Systems Analysis of Physical Absorption of CO₂ in Ionic Liquids for Pre-Combustion Carbon Capture

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Supporting Information

ABSTRACT: This study develops an integrated technical and economic modeling framework to investigate the feasibility of ionic liquids (ILs) for precombustion carbon capture. The IL 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]) is selected for the IL-based capture system, mainly because of its high nonvolatility, high CO₂ solubility and selectivity, and lower parasitic load. However, their high viscosity poses a challenge for large-scale applications.

INTRODUCTION

Ionic liquids (ILs) are under active development as emerging technologies for carbon dioxide (CO₂) capture because of their favorable properties, such as relative nonvolatility, high CO₂ solubility and selectivity, and endless tenability. ILs also can be used for CO₂ capture without water dilution, which reduces the parasitic load of capture systems. However, their high viscosity poses a challenge for large-scale applications.

Research on ILs has been emphasized on laboratory experiments, molecular and phase equilibrium simulations, and materials synthesis. More novel ILs with high capacity and low viscosity are being synthesized, especially for postcombustion CO₂ capture. While research activities on ILs focus mainly on the application to postcombustion CO₂ capture, there have been relatively few studies of ILs for precombustion CO₂ capture at integrated gasification combined cycle (IGCC) power plants. The shifted gas stream consists mainly of CO₂ (∼38%) and hydrogen (H₂) (∼56%), with CO₂ partial pressures that can be several tens of bars at IGCC plants. So, ILs also appear attractive as a potential physical solvent for precombustion CO₂ capture. Shiflett and Yokozeki measured and predicted the solubility of CO₂ in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]). Recent computational studies demonstrated the technical feasibility of absorption processes using [hmim][Tf₂N] and two TEGO ILs as a physical solvent for capturing CO₂ at an IGCC plant, but lacked cost evaluation.

A variety of thermodynamic models have been developed to predict the phase behavior of CO₂ and other gases in various ILs, such as classical cubic equations, activity coefficient and group contribution methods, and quantum chemistry calculations, and data mining algorithms. However, much less attention has been paid to the simulation and design of IL-based capture systems, and the cost of IL-based capture systems has rarely been evaluated. The major objectives of this study, therefore, are to evaluate the techno-economic feasibility of ILs for precombustion CO₂ capture at IGCC plants and to explore the measures needed to improve the viability of this technology.

MATERIALS AND METHODS

This section presents details of the performance and cost models developed to analyze the IL-based option for IGCC plants. Subsequent sections present plant-level results and comparisons with current commercial alternatives.

Performance Modeling of CO₂ Capture System. The performance modeling framework for precombustion CO₂ capture mainly includes the phase equilibrium model, plus
the mass and energy balance models for an IL-based capture system.

**Physical Properties of Solvent and Gases.** Solvent properties correlate with temperature and/or pressure. Basha et al. developed correlations for density, surface tension, viscosity, and heat capacity for [hmim][Tf2N] based on data from the literature. The vapor pressure of [hmim][Tf2N] is extremely low and negligible. The correlations of density, viscosity, and heat capacity with temperature and pressure are formulated for CO2 and H2 based on data available from the National Institute of Standards and Technology’s properties database for fluid systems. For CO2, the gas-phase diffusivity is predicted using the correlation equation developed by Fuller et al., whereas the liquid-phase diffusivity is predicted using the correlation equation developed by Fuller et al., whereas the liquid-phase diffusivity is estimated as a function of the solvent viscosity. Solvent and gas properties are summarized in Tables S1, S2, and S3 of the Supporting Information (SI).

**Phase Equilibrium based on Equation of State.** The generic Redlich–Kwong Equation of State (RK EOS), relating temperature, pressure, and volume of gases, can be applied to predict the phase behavior of gases in solvents, such as ILs. The modified RK EOS is expressed as follows:

\[
P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)}
\]

For N-component mixtures, mixing rules are applied to estimate the parameters \((a, b)\) in the RK EOS as

\[
a = \sum_{i,j=1}^{N} \sqrt{a_{i}a_{j}} f_{ij}(T)(1 - k_{ij})x_{i}x_{j}
\]

\[
a_{i} = 0.427480 \frac{RT_{ci}^{2}}{P_{ci} - \alpha(T)}
\]

\[
\alpha(T) = \begin{cases} \frac{\sum_{i=0}^{\leq 3} \beta_{i}(T/T_{c} - 1)^{i}}{\beta_{0} + \beta_{1}[\exp(2(1 - T/T_{c}))-1]}, & T/T_{c} \leq 1 \\ \beta_{0} + \beta_{1}[\exp(2(1 - T/T_{c}))-1], & T/T_{c} > 1 \end{cases}
\]

