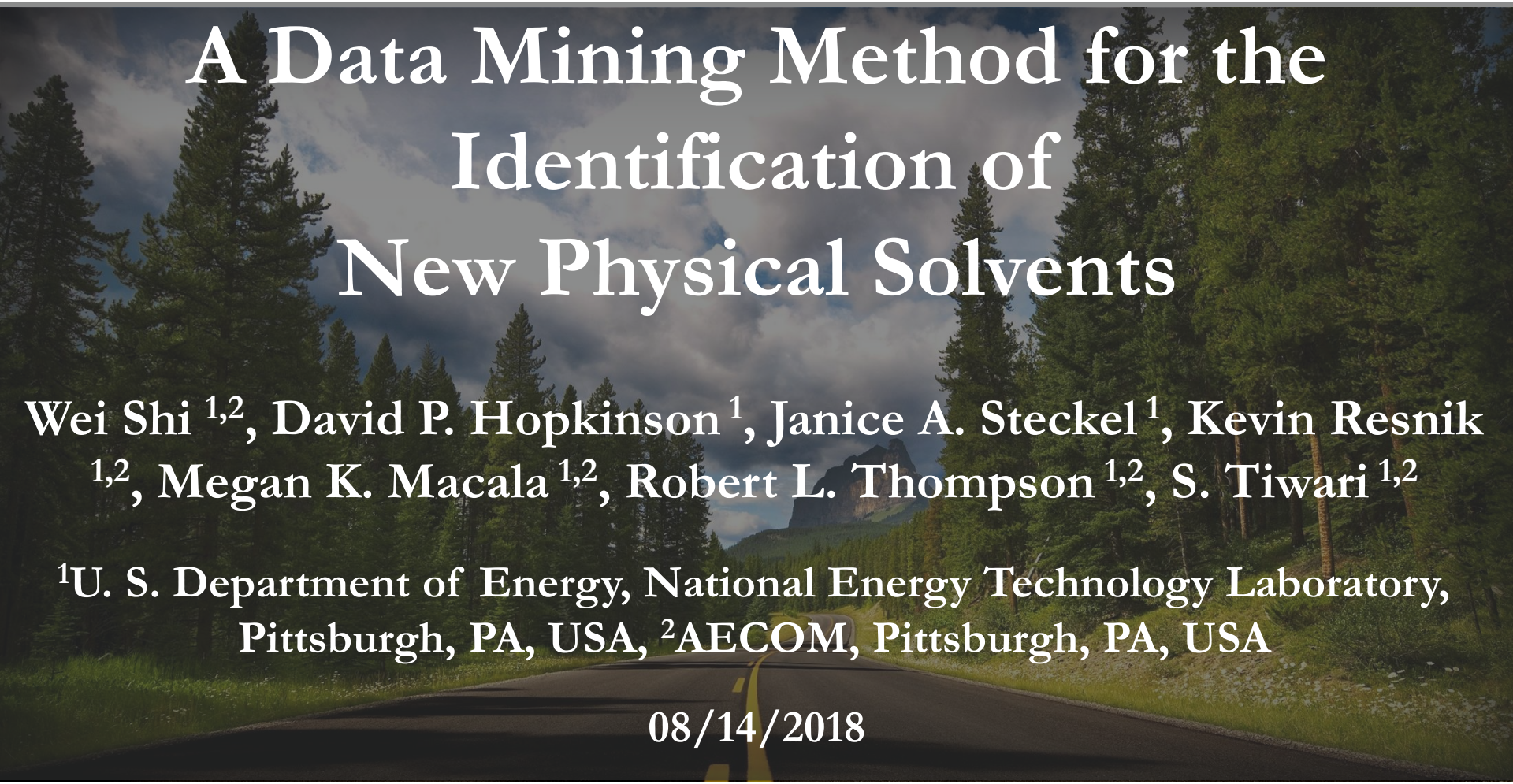


A Data Mining Method for the Identification of New Physical Solvents

Wei Shi [1,2], David P. Hopkinson [1], Janice A. Steckel [1], Kevin Resnik [1,2], Megan K. Macala [1,2], Robert L. Thompson [1,2], S. Tiwari [1,2]

