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Solvent Selection for Post-Combustion CO₂ Capture

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Abstract

This paper discusses using computational molecular modeling and process optimization to select solvents for post-combustion CO₂ capture from fossil fuel fired power plants. Post-combustion CO₂ capture processes require considerable energy thus reducing the output of the power plant. For solvent-based capture, the bulk of this required energy is the heat used to regenerate the solvent, and the balance is the electricity required for liquid pumping, the flue gas fan and the final compression of the CO₂ product. The approach is based on computer aided molecular design to generate novel solvents. Key properties for absorption and stripping are obtained for 50 candidate solvents. These solvents are then evaluated in detail with the integrated approach using equilibrium models and compared with the performance of monoethanolamine (MEA) with equilibrium models. We find that many of these new solvents reduce the equivalent energy required for capturing 90% of CO₂ emissions.

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1. Introduction

Various studies [1] of the available options for the large scale capture of CO₂ have concluded that solvent-based, post-combustion CO₂ capture technique is a promising approach. In addition to high capture efficiency and selectivity, this process can be retrofitted to existing power plants. A solvent-based process can potentially also be tuned for various levels of CO₂ capture and is more likely to find acceptance in a competitive market [2]. Given this potential of solvent-based processes in CO₂ capture, the focus of this

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current endeavor is to quantify key solvent properties that minimize energy consumption of CO₂ capture processes.

Two main questions arise in a solvent capture process: how to select an effective separating agent and how to design and synthesize this separation process. In most previous studies, new CO₂ capture solvents were devised using experimental methods which have limited capacity to develop large numbers of possible candidates. In this work, we used a computer aided molecular design (CAMD) method to obtain a large number of possible solvent candidates. These candidates are then evaluated by integrating the solvent selection and CO₂ capture process to find solvents that lower energy consumption.

1.1. The Process Description

CO₂ absorption in a solvent-based capture process is essentially based on the reversible, selective nature of the chemical reaction between the liquid solvent and CO₂ in the flue gas. As shown in Figure 1 [1], flue gas from the boiler is brought into contact with the solvent in the absorber after the removal of impurities such as NO_x, SO_x and particulate matter using processes that also cool the flue gas. A blower is used to compensate the pressure drop experienced in the absorber. In the absorber, CO₂ absorbs into and selectively reacts with the solvent. The flue gas leaving the absorber is relatively free of CO₂. The CO₂-rich solvent from the absorber is then pumped to the top of a stripper (or regeneration vessel), via a heat exchanger. Regeneration of the chemical solvent is done in the stripper at elevated temperatures and often at near atmospheric pressure. The desorption heat required for removing the absorbed CO₂ is provided to the reboiler section of the stripper. The CO₂-lean solvent, containing far less CO₂ is then pumped back to the absorber via a lean-rich heat exchanger to cool it to the operating temperature of the absorber.

1.2. Solvents

A wide variety of organic and inorganic chemicals [3] have been proposed as solvents for chemical absorption of CO₂. Among organic solvents, amines have been the most studied. In particular, aqueous monoethanolamine (MEA) has been the most studied and commercially demonstrated technique [4], though demonstrations have been at scales much smaller than that needed for power plants. In recent research studies, hindered amines have also been shown to be very beneficial [5]. Among inorganic solvents, ammonia [6] and potassium carbonate [7] have generated considerable interest in the research community.

1.3. Solvent Recovery Process & Energy Requirement

An important aspect of post-combustion CO₂ capture processes is the considerable energy requirement resulting in an energy penalty on the power plant. The bulk of this energy is required to supply the necessary heat to regenerate the solvent, and a lesser amount towards the electricity required for liquid pumping, the flue gas fan and the final compression of the CO₂ product. It has been reported that the power output of a coal-fired power plant can be reduced by as much as 30-35% with the inclusion of an aqueous amine based solvent extraction process for the capture of CO₂ [8]. Therefore, it is important to consider the integrated separation process with solvent selection.

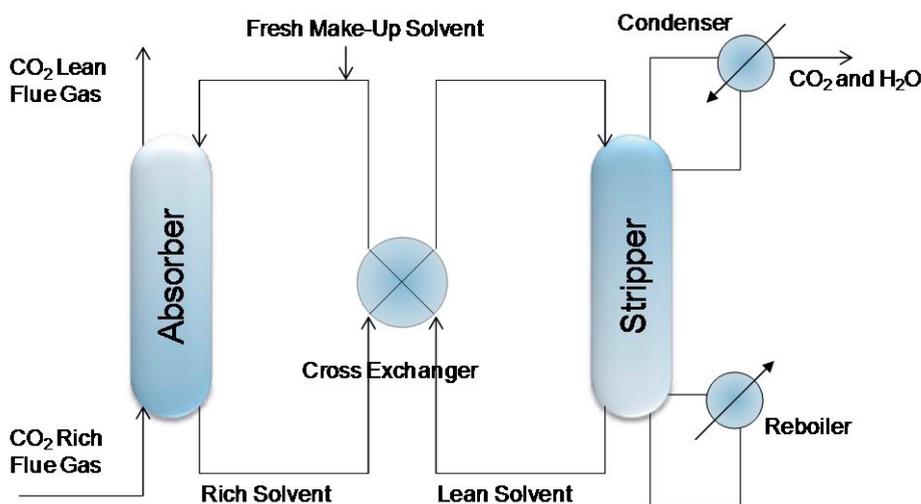


Figure 1
Absorption Process Flowsheet for CO₂ Capture [1]