\[
f_{ij}(T) = 1 + \frac{\tau_{ij}}{T}
\]

\[
k_{ij} = \frac{l_{ij}(x_{i} + x_{j})}{l_{ij}x_{i} + l_{ij}x_{j}}
\]

\[
b = \frac{1}{2} \sum_{i,j=1}^{N} (b_{i} + b_{j})(1 - k_{ij})(1 - m_{ij})x_{i}x_{j}
\]

\[
b_{i} = 0.08664 \frac{RT_{ci}}{P_{ci}}
\]

where \(T_{ci}\) is the critical temperature of the \(i\)th species (°K), \(P_{ci}\) is the critical pressure of the \(i\)th species (kPa), \(R\) is the universal gas constant, and \(x_{i}\) is the mole fraction of the \(i\)th species. There are four binary-interaction parameters for each pair of components in the system: \(l_{ij}, m_{ij},\) and \(\tau_{ij}\). However, two or three parameters are sufficient for most equilibrium applications. The fugacity coefficient of the \(i\)th component derived from the RK EOS is described as follows:

\[
\ln \Phi_{i} = \ln \left( \frac{RT}{P(V - b)} + b' \left( \frac{1}{V - b} - \frac{a}{RT(V + b)} \right) \right) + \frac{a}{RTb} \left( a' \left( \frac{1}{b} - \frac{1}{V + b} \right) + 1 \ln \frac{V}{V + b} \right)
\]

in which,

\[
a'_{i} = 2 \sum_{j=1}^{N} \sqrt{a_{i}a_{j}} f_{ij}(T)(1 - k_{ij})x_{i}x_{j}
\]

\[
b'_{i} = \sum_{j=1}^{N} (b_{i} + b_{j})(1 - m_{ij})x_{i}x_{j}
\]

For a component \((i)\), the K-value of vapor–liquid equilibrium (VLE) is calculated as the ratio of liquid versus vapor fugacity coefficients \((\Phi_{L}^{i}/\Phi_{V}^{i})\) from eq 9:

\[
K_{i} = \frac{\Phi_{L}^{i}}{\Phi_{V}^{i}}
\]

The critical component parameters and constants in the VLE model are summarized in Table S4 of the SI. The binary-interaction parameters can be estimated by correlating the experimental solubility data with the RK EOS. The binary parameters of interactions between CO2 and [hmim][Tf2N] and between CO2 and H2 come from the estimates by Shirleth and Yokozeki. The binary interaction parameters for H2 and [hmim][Tf2N] are determined by fitting the solubility data available from the literature. The binary-interaction parameters used for each pair are summarized in Table S5 of the SI. The phase equilibrium model of CO2 and H2 in [hmim][Tf2N] was incorporated in the absorption and stripping process simulation.

**Multistage Equilibrium Process Model for Gas Absorption.** Gas absorption using [hmim][Tf2N] for CO2 capture is treated as a steady-state vapor–liquid process that consists of multiple equilibrium stages. For any stage in a countercurrent cascade, vapor and liquid streams leave in phase equilibrium. Then, a multistage equilibrium model is developed to delineate the absorption process, including the mass balance (M), phase equilibrium (E), summation (S), and enthalpy balance (H) at each stage:

1. **Mass balance for each component at stage \((j)\):**

\[
L_{j} - x_{i,j-1} = L_{j}x_{i,j} + V_{j}y_{i,j+1} - V_{j}y_{i,j} = 0
\]

2. **Equilibrium for each component at stage \((j)\):**

\[
y_{i,j} = K_{i}x_{i,j}
\]

3. **Summation based on mole fractions at stage \((j)\):**

\[
\sum x_{i,j} = \sum y_{i,j} = 1
\]

4. **Enthalpy balance at stage \((j)\):**

\[
L_{j}H_{j}x_{i,j-1} - L_{j}H_{i,j} + V_{j}y_{i,j+1} - V_{j}y_{i,j} - Q = 0
\]

in which \(H_{i}\) is the enthalpy of liquid flow (kJ/kmole); \(H_{j}\) is the enthalpy of gas flow (kJ/kmole); \(L\) is the solvent molar flow rate (kmol/h); \(K\) is the phase equilibrium constant (ratio); \(Q\) is the cooling duty (kJ/h); \(V\) is the gas molar flow rate (kmol/h); \(x\) is the mole fraction in liquid phase; and \(y\) is the mole fraction in gas phase. An inside-out (I/O) algorithm is applied to solve
the coupled MESH equations, which employs two sets of thermodynamic property models: a simple, approximate, empirical set used frequently to converge inner-loop calculations, and a rigorous set used less often in the outer loop.\(^3\)^\(^1\),\(^3\)^\(^2\)

The pressure drop across an absorber is estimated as the product of pressure drop rate and absorber height. The generalized Sherwood-Leva/Eckert correlation is used to estimate the pressure drop rate.\(^3\)^\(^3\),\(^3\)^\(^4\) The absorber height is estimated based on the overall gas-phase mass transfer coefficient of physical absorption, using mass transfer correlations developed by Onda et al. for randomly packed vessels.\(^3\)^\(^5\) Details of the pressure drop estimation are given in Section S3 of the SI.

