A Guide to Evaluate Solvents and Processes for Post-Combustion CO2 Capture

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Abstract

The CO_2-capture literature is difficult to follow because the number of papers and patents has exploded, and the claims of the authors are difficult to substantiate. From a beginning in the early 90s with just a handful of papers each year, the number of yearly papers has grown exponentially, reaching almost 1,000 publications in 2011. If this exponential rate of increase continues – and there is reason to believe that it will do so – the number of yearly publications will exceed 10,000 before 2020! The number of patents shows a similarly explosive growth. We believe that scientists and engineers who follow this important technology will be aided if they had some structure to guide them, and this paper represents our attempt to initiate the development of such guidelines.

Keywords: CO_2 capture, chemical solvent; heat of solution; solvent evaluation, process innovations

1. Introduction

The CO_2-capture technical literature began in the early 1990s, and the growth has been exponential over these past two decades. Figure 1 shows that the number of publications was almost 1,000 in 2011, and is projected to exceed 10,000 by 2020 if exponential extrapolation is applicable. The number of patents exhibits similar exponential growth, delayed by a period of about 7-10 years. We believe that scientists and engineers who attempt to follow this important process technology will be aided if they had some guidelines to follow, and this paper represents our attempt to initiate the development of such guidelines. Post-combustion capture of CO_2 using amine solvents is likely to be the dominant CO_2-capture technology for the medium term,[1] and hence we limit our analysis to this process technology.
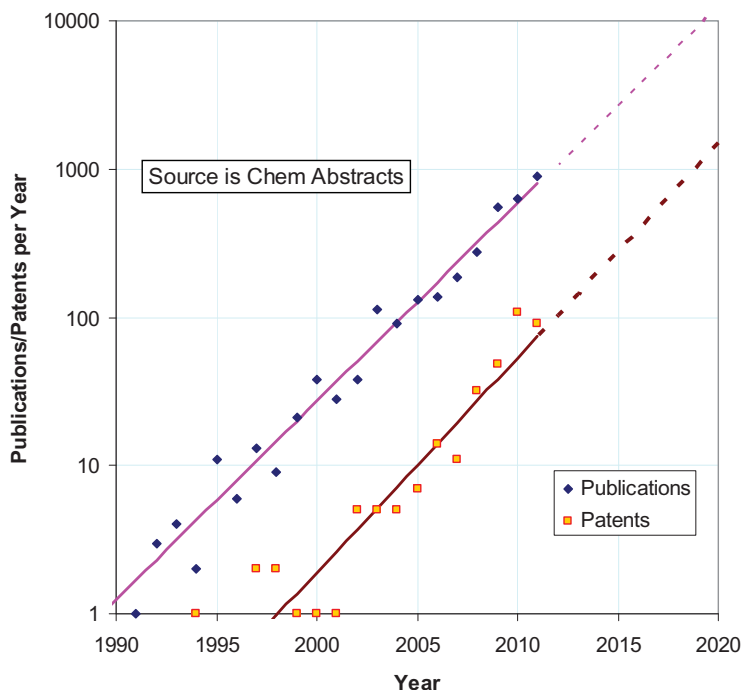
Figure 1 Yearly publications and patents in CO_2 capture. The source is Chem Abstracts, and the lines are best-fit exponential curves.

This work first presents an overview of solvents and process innovations for CO_2 capture, and then describes a systematic simulation process study to evaluate and understand the inherent (thermodynamics based) effectiveness of amine solvents.

2. Overview of Solvents and Processes for CO_2 Capture

The post-combustion CO_2-capture process using amines is based upon absorbing CO_2 in the solvent at low (atmospheric) pressure, and then releasing the CO_2 in a stripper by applying heat and/or another solute like steam. Analogous processes are used for gas purification[2] starting with Bottom's patent,[3] which was filed over 80 years ago. The initial application of CO_2-capture technology is expected to be flue gas from coal-fired power plants.[4] Since the pressure of flue gas is close to atmospheric and significant pressurizing of the flue gas is not energetically feasible, a strong solvent is required, and hence chemical solvents are preferred over physical solvents. Amine scrubbing technology is mature, and will probably be the first to be applied on a large scale, and the initial application will likely be to coal-fired power plants.[1]