[1]U. S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA, USA, [2]AECOM, Pittsburgh, PA, USA

08/14/2018

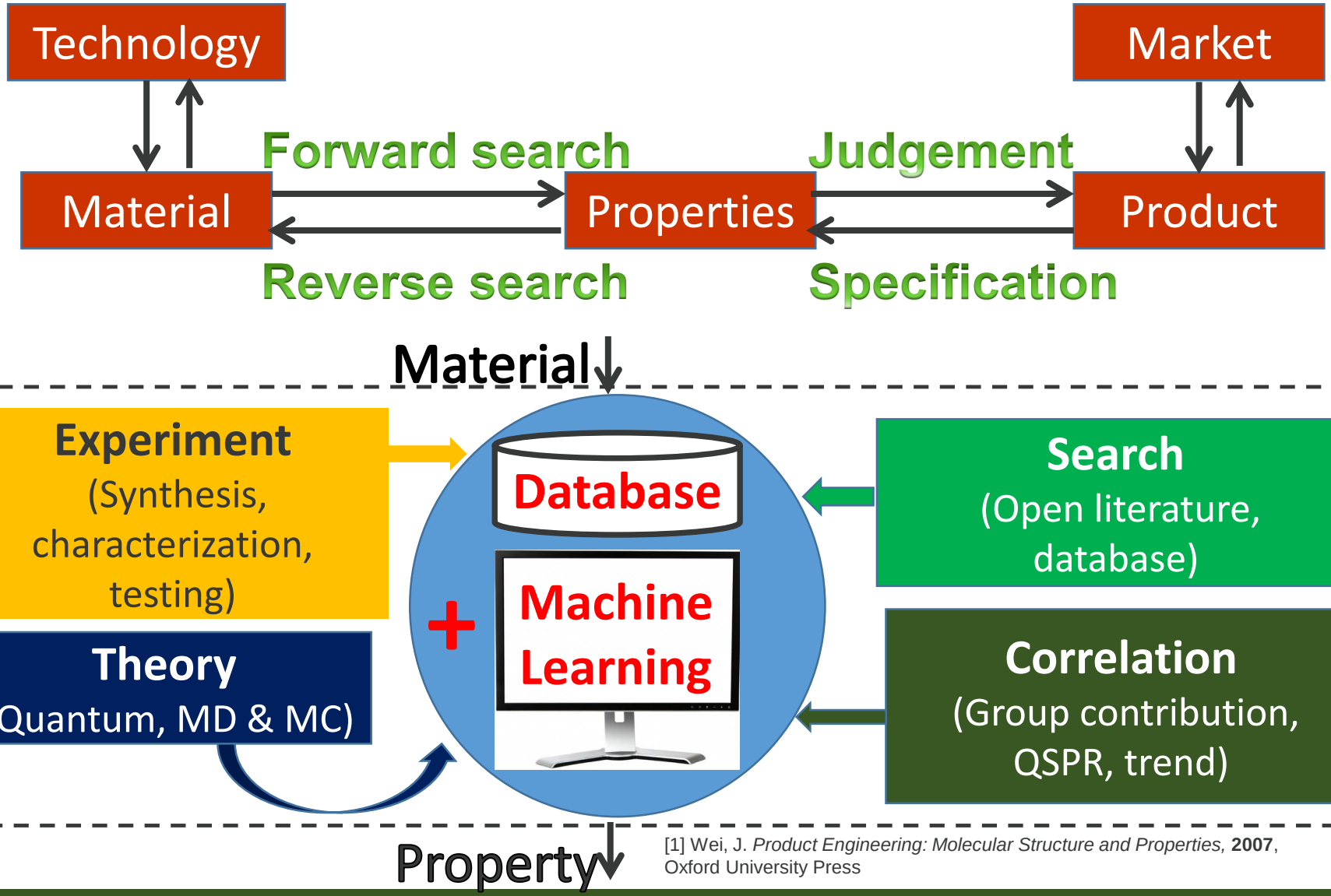
Objectives

- **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

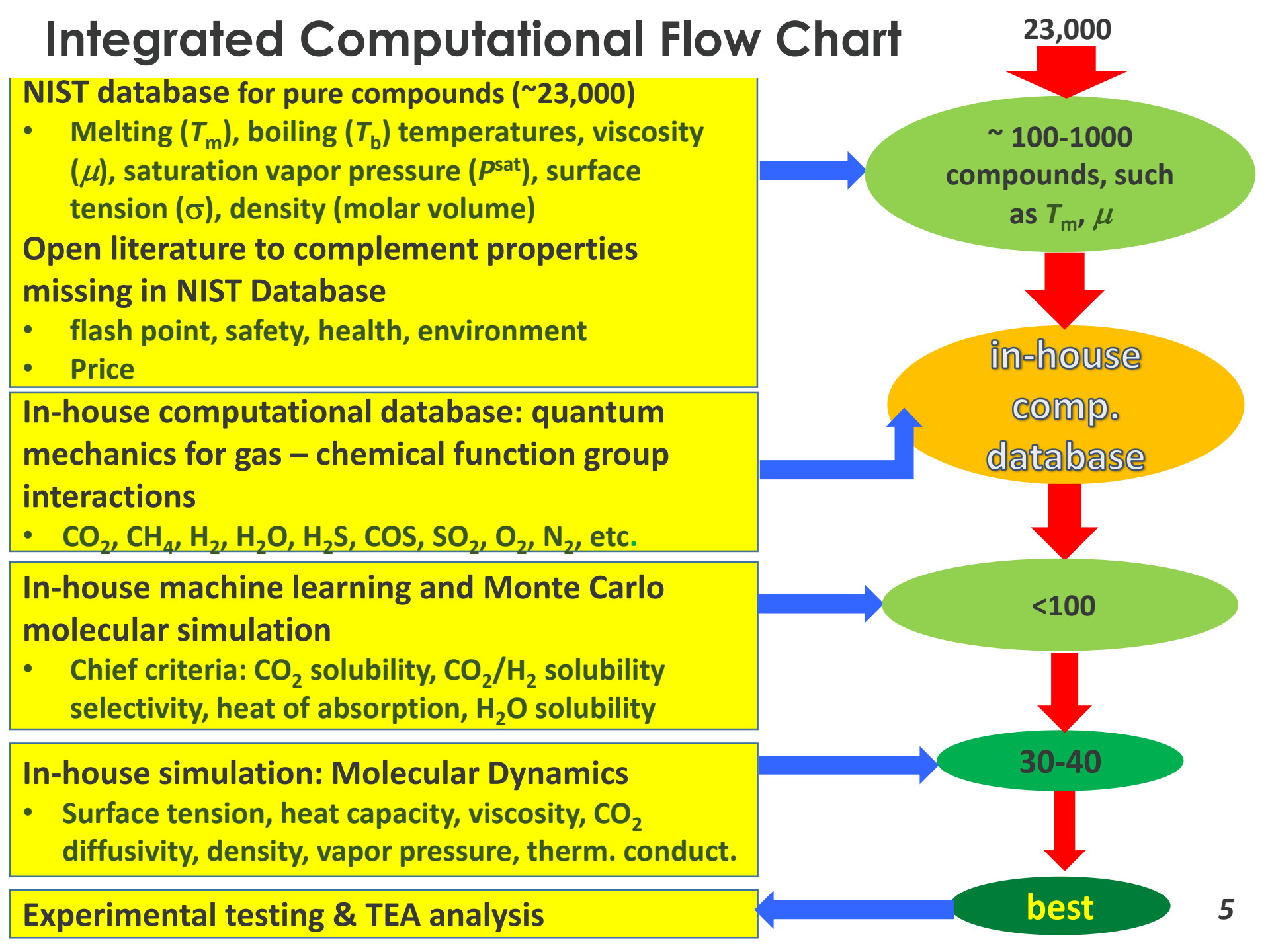
- **Background**
  - Search and screening
  - Required physical properties
  - Challenges
- **Results**
  - One (CASSH-1) very promising hydrophobic physical solvent has been identified from computational screening for CO_2 pre-combustion capture.
- **Future work**