**Flashing for Solvent Regeneration.** For solvent regeneration, the CO\(_2\)-rich solvent stream exiting the absorber with a much high pressure can enter multiple flash drums with lower pressures, which is similar to the design adopted for Selexol-based CO\(_2\) capture.\(^3\)^\(^6\) The solvent is regenerated and recirculated to the absorber, while the CO\(_2\) is released from the solvent in a series of flash drums and further compressed for transport to a storage site. The calculation of TP-flash based on the phase equilibrium model discussed above is performed to assess the stripping process.

**Key Power Equipment.** There is no thermal energy required for the IL-based capture process. However, electric power is required for process and CO\(_2\) product streams compression and solvent pumping. In the pressure swing for solvent regeneration, some energy from high-pressure solvent streams can be recovered by hydraulic power turbines.\(^3\)^\(^7\) Equipment power use calculations are detailed in Section S4 of the SI.

**Engineering-Economic Analysis of CO\(_2\) Capture System.** This study adopts the costing method presented in the Electric Power Research Institute’s Technical Assessment Guide.\(^3\)^\(^8\),\(^3\)^\(^9\) The performance models discussed above are integrated with engineering-economic models that estimate the capital cost, annual operating and maintenance (O&M) costs, and total annual levelized cost of an IL-based capture system. Table 1 summarizes the costing method.

The total capital requirement (TCR) includes the direct process facilities cost (PFC) plus a number of indirect cost categories. Major direct cost components are given in Table 1. The cost model developed by Chen for a Selexol-based CO\(_2\) capture system was adopted to estimate the major direct costs.\(^3\)^\(^7\) In the model, the direct costs of absorber and flash drums per train are estimated as a function of stream mass flow rates and process pressure if applicable, while the direct costs of compressor, pump, and hydraulic power turbine per train are estimated as a function of equipment power use.\(^3\)^\(^7\) These individual direct cost estimates were further updated mainly based on more recent cost studies by the U.S. National Energy Technology Laboratory.\(^4\)^\(^0\)−\(^4\)^\(^4\) Details of the direct cost estimation are available in Section S5 of the SI.

Indirect costs such as the general facilities cost (GFC) and engineering and home office fees are estimated empirically as a percentage of PFC. The process contingency depends on the status of technology development and is estimated as a percentage of PFC, whereas the project contingency depends on the project design level and is estimated as a percentage of the sum of PFC, GFC, and process contingency.\(^3\)^\(^8\) Other indirect cost categories considered include interest charges, royalty fees, preproduction cost, and inventory capital cost.

Table 1 also summarizes variable and fixed O&M cost components. Variable O&M costs are estimated as the product of the quantity used times the unit price. Operating labor is estimated in terms of hourly labor rate, personnel per shift, and number of shifts. Total maintenance cost is estimated as a percentage of total plant cost, while administrative and support labor is estimated as a percentage of operating plus maintenance labor.

The LCOE of an overall plant or a system is then calculated as follows:\(^4\)^\(^5\)

\[
\text{LCOE} = \frac{\text{TCR} \times \text{FCF} + \text{FOM} + \text{VOM}}{(\text{CF} \times 8760) \times \text{MW}} + \text{HR} \times \text{FC}
\]

(15)

where LCOE is the levelized cost of electricity ($/MWh); TCR is the total capital requirement ($); CF is the capacity factor (%); FCF is the fixed charge factor (fraction/yr); FOM is the fixed O&M costs ($/yr); VOM is the nonfuel variable O&M costs ($/yr); HR is the net heat rate (MBtu/MWh); FC is the unit fuel cost ($/MBtu); and MW is the net power output (MW).

The LCOE is also used to calculate the cost of CO\(_2\) avoided—a key measure of the overall cost of carbon capture and storage (CCS):\(^4\)^\(^5\)

\[
\text{cost of CO}_2 \text{ avoided ($/t CO}_2) = \frac{(\text{LCOE})_{\text{CCS}} - (\text{LCOE})_{\text{ref}}}{(\text{ER})_{\text{ref}} - (\text{ER})_{\text{CCS}}}
\]

(16)

where ER is the CO\(_2\) emission rate (t/MWh). The subscripts of “CCS” and “Ref” indicate an IGCC plant with CCS and a reference IGCC plant without CCS, respectively. A plant-level assessment will be conducted to estimate LCOE and ER for both plants with and without CCS.