Table 1 Desired solvent characteristics – single solvent

Desired Solvent Characteristic	Comments
1. High capacity and low heat of absorption	This characteristic is most important as it directly relates to the energy expended (megawatt-hours per metric ton of CO_2), but the laws of thermodynamics connect the absorption capacity and heat,[5] and thus independent variation may be restricted.
2. High mass transfer and chemical kinetics	This characteristic is desirable because it reduces equipment sizes, and for the same equipment and flow will increase capacity because the system will operate closer to the equilibrium limit.
3. Low viscosity	Lower viscosity reduces pumping costs, and usually leads to faster mass transfer and higher heat-transfer rate.[6]
4. Low degradation tendency	Lower degradation tendency reduces the need for solvent replacement or reclaiming, and allows the regenerator to operate at higher pressure (i.e., higher temperature), which increases thermal efficiency.
5. Low volatility	Lower solvent volatility decreases solvent slip in the absorber, and hence reduces the capacity required for the wash system.
6. Toxicity/environmental	Of particular concern here is the formation of toxic by-products like nitrosamines,[7] or environmental impacts from volatility losses.
7. Cost and availability	A readily available chemical that has other uses is often preferred.
8. Low Fouling Tendency	This characteristic is closely related to the solvent melting point and indicates whether it may precipitate as a solid. Solvent degradation may also cause fouling.

Table 2 Process improvements for post-combustion CO_2 capture

Process Improvement	Comments
1. Absorber intercooler	The absorber heats up since absorption is an exothermic process, and higher temperatures reduce the capacity of the solvent for CO2. Absorption intercooling increases the solvent carrying capacity, which reduces the solvent circulation rate.[8]
2. Lean-vapor compressor	The hot lean solvent is flashed at low pressure to produce a vapour stream containing mainly steam with small amounts of CO_2 and solvent. This stream is compressed in a thermo-compressor and returned to the bottom of the stripper. The stream requirement is significantly reduced since a portion of the steam requirement is supplied by the flashed vapor.[8]
3. Multiple-pressure stripping	The stripper is integrated with the first two stages of the CO2 compressor. The stripper operates at several pressure levels (typically three). Studies have revealed that multiple-pressure stripping reduces the overall work requirement.[9]
4. Interheated stripper	The study of Van Wagener and Rochelle concluded that interheated columns gave the most significant overall energy improvement.[10]
5. Novel solvent regeneration	The solvent characteristic may enable step changes in solvent regeneration. For example, Heldebrandt et al.[11,12] have proposed that an antisolvent may be used to regenerate s switchable solvent at relatively low temperature.

Table 1 lists the desired characteristics of a CO_2-capture solvent, and provides a brief comment on each one. In this work we focus on the first characteristic because it is the most important.

Table 2 summarizes key process enhancements that have either improved the efficiency of post-combustion CO_2 capture or promise improvements in the future. Most of these enhancements are largely independent of the particular solvent, but other enhancements (e.g., #5) require specific features of the solvent. However, process improvements confuse the evaluation of solvents. In this work, we evaluate solvents by keeping the process specifications constant.

3. Solvent Study: Evaluation of the Effects of CO_2 Capacity and Heat of Absorption

Theoretical and experimental approaches have been used to find the "best" solvent for CO_2 capture. Xie et al.[13] built upon the earlier work of Chakraborty et al.,[14] and used ab initio computational chemistry to identify the best balance between chemical reaction extent and the energy of regeneration. Chowdhury et al.[15] synthesized nine secondary and tertiary amines to find a target solvent with high absorption and low heat of reaction. Researchers have generally assumed that the goal is to identify solvents with large capacity and low heat of regeneration. We propose and use a third approach, which invents artificial solvents that have a systematic variation in CO_2 capacity and heat of solution, and test these solvents in an Aspen Plus simulation model. We hope that our approach will improve the understanding of the performance of proposed solvents, and fine-tune our ability to identify and evaluate new solvents.