2. Novel Solvent Selection and Solvent Recovery

In this paper we present the first attempt at using group contribution based CAMD to derive new solvents for CO₂ capture. Here we concentrated on various amines. In order to use group contribution methods, we first considered the equilibrium performance for these new amines for absorbing and stripping CO₂. We found that for MEA, a rate-based model with detailed kinetics shows the same trends as an equilibrium based model, although the equilibrium models predict slightly different energy requirements. Since the solvents we are generating are new solvents, we do not have detailed kinetic information so we assumed that equilibrium based models will show the same trends as kinetic models. In the future, we will generate kinetic parameters for selected solvents for further studies.

In order to predict the absorption capacity of the solvent, we considered both the reactive contribution and the physical absorptive contribution.

2.1. Carbon Dioxide Reactivity

The overall reaction of carbon dioxide with primary or secondary amines is given by:



The Gibbs energy of this reaction can be expressed in terms of the Gibbs energy of formation of each product and reactant:

$$\Delta G_R^\circ = \sum_{\text{prods}} \Delta G_{f,i}^\circ - \sum_{\text{reacts}} \Delta G_{f,i}^\circ \quad (2)$$

Group contribution estimation techniques can be used to adequately predict a chemical's Gibbs energy of formation [9]. These techniques assume each group's contribution is dependent only upon its local structure, not upon the compound's overall molecular structure. For example, using the groups from Jankowski et al.'s method [10] to dissect the structure of monoethanolamine

HO-CH₂-CH₂-NH₂

gives us the following group occurrences:

-OH -CH₂- -CH₂- -NH₂

Each group describes only its internal atoms, and the contribution of the alcohol group is assumed not to be affected by the presence or absence of the amine group.

Using a linear, first order group contribution technique, we can rewrite Equation 2 as:

$$\Delta G_R^\circ = \sum_{\text{prods}} \left(\sum_{\text{groups}} \Delta_{\Delta G_{f,i}^\circ} \right)_j - \sum_{\text{reacts}} \left(\sum_{\text{groups}} \Delta_{\Delta G_{f,i}^\circ} \right)_j \quad (3)$$

Here the value for each compound's Gibbs energy of formation has been replaced by the sum of its group contributions. Table 1 lists the groups for the products and reactants in the reaction of carbon dioxide with monoethanolamine.

Table 1. Groups Used in the Reaction of CO₂ with Monoethanolamine

Compound	Role	Groups
Monoethanolamine	Reactant	2 (-OH -CH ₂ - -CH ₂ - -NH ₂)
Carbon dioxide	Reactant	- - -
Amine ion	Product	-OH -CH ₂ - -CH ₂ - >NH ₃ ⁺
Carbamate ion	Product	-OH -CH ₂ - -CH ₂ - -NH- -COO--

Inserting the contributions for each of these groups into Equation 3 gives:

$$\Delta G_R^\circ = \Delta_{-NH_3^+} + \Delta_{-NH-} + \Delta_{-COO^-} - 2\Delta_{-NH_2} - \Delta G_{f,CO_2}^\circ \quad (4)$$

Equation 4 shows that only those groups created or destroyed by the reaction are used in the computation of the Gibbs energy. The remaining groups do not affect the estimated Gibbs energy and thus do not affect the overall chemical equilibrium. Reacting carbon dioxide with ethanolamine, propanolamine or butanolamine would give the same Gibbs energy. It is likely that a more refined group contribution would predict a different Gibbs energy for each different structure, but for this work, we assumed these differences are less significant than changes in the groups themselves. Therefore, for simulation of the new compounds we decided to start with models for MEA and DEA as extensive data is available for these systems. The reaction system in the process is based on the idea that MEA (DEA) associates either with H₃O⁺ to form an ion MEAH⁺(DEAH⁺) or reacts with CO₂ to form a carbamate ion MEACOO⁻(DEACOO⁻). As in literature [11], chemical equilibrium is assumed with all the ionic reactions similar to MEA or DEA. The equilibrium expressions for the reactions are taken from the literature [11].

2.2. Carbon Dioxide Solubility

Equation 5 is a common simple model used to calculate the solubility of a gas in a liquid [12].

$$\ln x_i = \ln \left(\frac{f_i}{f_{i,l}} \right) - \frac{V_{i,l}}{RT} (\delta_i - \delta_{\text{solvent}})^2 \quad (5)$$

In Equation 5, x_i is the mole fraction of the gas in the solvent, $f_i/f_{i,l}$ is the ratio of the gas fugacity in its pure state to its fugacity in a hypothetical liquid state, $V_{i,l}$ is the molar volume of the hypothetical liquid, δ_i is the gas solubility parameter and δ_{solvent} is the solvent (pure amine) solubility parameter.