Some studies of CO\(_2\) capture processes also report the cost of CO\(_2\) separation ($/t CO\(_2\)\(_s\)). This is typically based on a “stand-alone” analysis of a capture process in which the cost of

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**Table 1. Costing Method and Nomenclature**

<table>
<thead>
<tr>
<th>category</th>
<th>cost component</th>
</tr>
</thead>
<tbody>
<tr>
<td>capital cost</td>
<td>process facilities capital</td>
</tr>
<tr>
<td></td>
<td>absorbers</td>
</tr>
<tr>
<td></td>
<td>high-pressure flash drums</td>
</tr>
<tr>
<td></td>
<td>middle-pressure flash drums</td>
</tr>
<tr>
<td></td>
<td>low-pressure flash drums</td>
</tr>
<tr>
<td></td>
<td>solvent pumps</td>
</tr>
<tr>
<td></td>
<td>high-pressure stream compressors</td>
</tr>
<tr>
<td></td>
<td>low-pressure stream compressors</td>
</tr>
<tr>
<td></td>
<td>CO(_2) product compressors</td>
</tr>
<tr>
<td></td>
<td>hydraulic power recovery turbines</td>
</tr>
<tr>
<td></td>
<td>sump tanks</td>
</tr>
<tr>
<td></td>
<td>heat exchangers</td>
</tr>
<tr>
<td></td>
<td>general facilities capital</td>
</tr>
<tr>
<td></td>
<td>engineering and home office fees</td>
</tr>
<tr>
<td></td>
<td>project contingency</td>
</tr>
<tr>
<td></td>
<td>process contingency</td>
</tr>
<tr>
<td></td>
<td>interest charges</td>
</tr>
<tr>
<td></td>
<td>royalty fees</td>
</tr>
<tr>
<td></td>
<td>preproduction cost</td>
</tr>
<tr>
<td></td>
<td>inventory capital</td>
</tr>
<tr>
<td>variable O&amp;M cost</td>
<td>solvent makeup</td>
</tr>
<tr>
<td></td>
<td>electricity</td>
</tr>
<tr>
<td></td>
<td>CO(_2) transport and storage when applicable</td>
</tr>
<tr>
<td>fixed O&amp;M cost</td>
<td>operating labor</td>
</tr>
<tr>
<td></td>
<td>maintenance labor</td>
</tr>
<tr>
<td></td>
<td>maintenance material</td>
</tr>
<tr>
<td></td>
<td>administrative and support labor</td>
</tr>
</tbody>
</table>

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energy to operate the system is assumed to be purchased externally. This measure of cost is given by the following:

\[
\text{cost of CO}_2 \text{ separation} = \frac{\text{TCR} \times \text{FCF} + \text{FOM} + \text{VOM}}{(\text{CF} \times 8760) \times m_{\text{CO}_2}}
\]  

(17)

**Integrated Environmental Control Model for Power Plant Assessments.** The Integrated Environmental Control Model (IECM) is a computer-modeling tool developed by Carnegie Mellon University for power plant assessments.\(^{44}\) The IECM provides systematic estimates of the performance, emissions, and costs for a variety of fossil-fuel fired power generation systems with and without CCS, including IGCC systems.\(^{36,37,40,46}\) To evaluate the effects of CCS deployment on the overall plant performance and cost, the 2017 release of IECM (Version 9.5) was employed for this study.\(^{44}\) The new performance and cost models developed for IL-based CO\(_2\) capture were integrated with the IECM framework and used to conduct techno-economic assessments at both process and plant levels.

![Figure 1. PT-x phase diagram for a binary system (a) CO\(_2\) in [hmim][Tf\(_2\)]N; (b) H\(_2\) in [hmim][Tf\(_2\)]N.](image)

**BASE CASE RESULTS**

Here we present results for base case assumptions using current IL properties. First we show results for the stand-alone IL-based capture process. Then we show results for a complete power plant with precombustion capture. Following this, we look at potential process improvements that can enhance the viability of ILs for precombustion CO\(_2\) capture applications.

**Phase Equilibrium of CO\(_2\) and H\(_2\) in [hmim][Tf\(_2\)]N.** The calibrated VLE model based on the modified RK EOS can predict the CO\(_2\) and H\(_2\) phase behavior under different temperatures and pressures. Figure 1(a) and (b) present the PT-x phase diagram for CO\(_2\) and H\(_2\) in a binary system, respectively. CO\(_2\) has a much larger solubility than H\(_2\). When the interaction between CO\(_2\) and H\(_2\) in a tertiary system is considered, the EOS-based VLE model needs to be further adjusted by incorporating the binary interaction parameters of CO\(_2\) and H\(_2\) to predict the simultaneous solubility of CO\(_2\) and H\(_2\) in [hmim][Tf\(_2\)]N. The predicted pressure of the tertiary system matches well with an experimental study conducted by Kumelan et al.,\(^{47}\) resulting in an R\(^2\) value of 0.996.