Forward & Reverse Search

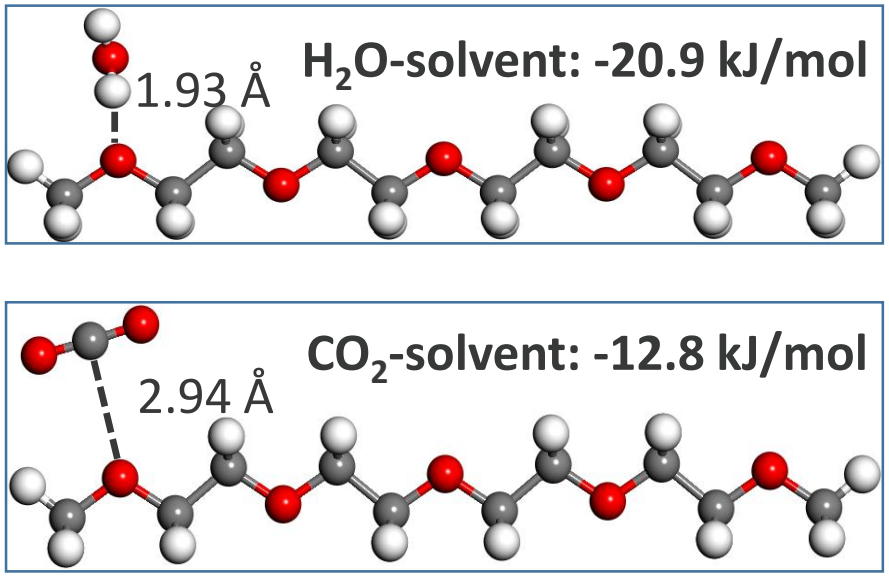


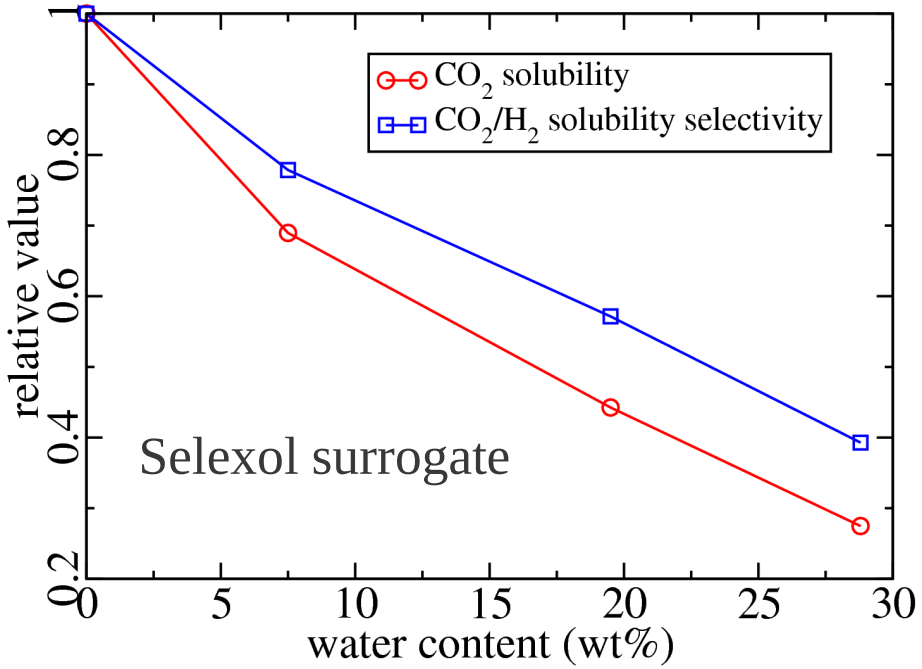
[1] Wei, J. *Product Engineering: Molecular Structure and Properties*, **2007**, Oxford University Press