Table 3 Solvents used to understand correlation between CO_2 capacity and enthalpy of solution

ID	Formula	Molecular Weight	Name
MDEA	$C_5H_{13}NO_2$	119.2	Methyldiethanolamine
TEA	$C_6H_{15}NO_3$	149.2	Triethanolamine
AMP	$C_4H_{11}NO$	89.1	1-Propanol, 2-amino-2-methyl-
NH3	H_3N	17.0	Ammonia
MEA	C_2H_7NO	61.1	Monoethanolamine
PZ	$C_4H_{10}N_2$	86.1	Piperazine
DGA	$C_4H_{11}NO_2$	105.1	Diglycolamine

The seven common CO_2-capture solvents presented in Table 3 were used to understand and quantify the relationship between the CO_2 capacity and the enthalpy of solution; the solvents are listed approximately in the order of increasing magnitude of heat of solution. For the purpose of standardization, a representative condition of 40°C, CO_2 loading of 0.15, and a solvent strength of 7m was chosen. The thermodynamic models for the seven solvents were standard models from the AspenTech support web site,[16] or were developed by the present authors through data regression of VLE data. The solvents covered a range of primary to tertiary amines, yet Figure 2 indicates that there appears to be a simple relationship between the solvent strength and its heat of solution, i.e., solvents with a higher CO_2 capacity (low CO_2 partial pressure) have a larger heat of solution. We have used this relationship to "invent" solvents that can be readily studied in a standardized process model. Primary amines like MEA and DGA form stable carbamates, and hence only half a mole of CO_2 is absorbed per mole of amine, whereas tertiary amines (MDEA and TEA) and hindered amines (AMP) do not form stable carbamates, and hence can absorb up to one mol of CO_2 per mole of amine.[15] The eight artificial solvents shown in Figure 2 were created by modifying the parameters (specifically the enthalpy and Gibbs energy of formation at infinite dilution in water of the amine cation) of the AspenTech MDEA model, and thus they effectively behave as tertiary or hindered mines.
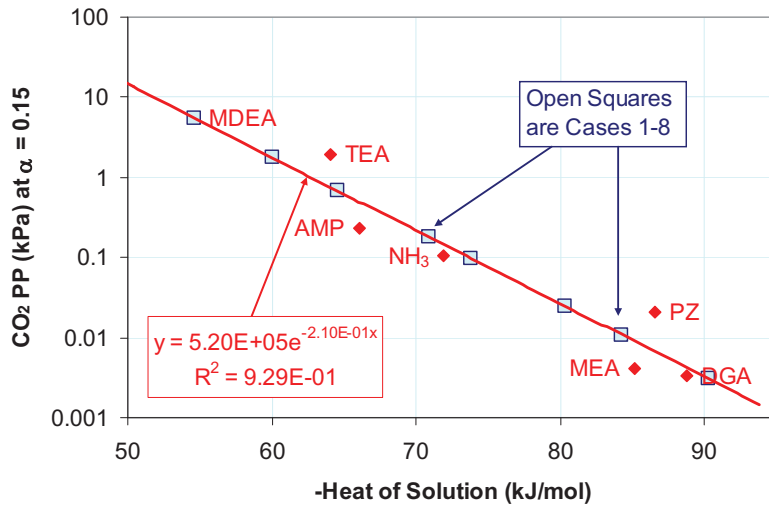
Figure 2 Relationship between the CO_2 partial pressure and the het of solution for seven common solvents. The calculations were done at 40C, CO_2 loading of 0.15 and a solvent strength of 7m. The line is an exponential correlation of the data. The open squares represent the eight artificial solvents created for this study.
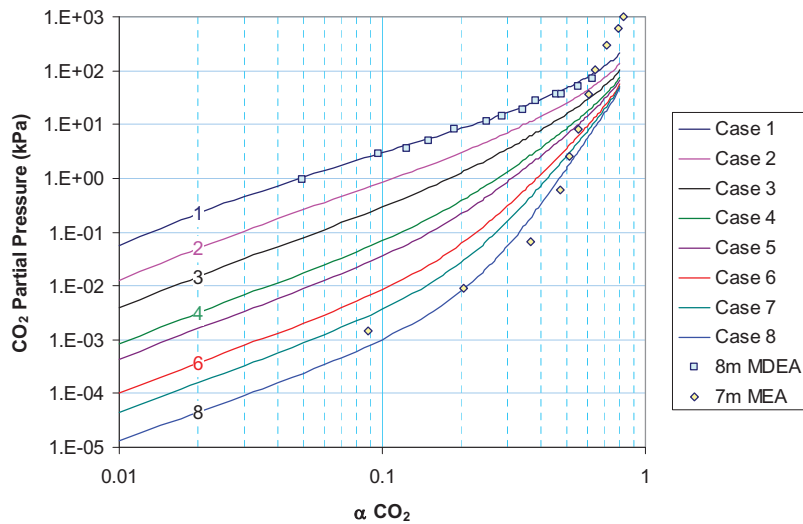