![Figure 2. Precombustion CO\(_2\) capture system using [hmim][Tf\(_2\)]N.](image)
Table 2. Major Technical and Economic Parameters and Assumptions for IL-Based Pre-combustion CO₂ Capture

<table>
<thead>
<tr>
<th>Technical Parameter</th>
<th>Value</th>
<th>Economic Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of trains</td>
<td>#</td>
<td>Discount rate</td>
<td>%</td>
</tr>
<tr>
<td>Capacity factor</td>
<td>%</td>
<td>Fixed charge factor</td>
<td>fraction</td>
</tr>
<tr>
<td>Total syngas flow rate</td>
<td>kmol/h</td>
<td>Construction time</td>
<td>yr</td>
</tr>
<tr>
<td>Syngas pressure</td>
<td>kPa</td>
<td>General facilities</td>
<td>% PFC</td>
</tr>
<tr>
<td>Syngas temperature</td>
<td>°C</td>
<td>Engr. and overhead fees</td>
<td>% PFC</td>
</tr>
<tr>
<td>CO₂ concentration in syngas</td>
<td>%</td>
<td>Process contingency</td>
<td>% PFC</td>
</tr>
<tr>
<td>CO₂ removal efficiency</td>
<td>%</td>
<td>Project contingency</td>
<td>% (PFC + overhead + process conting.)</td>
</tr>
<tr>
<td>Absorber pressure</td>
<td>kPa</td>
<td>Royalty fees</td>
<td>% PFC</td>
</tr>
<tr>
<td>High/middle/low flashing pressures</td>
<td>kPa</td>
<td>Misc. capital cost</td>
<td>% TPCI</td>
</tr>
<tr>
<td>Flashing temperature</td>
<td>°C</td>
<td>Inventory capital</td>
<td>% TPC ^b</td>
</tr>
<tr>
<td>Solvent loss rate</td>
<td>kg IL/tonne CO₂</td>
<td>Total maintenance cost</td>
<td>$/h</td>
</tr>
<tr>
<td>Compressor efficiency</td>
<td>%</td>
<td>Labor fee</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Pump efficiency</td>
<td>%</td>
<td>Makeup solvent price</td>
<td>$/tonne</td>
</tr>
<tr>
<td>Recovery turbine efficiency</td>
<td>%</td>
<td>Reclaimer waste disposal</td>
<td>$/tonne</td>
</tr>
<tr>
<td>CO₂ product pressure</td>
<td>MPa</td>
<td>CO₂ transport and storage</td>
<td>$/tonne</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electricity price</td>
<td>$/MWh</td>
</tr>
</tbody>
</table>

*This is derived based on the study by Maginn et al. ^48* ^TPI is the total plant investment. TPC is the total plant cost.

**Process-Level Evaluation.** An IL-based process based on the newly developed models was assumed to capture CO₂ from the shifted syngas of an IGCC plant. A parametric analysis was further conducted to explore the effects of process design variables on process performance and cost for a “stand-alone” capture system.

**Base Case Studies.** Basha et al. proposed a process configuration for precombustion CO₂ capture using ILs. ^17,18* Figure 2 shows a similar process configuration: CO₂ is absorbed by [hmim][Tf₂N] in a packed column, then the CO₂-rich solvent stream exiting the absorber is regenerated in pressure-swing flash drums arranged in series. Since the gas stream out of the high-pressure flash drum has a high hydrogen concentration, it is recirculated to the absorber to avoid hydrogen losses. The CO₂ streams out of the medium- and low-pressure flash drums for solvent regeneration are combined, while the CO₂-lean solvent stream out of the low-pressure flash drum is recirculated to the absorber. A hydraulic turbine is used to recover energy from pressure changes in the CO₂-rich solvent stream. ^37* Table 2 summarizes the major technical and economic parameters and assumptions for the precombustion IL-based capture system based on the syngas characteristics of an IGCC plant employing Shell gasifiers. ^37,44* Our process simulation results of stream mass flow rates and compositions for a single train are presented in Figure 2 (the second train is identical).

The capture system is designed as an isothermal process (at about 29 °C) with two trains for 90% CO₂ capture. The designated absorption pressure is 2960 kPa. The CO₂-rich solvent is regenerated in three flash drums with pressures that decrease from 1000 to 80 kPa. Figure 2 shows the mass flow rate and composition for each stream in each train. The H₂-rich stream delivered as fuel to the gas turbines has a H₂ purity of 94%, while the final CO₂ product stream has a purity of over 99% CO₂. Figure 2 also shows that the hydrogen loss and [hmim][Tf₂N] in the CO₂ product stream are negligible.

