The strategy is to apply chemical engineering science to understand and quantify the performance of MEA and piperazine (PZ) absorption/stripping, then to develop innovative, evolutionary improvements.

Background

CO_2 capture by absorption/stripping with aqueous monoethanolamine (MEA) is the benchmark technology for addressing CO_2 emissions from existing coal-fired power plants. Conventional coal-fired power plants represent a large fraction of the existing capacity and capacity to be built before advanced power systems can be deployed. These conventional plants cannot be abandoned in any comprehensive strategy to address global climate change by reducing CO_2 emissions. With the availability of cheap natural gas, new combined cycle, gas-fired power plants will also be a significant source of CO_2 emissions that must be addressed. Alberta has an urgent need to reduce the carbon footprint from gas-fired boilers and turbines used to produce petroleum from oil sands. The lean and rich partial pressure of coal-fired CCS is comparable to CO_2 capture for LNG production.

The economics of the first generation MEA technology are not attractive. The energy requirement can reduce the power output of a coal-fired plant by as much as 30%. However, the alternatives for existing coal-fired power plants can be equally unattractive. Like limestone slurry scrubbing for flue gas desulfurization, aqueous absorption/stripping for CO_2 capture is the first technology to receive serious consideration and it will probably survive as the primary technology to be used for this application.

The TxCMP has identified aqueous PZ with a flash stripper at 150 ^oC as an attractive alternative to MEA. We will continue to minimize energy use and capital cost with innovations of absorber intercooling and stripper configurations and to address the secondary impacts of solvent degradation and amine aerosol emissions. Aqueous blends of PZ with thermally resistant tertiary amines and other amines will be developed to permit economic operation at lower lean loading and greater rich loading consistent with a range of inlet CO_2 partial pressure from 3 kPa (gas-fired turbine) to 4 bar (natural gas treating). This fully disclosed, comprehensive case study of solvent and process development will develop fundamental understanding and applied methods that will be applicable to the evaluation and development of proprietary solvents and processes.

The deployment of this technology will require a demonstration of CO_2 capture and sequestration on an absorber module at a commercial scale. The purpose of this integrated research effort is to provide the technical basis for such a demonstration on an existing coal-fired power plant, on a new gas-fired combined cycle, and on a gas-fired boiler in the Alberta oil sands.

Focus of Effort

The program includes 13 Ph.D. students, 2 faculty, and 2 Ph.D. professionals working on CO_2 rate and solubility measurements, amine degradation, systems modeling, and pilot plant testing. The effort is funded by more than \$400,000/yr from 13 sponsors in the Texas Carbon Management Program and other affiliated activities including 3 process suppliers (Shell/Cansolv, AECOM, Powerspan), 4 power companies (Southern Company, E.ON Technologies, EPRI, LG&E-KU), 4 oil companies (Chevron, Phillips 66, ExxonMobil, Statoil), the U.S. DOE, and one equipment donor (Emerson).

Solvent Performance

More than 50 solvents have been quantitatively characterized for properties that determine energy performance and capital costs. Future work will focus on thermally stable blends of piperazine (PZ) with tertiary amines and other promising amines. Systematic work with homologous series of amines and amines with commercial potential will continue to build the database to predict amine performance as a function of structure. This work is being done by Yang Du and Ye Yuan.

1. The normalized rate of CO_2 absorption, kg', the CO_2 solubility, and the intrinsic capacity of each solvent are measured in a wetted wall column at absorber and stripper conditions (20–100 ^oC). The total surface area of absorber packing varies directly with the kg'. The size of the cross exchanger varies directly with the capacity normalized by the measured viscosity.
2. Total vapor pressure of loaded solution is measured in an autoclave at 100–160 ^oC. When combined with CO_2 solubility from the wetted wall column, these data determine the heat of CO_2 absorption, $-\Delta H_{abs}$. In a thermal swing regeneration process, greater $-\Delta H_{abs}$ enhances stripper energy performance by resulting in greater stripper pressure or reduced reboiler temperature.
3. Thermal stability of loaded solvent is determined by degradation in sealed cylinders at 100–175 ^oC. The parent amine and degradation products are analyzed by ion and liquid chromatography and identified by mass spectrometry. Systematic measurements with variation of solution composition define the kinetic mechanisms of thermal degradation. T_{max} is the stripper T that would give the same degradation rate as MEA. Greater T_{max} permits greater stripper P and T with reduced compression capital and energy cost.
4. Additional thermodynamic measurements support rigorous predictions by the electrolyte-NRTL model. Amine volatility in loaded solutions is measured by hot gas FTIR at absorber conditions. Solutions are speciated by H^1 and C^{13} NMR at 25–60 ^oC to provide a fundamental basis for rate modeling. Liquid heat capacity is measured with a differential scanning calorimeter.

