A Data Mining Method for the Identification of New Physical Solvents

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Objectives

• Identify promising & commercially available physical solvents for CO$_2$ pre-combustion capture from computational screening

1. Solvents to be used around room temperature (25-80°C) and some important property requirements
   √ Hydrophobic
   √ High CO$_2$ loading & high CO$_2$/H$_2$ selectivity
   √ Low vapor pressure & low viscosity
   √ Non-foaming, non-harmful, non-environmental and non-safety issues
   √ Reasonable price

2. Solvents to be used at low temperatures (below 0°C)

• The best identified solvents will be experimentally tested at NETL and further modified, if needed.

• Perform Techno-Economic Analysis (TEA) & pilot plant testing
Outline

• Background
  – Search and screening
  – Required physical properties
  – Challenges

• Results
  – One (CASSH-1) very promising hydrophobic physical solvent has been identified from computational screening for CO₂ pre-combustion capture.

• Future work
Forward & Reverse Search

Material → Properties → Product → Market → Technology

Forward search

Material

Reverse search

Properties

Judgement → Specification

Machine Learning + Database

Experiment

(Search, characterization, testing)

Theory

(Quantum, MD & MC)

Search

(Open literature, database)

Correlation

(Group contribution, QSPR, trend)

NIST database for pure compounds (~23,000)
- Melting ($T_m$), boiling ($T_b$) temperatures, viscosity ($\mu$), saturation vapor pressure ($P^{\text{sat}}$), surface tension ($\sigma$), density (molar volume)

Open literature to complement properties missing in NIST Database
- flash point, safety, health, environment
- Price

In-house computational database: quantum mechanics for gas – chemical function group interactions
- CO$_2$, CH$_4$, H$_2$, H$_2$O, H$_2$S, COS, SO$_2$, O$_2$, N$_2$, etc.

In-house machine learning and Monte Carlo molecular simulation
- Chief criteria: CO$_2$ solubility, CO$_2$/H$_2$ solubility selectivity, heat of absorption, H$_2$O solubility

In-house simulation: Molecular Dynamics
- Surface tension, heat capacity, viscosity, CO$_2$ diffusivity, density, vapor pressure, therm. conduct.

Experimental testing & TEA analysis

Integrated Computational Flow Chart

- 23,000 compounds, such as $T_m$, $\mu$
- ~100-1000 compounds, such as $T_m$, $\mu$
- <100 compounds
- 30-40 compounds
- best

Integrated Computational Flow Chart

Experimental testing & TEA analysis
Why Do We Care About Hydrophobicity?

• $\text{H}_2\text{O}$ competes for $\text{CO}_2$ interaction with solvent.
• Presence of water significantly & unfavorably decreases both $\text{CO}_2$ loading and $\text{CO}_2/\text{H}_2$ selectivity.
Developing a Hydrophobic CO$_2$ Capture Solvent Is Challenging

• Minimizing water absorption by adding functional groups could decrease CO$_2$ absorption
Why Low Solvent Viscosity is Desirable?

- Low viscosity increases CO₂ diffusivity → faster absorption
  - decrease capital cost

\[ D_{\text{CO}_2} = 2.6482 \times 10^{-9} / \mu_{\text{solv}}^{0.61776} \]

\[ R = -0.96 \]

298 K
Compromise Between Solvent Viscosity and Vapor Pressure

- 53 solvents exhibit both smaller vapor pressure and smaller viscosity than Selexol.
• ~600 compounds were found in NIST database with

\[ T_m < 30 \, ^\circ\text{C} \, \& \, T_b > 260 \, ^\circ\text{C} \]
In-house Computation Database: Chemical Functional Group Interactions with CO$_2$

202 chemical functional groups$^1$

- PHO$_4$, C=N, etc. interact most strongly with CO$_2$ (> 15 kJ/mol)
- -O-, COO$^-$ groups interact strongly with CO$_2$ (~ 10-12 kJ/mol)
- -CH, -CH$_2$, -CH$_3$ interact most weakly with CO$_2$ (< 1 kJ/mol)