In each train, two compressors are used to increase the pressure of the regenerated gas stream out of the HP flash drum from 1000 to 2960 kPa, and of the CO₂ product stream out of the LP flash drum from 80 to 500 kPa. The regenerated solvent is pumped back to the absorber. The final CO₂ product stream is then further compressed to a supercritical fluid phase for transport and storage (T&S). Table 3 summarizes the equipment power use and recovered energy. CO₂ product compression is the largest power user.

**Table 3. Performance and Costs of IL-Based CO₂ Capture System**

<table>
<thead>
<tr>
<th>Category</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>System power use (MW)</td>
<td></td>
</tr>
<tr>
<td>Solvent pumping</td>
<td>18.1</td>
</tr>
<tr>
<td>Process compression</td>
<td>14.0</td>
</tr>
<tr>
<td>CO₂ product compression</td>
<td>30.4</td>
</tr>
<tr>
<td>Hydraulic turbine recovery power</td>
<td>9.4</td>
</tr>
<tr>
<td>Total net system power use</td>
<td>53.1</td>
</tr>
<tr>
<td>Process facilities capital (2011 M$)</td>
<td>99.3</td>
</tr>
<tr>
<td>Absorbers</td>
<td>19.1</td>
</tr>
<tr>
<td>Flash drums</td>
<td>7.9</td>
</tr>
<tr>
<td>Solvent pumps</td>
<td>4.9</td>
</tr>
<tr>
<td>Heat exchangers</td>
<td>2.4</td>
</tr>
<tr>
<td>Slump tanks</td>
<td>3.9</td>
</tr>
<tr>
<td>Process compressors</td>
<td>22.1</td>
</tr>
<tr>
<td>CO₂ product compressors</td>
<td>35.5</td>
</tr>
<tr>
<td>Power recovery turbines</td>
<td>3.5</td>
</tr>
<tr>
<td>Total capital requirement (2011 M$)</td>
<td>168.3</td>
</tr>
<tr>
<td>Annualized capital cost (2011 M$/yr)</td>
<td>19.0</td>
</tr>
<tr>
<td>Fixed O&amp;M cost (2011 M$/yr)</td>
<td>9.4</td>
</tr>
<tr>
<td>Variable O&amp;M cost, excluding CO₂ T&amp;S (2011 M$/yr)</td>
<td>17.4</td>
</tr>
<tr>
<td>CO₂ separation cost, excluding CO₂ T&amp;S (2011 $/tonne CO₂)</td>
<td>17.1</td>
</tr>
</tbody>
</table>

Table 3 also presents the capital and O&M costs of the IL-based capture system, excluding CO₂ T&S costs. The major capital cost components are the absorbers, process compressors, and product compressors, which account for 19%, 22%, and 36% of the TCR, respectively. Given the assumptions in Table 2, capital cost accounts for more than a half the total annualized cost and the separation cost for the IL-based system is about $17 per tonne of CO₂ separated. We note, however, that the separation cost for energy-intensive processes is strongly affected by the assumed price of purchased electricity for a stand-alone process. ^39* In this example, doubling the
assumed price of electricity increases the separation cost to about $24 per tonne of CO₂ separated.

**Effects of Process Parameters.** A sensitivity analysis also was conducted to evaluate the effects of major process parameters on the net process power requirement and the separation cost for CO₂ capture. The parameters considered include the CO₂ capture efficiency, process operating temperature, and absorption and stripping pressures. When a parameter was assessed, other parameters were held at their base case values given in Table 2, unless otherwise noted.

The process operating temperature affects the solvent properties such as CO₂ solubility and solvent viscosity. When it increases, the solvent requirement increases for the given CO₂ removal efficiency due to the decreased solubility. As shown in Figure 3(a), both the power use and separation cost increase when the temperature increases. When the pressures of the HP and MP flash drums increase from 800/400 kPa to 1050/525 kPa, the gas stream flow rate recirculated from the HP flash drum to the absorber decreases and the required pressure ratio for the process compressor decreases as well, which collectively lower the corresponding compression power use. Figure 3(c) shows that for the given three-stage stripping designs, elevating the absorption pressure from 2960 to 5000 kPa increases the system power use and separation cost by 28% and 38%, respectively. This result indicates that when an absorption process occurs at a much high pressure, stripping pressures need to be elevated accordingly.

The CO₂ removal requirement largely determines the capture system size, power use, and cost. Figure 3(d) shows that both the net normalized power use and separation cost decrease when the CO₂ removal efficiency increases from 50% to 95%. To achieve 95% CO₂ capture, the three stripping pressures have to be lowered from the base designs to 800, 400, and 60 kPa, respectively. Otherwise, the process simulation could not converge. As a result, both the normalized power use and separation cost increase when the CO₂ removal efficiency is elevated from 90% to 95%. Figure 3(d) shows that the optimal removal efficiency is 90%.