Solvent Management

Solvent management is required to minimize secondary environmental impacts and costs of solvent make-up. This effort includes fundamental studies of loss mechanisms and more applied measurements to deal with each of the mechanisms. It includes case studies with PZ and MEA and screening of other amines but will start to develop more detailed information on these other amines. Paul Nielsen, Steven Fulk, Matt Beaudry, and Kent Fischer are performing this research.
5. Oxidative degradation is being elucidated by comprehensive analysis of degraded samples from pilot plants and bench-scale experiments. The solutions are analyzed by cation and anion chromatography, HPLC, mass spectrometry, and NMR to determine and quantify the parent amine and degradation products including aldehydes, organic acids, amino acids, and amides. A simple bench-scale experiment with intensive exposure to oxygen for 1 to 3 weeks is used to screen amines at absorber conditions. Temperature cycling in another apparatus is used to simulate absorber/stripper conditions. The cycling system uses hot gas FTIR to determine ammonia and other volatile degradation products.
6. Solvent reclaiming by evaporation is being tested with batch operation at the bench scale and continuous operation at the pilot scale. Ion exchange is being evaluated to selectively remove dissolved metals from aqueous amine solvents.
7. Amine aerosol formation is being examined in a bench-scale scrubber equipped with measurements of aerosol size and composition by hot gas FTIR and by phase doppler interferometry (PDI). The results will validate a numerical model of aerosol growth. The FTIR and PDI are being used intermittently in field measurements of amine aerosols at two coal-fired pilot plants operated by others.
8. Nitrosamine formation and decomposition kinetics have been determined in PZ and a number of other amines. NO_x absorption rate and stoichiometry are being measured in the wetted wall column and the cyclic oxidation apparatus. We are developing a method of removing NO_2 with sulfite or a tertiary amine in the SO_2 polishing scrubber. This method will be tested at the National Carbon Capture Center.

9. Corrosion rates of carbon and stainless steel are being measured by an electrical resistance probe at 100–150 ^oC in a cyclic flow system with loaded solutions of amine. We are also inferring corrosion by analysis of dissolved metals in thermal stability samples and in samples from pilot plant testing.

Modeling

Brent Sherman, Yu-Jeng Lin, Matt Walters, Junyuan Ding, and Yue Zhang are developing rigorous models of the amine scrubbing process and using them to evaluate solvents and innovative flowsheets and to optimize the process conditions and configuration to minimize energy and total costs. Most of this work is being performed in Aspen Plus® with rigorous models for the piperazine solvent.

10. Rigorous thermodynamic and rate models of the solvent data are correlated with the Aspen Plus® electrolyte-NRTL model. We have a fully functional model for MDEA/PZ. Rigorous solvent models are being developed for blends of PZ with 2-methyl piperazine, AMP, 2PE, and other hindered and tertiary amines.

11. Rigorous stripper process models are being developed to predict energy requirements and model innovative stripper configurations. This activity includes model reconciliation with pilot plant data. Transparent methods will be developed to estimate equipment costs for exchangers and compressors. These tools will be used to optimize lean loading, exchanger ΔT, and other important stripper design variables.

12. Rigorous absorber models are being developed in Aspen Plus® to represent and extrapolate pilot plant data. The absorber model is being used to evaluate advanced configurations for intercooling and to evaluate performance with other applications including gas-fired combined cycles, gas-fired boilers, and hybrid systems of amine scrubbing and membranes.

13. System models are being developed for optimization and control. gPROMS is being used to build a dynamic model of PZ absorption/stripping to develop control strategies for the entire process.

Pilot plant

Pilot-scale testing at the facilities of the Separations Research Program is used to implement ideas developed by the TxCMP and characterize packing at a larger scale. Di Song is characterizing packing in a 16.8-inch ID column processing air/water. Dr. Eric Chen is supervising pilot testing of amine scrubbing in an integrated pilot plant funded by DOE and the CO_2 Capture Pilot Plant Project (C2P3, an associated industrial associates program). The pilot plant facility is managed by Dr. Frank Seibert.

14. The wetted area and liquid film coefficient of packing alternatives has been measured by CO_2 absorption in 0.1 M NaOH and by toluene desorption. Methods have been developed to measure gas and liquid film mass transfer coefficients with structured and random packing. This work will be expanded to other types of packing and will measure the effect of viscosity on the liquid film mass transfer coefficient with the addition of glycerol to vary viscosity.

15. Pilot plant testing of process and solvent concepts is conducted by C2P3. Interpreted pilot plant results are shared with participants of the TxCMP. A carefully controlled pilot plant facility has been constructed and is being used to provide quantitative screening of contactor alternatives and to demonstrate important process concepts. This facility is currently being used with concentrated PZ and the advanced flash stripper. It will be used to test other advanced solvents and innovative stripper configurations. It is available for proprietary testing by our industrial sponsors.

Participation

Please consider participating in this research program by providing $30,000/yr. If you wish formal participation, you may execute a Memorandum of Agreement. We will provide you with an invoice for payment. You may also implement this support as a gift by sending payment with cover language such as "Enclosed is an unrestricted gift of $30,000 to support the research effort of Dr. Rochelle in carbon management." Neither mode of participation includes contractual deliverables. As a courtesy we will provide you with copies of preprints and publications generated by the research and you will be invited to attend semi-annual research review meetings and to contribute to discussions of future work.

Our next review meeting will be in Lausanne, Switzerland before GHGT-13 on November 14, 2016.