Experimental Validation of Simulation

- **CO₂ solubility values agree (14.2% difference)**
  - Consistent trends

PDMS: polydimethylsiloxane [1]
TBP: Tributyl phosphate [3]
PEGS: NETL PEG-Siloxane-1 [2]
PC: propylene carbonate [3]
NMP: N-Methyl-2-pyrrolidone [3]

- **CO₂/H₂ selectivity values agree**
  - (17.3% difference)
  - Same trends

CAS 143-24-8: Selexol surrogate

Simulated CO$_2$ Solubility Values in ~30 Solvents: Identify One of the Best

- One of the best solvents, CASSH-1, was identified from the computational screening.
- Similar CO$_2$ solubility trend
  - Sim.: CASSH-1 > Selexol > PEG-PDMS-3 > decane > H$_2$O
  - Exp.: Selexol ~ CASSH-1 ~> PEG-PDMS-3 > decane > H$_2$O

298 K
Simulated High CO$_2$/$H_2$ Solubility Selectivity in CASSH-1

• CASSH-1 exhibits high CO$_2$/$H_2$ selectivity
  – needs experimental validation
CASSH-1 is non-foaming

Hand shaken for 1 min., then photographed immediately

Hand shaken for 1 min., then photographed after 1 min.
## Physical Properties at 298 K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Selexol</th>
<th>PEG-PDMS-3</th>
<th>CASSH-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (cP)</td>
<td>5.8</td>
<td>12.2</td>
<td>5.1</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.030</td>
<td>0.9847</td>
<td>0.960</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>280</td>
<td>620</td>
<td>260</td>
</tr>
<tr>
<td><strong>Vapor pressure (mmHg)</strong></td>
<td>7.3×10⁻⁴</td>
<td>small</td>
<td>1/100 of Selexol</td>
</tr>
<tr>
<td>Freezing point (°C)</td>
<td>-28</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Normal boiling point (°C)</td>
<td>275</td>
<td>high</td>
<td>300</td>
</tr>
<tr>
<td><strong>Hydrophobicity</strong></td>
<td>Very hydrophilic</td>
<td>hydrophobic</td>
<td>Very hydrophobic</td>
</tr>
<tr>
<td>Foaming</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Safety, health, environment</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>
Future Work: TEA Analysis for ~30 Solvents

- CO$_2$ solubility, CO$_2$/H$_2$ selectivity at T, P
- Viscosity, heat capacity, vapor pressure, density, critical T & P, price
Extending the Same Approach to Polymer Screening for CO$_2$ Capture Membrane (New Project)

- **Polymer database**
  - Over 800 organic polymers involving 9 species (C, H, O, N, S, F, Cl, Br, I) \[^{[1]}\]
  - Experimental database development
    - $\sqrt{\text{CO}_2}$, CH$_4$, H$_2$O, N$_2$, O$_2$ and H$_2$ permeability, solubility, and diffusivity in polymers
    - $\sqrt{\text{Glass transition temperature, melting point, mechanic properties}}$
    - $\sqrt{\text{Data for } \sim 50 \text{ polymers collected so far}}$
  - Computational polymer database development
    - $\sqrt{\text{CO}_2}$ interactions with dimer built from monomer functional groups
    - $\sqrt{\text{Free volume fraction, gas-functional group interaction, and functionality availability}}$

- **Polymer molecular simulation tools to calculate permeability**
  - Tools development to generate polymer initial configurations
  - In-house simulation tools ready for polymer simulation

Conclusions

• Integrated automatic computational approach developed

• In-house computational database built

• 23,000 compounds from NIST database screened

• One (CASSH-1) very promising commercially available hydrophobic solvent identified from screening for CO$_2$ pre-combustion capture
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