**Effects of Process and Project Contingencies.** The process and project contingencies represent indirect capital costs that are expected to occur. The process contingency depends on the level of technology maturity and lies within the range from 30% to 70% of PFC for a conceptual system with bench-scale data and 5% to 20% for an operational full-size system. The project contingency is related to the level of project design and typically lies within 30% to 50% of the sum of process capital, engineering and home office fees, and process contingency for a
simplified project design, and 10% to 20% for a detailed project design.\textsuperscript{48} Our base case assumes a hypothetical mature plant, akin to analyses by the U.S. Department of Energy’s National Energy Technology Laboratory and others.\textsuperscript{50} To illustrate cost sensitivity, both contingency factors are increased from their base values to 30%. As a result, the total capital requirement increases by 29%, and the separation cost increases by 17% in comparison to the base case.

### Plant-Level Evaluation

To analyze a complete IGCC plant with CO\textsubscript{2} capture and storage (CCS), we use IECM 9.5 to model a plant employing Shell gasifiers. The plant design includes a two-stage water gas shift (WGS) reactor and a combined cycle power plant employing GE 7FB gas turbines.\textsuperscript{37} Because the cost of CO\textsubscript{2} avoided offers a more rigorous metric than the separation cost calculated for a stand-alone process with purchased energy,\textsuperscript{49} it is used to measure the overall cost of CCS. To estimate the avoidance cost, the IECM was employed to calculate plant-level CO\textsubscript{2} emission rates and LCOE for Shell-IGCC plants with and without CCS. For the plant with CCS, the designated CO to CO\textsubscript{2} conversion efficiency is 95% for the WGS reactor, while the designated CO\textsubscript{2} removal efficiency is 90% for the CO\textsubscript{2} capture system. The parametric values in default were adopted for other power plant components. For the assumptions given in Table 2, the addition of the IL-based CCS system decreases the net plant efficiency by 9.3 percentage points. The resulting cost of CO\textsubscript{2} avoided is $63 per ton of CO\textsubscript{2} in constant 2011 dollars.

The IL-based technology is further compared to a Selexol-based two-stage system that also employs physical absorption for CO\textsubscript{2} capture.\textsuperscript{36,37,44} IECM 9.5 also was applied to evaluate the performance and cost of an IGCC plant with Selexol-based CCS. The plant-level assessment results are provided in Table 4. The addition of the Selexol-based CCS for 90% CO\textsubscript{2} capture also leads to significant reductions in the net plant efficiency. The cost of CO\textsubscript{2} avoided by the Selexol-based CCS system is $65 per ton of CO\textsubscript{2}. So, the two capture systems have similar effects on overall plant performance and cost of electricity generation. Thus, on the basis of current solvents, this analysis suggests that there is no compelling case for ILs replacing the more established Selexol system.

## ANALYSIS OF HYPOTHETICAL IMPROVED SOLVENTS

ILs have tunable properties for gas absorption. To help guide the development of novel materials for CO\textsubscript{2} capture, there is a need for quantitative targets for material properties based on a system-level analysis. The model described in this paper provides that capability and is applied to investigate the material properties needed to improve the IL technology’s viability.

Given that CO\textsubscript{2} solubility is the most important property affecting capture process performance, we evaluate a hypothetical IL with improved solubility for CO\textsubscript{2}. As shown in Figure S1 in the SI, the concentration of CO\textsubscript{2} in equilibrium with the hypothetical IL is assumed to be 10 percentage points more than that of [\text{[hmmim]}][\text{[Tr}_{2}\text{N}]] on an absolute basis for a given temperature and pressure, while other properties are kept the same as those of [\text{[hmmim]}][\text{[Tr}_{2}\text{N}]]. No deviations from the ideality are also assumed.\textsuperscript{51,52} A new phase equilibrium model was developed based on the hypothetical solubility and incorporated in the process model for performance and cost assessments.

Because of the improved solubility, the CO\textsubscript{2}-rich solvent stream exiting the absorber has a higher CO\textsubscript{2} concentration compared to the base case. If the three flash drums in Figure 2 are employed for solvent regeneration, then the gas stream out of the HP drum has a higher CO\textsubscript{2} purity. Recycling this CO\textsubscript{2}-rich gas stream back to the absorber would waste a lot of the separation work. Thus, the HP flash drum and its associated compressor can be removed from the process configuration. Figure S2 in the SI shows the simplified capture process employing the hypothetical solvent. The design temperatures and pressures for the absorber and two flash drums are held the same as the base case system.