Equation 5 shows that gases and solvents with similar solubility parameters will have greater solubility. This is essentially the quantification of the old adage “like dissolves like”. We will use this similarity of solubility parameters as simply a metric for our design of absorption solvents.

For our initial solvent selection we have chosen to use a value of 21.8 MPa^{1/2} for carbon dioxide’s solubility parameter [17]. We thus want to design solvents as close to the solubility parameter of carbon dioxide as possible (see Equation 5).

The other property we concentrated on is related to the stripping operation. Increasing the difference in boiling points of components in a mixture results in an easier separation of that mixture. Therefore, the second metric we selected is the boiling point of the solvent. Since these amines are used in aqueous solution, the boiling point of the new solvent should be as high as possible as compared to water and CO₂ in order to avoid solvent volatility.

The CAMD resulted in a list that included a group of more than 50 alkyl alcohol amines which may not be commercially available and whose CO₂ solubility properties have not been experimentally determined, as far as we know. For these compounds it is expected that those having appropriate solubility parameter will enhance the capture process by modifying the phase equilibrium. The reason for this expectation is that the group contribution methodologies used to estimate chemical equilibrium behavior employ only the reacting part of the molecular structure which is identical for all these compounds.

Although, one of the selection criteria is the solubility of CO₂ in the new compounds, the amines are not used for carbon capture in their pure state but in aqueous solutions. Therefore, the performance of these chemicals as potential CO₂ absorbents needs to be evaluated in such condition.

The absorption and solvent stripping process modeled in ASPEN Plus is used to simulate the process performance.

3. Results and Discussions

We evaluated each of these 50 candidate solvents using ASPEN Plus models and group contribution methods like UNIFAC to evaluate the nonideality. We derived NRTL parameters for new solvents based on UNIFAC groups. Lean solvent flow is adjusted using design specification block so that more than 90% CO₂ is captured in the absorber. In the stripper, distillate flow is adjusted so that solvent leaving stripper has the same concentration as that of fresh solvent solution. Table 2 show three promising solvents, and MEA with energy requirements in GJ per tonne of CO₂ removed. The table also shows regeneration temperature. This variable is important for heat integration. This table shows that the reboiler temperature for the new solvents is in the vicinity of MEA so heat integration should be similar. We also calculated the equivalent energy using the following formula for each solvent [18, 19]:

$$E_{eq} = 0.75\eta Q_{reb} + W_{comp} \quad (4)$$

where E_{eq} is the equivalent energy, η is the Carnot efficiency calculated using regeneration temperature, Q_{reb} is the reboiler heat duty (energy required for regeneration) and W_{comp} is the compressor work for compressing CO_2 to 150 bar.

Table 2. Energy Requirements for New Solvents. Solvent numbers shown are their research ID numbers.

Solvent	Pressure atm	Energy GJ/Tonne	Equivalent Energy, GJ/Tonne	Regeneration Temp. °K
194	1.5	1.67	0.62	378.5
	1	1.798	0.6409	371.2
	0.8	1.793	0.6505	359.2
	0.7	1.92	0.673	356.6
202	1.5	1.88	0.6742	380
	1	1.96	0.6913	369.6
	0.9	2.1	0.7166	367.3
	0.7	2.34	0.756	362.9
198	1.5	1.88	0.6816	383
	1	1.49	0.601	369.8
	0.9	1.9	0.687	367
	0.75	1.91	0.6892	364
MEA	1	4.67	1.17	368

From these preliminary results in Table 2, it can be seen that the new solvents reduce the energy required for solvent recycling process as well as equivalent energy significantly. This can be attributed to the boiling point difference and non-ideality of the solvent.

4. Conclusions and Future Work

This paper presented our methodology of novel solvent selection and solvent stripping for CO_2 capture from the flue gas of fossil-fired power plants. The approach is based on computer aided molecular design for solvent selection, and integrating solvent selection and solvent stripping process design to obtain better CO_2 capture and reduce energy requirements. As a first step, solubility parameter and boiling point of the components are used for selecting 50 possible primary amines. These solvents were further studied using equilibrium models for energy requirements. The integration of these solvents with the solvent stripping process provided a platform to study these solvents for CO_2 capture. We found that these

solvents not only reduced the energy requirement of the process but have better capacity for CO₂ capture. In the future, we plan to synthesize these solvents in laboratory and study their properties. These properties will then be used to obtain optimal process configuration and design for each solvent.

Integration of the absorption process with an existing power plant will require modifications of the low-pressure part of the steam cycle. This is because a considerable fraction of the steam is extracted and hence is not available to contribute towards the plants electricity output [13-16]. In steam cycle based power plants, more than 50% of the thermal energy in the steam cycle is disposed off in the steam condenser. To utilize this heat, the steam cycle system and CO₂ recovery can be integrated and hence part of the waste heat disposed by the steam condenser can be utilized for regeneration of the chemical solvent. Therefore, we plan to carry out the complete process integration of a power plant with these novel solvents in the future.

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