Figure 3 Calculated CO_2 partial pressure of the eight artificial solvents. The points show data for MDEA[18] and MEA.[17]

Figure 3 presents the calculated CO_2 partial-pressure curves for the eight artificial solvents and compares the results with experimental data for MEA[17] and MDEA.[18] The Case-1 solvent is very similar to MDEA, and the subsequent seven solvents show increasingly stronger CO_2 absorption, with increasingly higher heat of solution. MEA is similar to the Case-7 and Case-8 solvents, but MEA's chemical absorption effectively ends as the CO_2 loading approaches 0.5, while the Case-7 and Case-8 solvents continue to chemically absorb CO_2 up to a loading approaching unity.

These eight solvents have been studied in Aspen Plus simulation models with the same process specifications that are summarized below:

1. The flowsheet is a standard absorber-stripper arrangement with a cross exchanger.[8] The only process innovation applied (see Table 2) in that the absorber has an intercooler.
2. The flue gas is representative of a coal-fired power plant with about 13 mole% CO_2.
3. The absorber and stripper models use a rate-based model, but the kinetics are assumed to be very fast. In effect the modelling tests evaluate the thermodynamics rather than the kinetics of absorption.
4. The absorber pressure is assumed to be approximately atmospheric.
5. The absorber has an intercooler that reduces the cools the temperature of the liquid near the bottom using cooling water at 35˚C.
6. The stripper reboiler pressure is set to 186 kPa, with a pressure drop of 7.5 kPa over the column.
7. The solvent flow rate is set to capture 90% of the CO_2 in the flue gas.
8. The approach temperature in the cross exchanger is set to 10˚C.
9. The CO_2 lean loading is set to 0.16.

The process specifications are typical of a CO_2 capture process, but, more importantly, they are kept constant across the eight cases and hence the results are representative of the relative solvent characteristics. Figure 4 presents relative results for the relative reboiler duty and required solvent flow rate. Case-3 has been chosen as the base case. Note that Case-1 and Case-2 absorbents are too weak to capture 90% of the CO_2 in the feed flue gas.

Figure 4 provides insight into some of the findings of this theoretical study. A reduction in the solvent strength results in a (small) decrease in heat rate, but the increase in solvent circulation rate is detrimental and quite significant. More studies on the artificial solvents are planned, and the results will be reported in the near future.

Another set of artificial solvents that can be conceived are those with a fixed heat of solution, but increasingly stronger CO_2 capacity. Chowdhury et al.[15] attempted to synthesize these kinds of chemicals. A study of these kinds of materials has been initiated, and will be reported soon.

4. Summary and Conclusions

The purpose of this paper is to initiate the objective analysis of solvents and processes for CO_2 capture. Objective analysis of this technology is needed because the technical papers/presentations and patents are numerous, and growing exponentially. We have summarized the desired characteristics of solvents and process innovations, and focussed our attention on one important solvent characteristic, i.e., the interplay between CO_2 capacity and heat of regeneration.
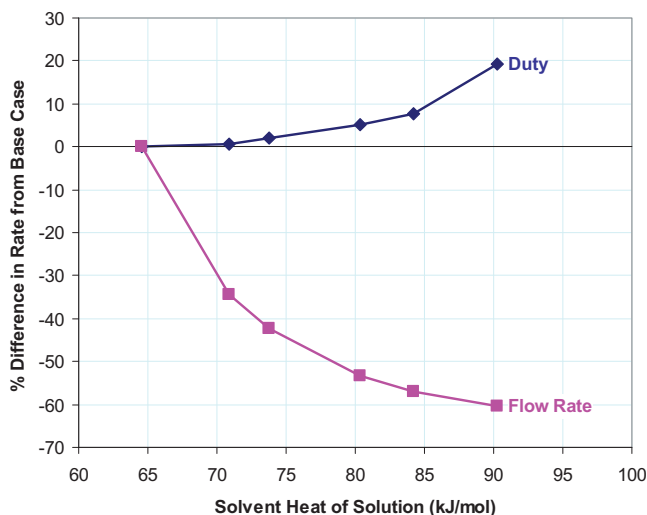
Figure 4 Percentage differences in reboiler duty and solvent flow rate from Case-3. Note that Case-1 and Case-2 were not able to capture 90% of the CO_2.

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