Results of the process simulation show that the CO\textsubscript{2} concentration of the solvent stream leaving the absorber increases to 46% while the CO\textsubscript{2} purity of the final product stream is 98% (comparable to the base case). However, the CO\textsubscript{2}-lean solvent requirement decreases by about 70%, which significantly reduces the power requirement for solvent pumping. The resulting system power use and separation cost are 34.6 MW and $12 per tonne of CO\textsubscript{2} separated, which are 35% and 29% less than the respective base case values. These results illustrate how an increase of 10 percentage points in CO\textsubscript{2} solubility can significantly improve the economic viability of this technology, offering targets for future IL developments. Whether and when such improvements can indeed be achieved, however, remains an open question.

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Table 4. Comparisons of Performance and Costs of IGCC Plants with and without CCS

<table>
<thead>
<tr>
<th>parameter</th>
<th>IGCC w/o CCS</th>
<th>IGCC w/Selexol-CCS</th>
<th>IGCC w/IL-CCS</th>
</tr>
</thead>
<tbody>
<tr>
<td>gross power output (MW)</td>
<td>681</td>
<td>656</td>
<td>656</td>
</tr>
<tr>
<td>net power output (MW)</td>
<td>595</td>
<td>533</td>
<td>534</td>
</tr>
<tr>
<td>CO\textsubscript{2} capture system</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>power use (MW)</td>
<td></td>
<td>54</td>
<td>53</td>
</tr>
<tr>
<td>TCR (2011$/\text{kWnet})</td>
<td>365</td>
<td>315</td>
<td></td>
</tr>
<tr>
<td>net plant efficiency (HHV, %)</td>
<td>44.3</td>
<td>34.9</td>
<td>35.0</td>
</tr>
<tr>
<td>plant CO\textsubscript{2} emission rate (kg/kWh)</td>
<td>0.710</td>
<td>0.131</td>
<td>0.130</td>
</tr>
<tr>
<td>plant TCR (2011$/\text{kWnet})</td>
<td>3211</td>
<td>4381</td>
<td>4323</td>
</tr>
<tr>
<td>plant LCOE (2011$/MWh) \textsuperscript{a}</td>
<td>86.6</td>
<td>124.4</td>
<td>123.2</td>
</tr>
<tr>
<td>added LCOE for CCS \textsuperscript{b} (2011$/MWh)</td>
<td>37.8</td>
<td>44</td>
<td>42</td>
</tr>
<tr>
<td>(relative %)</td>
<td>65</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>cost of CO\textsubscript{2} avoided (2011$/tonne CO\textsubscript{2}) \textsuperscript{a}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}The assumed coal price is $1.62/GJ. \textsuperscript{b}This also includes CO\textsubscript{2} transport and storage costs.
This study has analyzed the use of [hmim][Tf2N] as a physical solvent for precombustion CO2 capture at IGCC power plants. The energy penalty of the IL-based system comes mainly from the process and product compression and solvent pumping, while the major capital cost components are the compressors and absorbers. Both the parasitic load and cost vary to some extent with process design choices. The minimum cost of separation ($/ton CO2 separated from the syngas stream) for the base case design was found to occur at a CO2 removal efficiency of 90%, indicating that a bypass design treating only a portion of the syngas would be cost-effective for an IL-based system that required only partial CO2 capture (e.g., 50% removal). Comparisons of plant-level performance and cost between IGCC plants employing [hmim][Tf2N]-based and Selexol-based capture systems showed very similar results, implying that an IL-based CCS system could be a viable alternative to current solvent processes.

Advances in multiple areas are needed to improve the viability of IL-based capture technology. Improvements in the CO2 solubility of ILs are needed to simplify the capture system configuration and lower the energy penalty and cost for CO2 capture. Novel compression technology also is needed to further reduce power needs and system cost. In addition, since the CO2 capture system accounts for less than 10% of an IGCC plant’s total capital requirement (see Table 4), large-scale deployment of IGCC plants with CCS will require system-wide cost reductions in other major plant components as well as in overall plant integration, configuration, and design.

Two further caveats accompany this study. First, the models presented here do not consider the potential influence on process performance of other minor gas species such as water vapor and carbon monoxide. Second, to estimate the absorber pressure drop, this study employed mass transfer and pressure drop rate correlations derived empirically for conventional solvents with lower viscosity than ILs. Thus, there is a need for additional data in these areas to more rigorously evaluate the effectiveness of ionic liquids as a cost-effective sorbent for precombustion CO2 capture.

**DISCUSSION**

This work was supported in part by Stanford University’s Global Climate and Energy Project. All opinions, findings, conclusions, and recommendations expressed in this paper are those of the authors alone and do not reflect the views of any agencies.

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