Integrated Computational Flow Chart



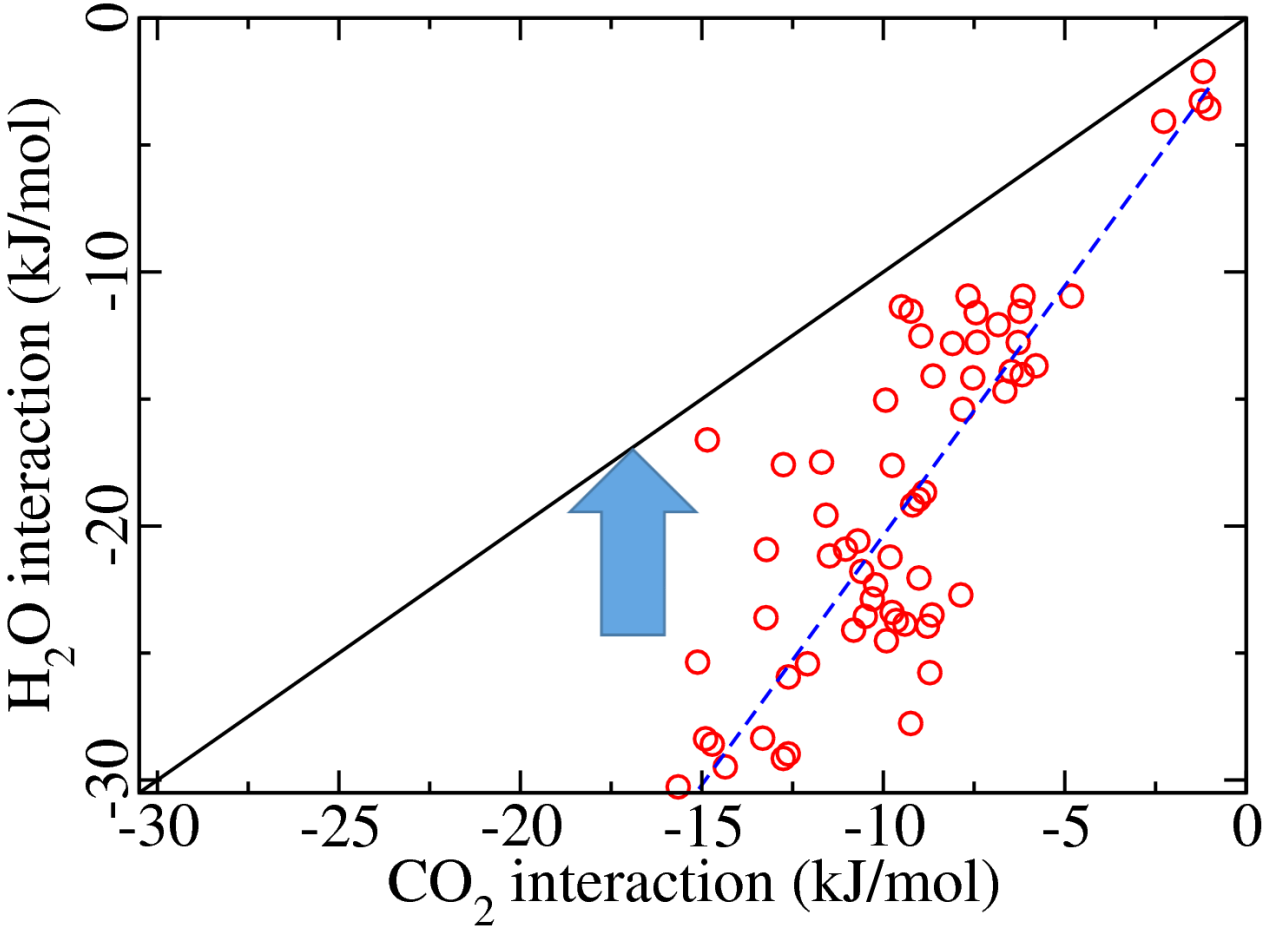
Why Do We Care About Hydrophobicity?





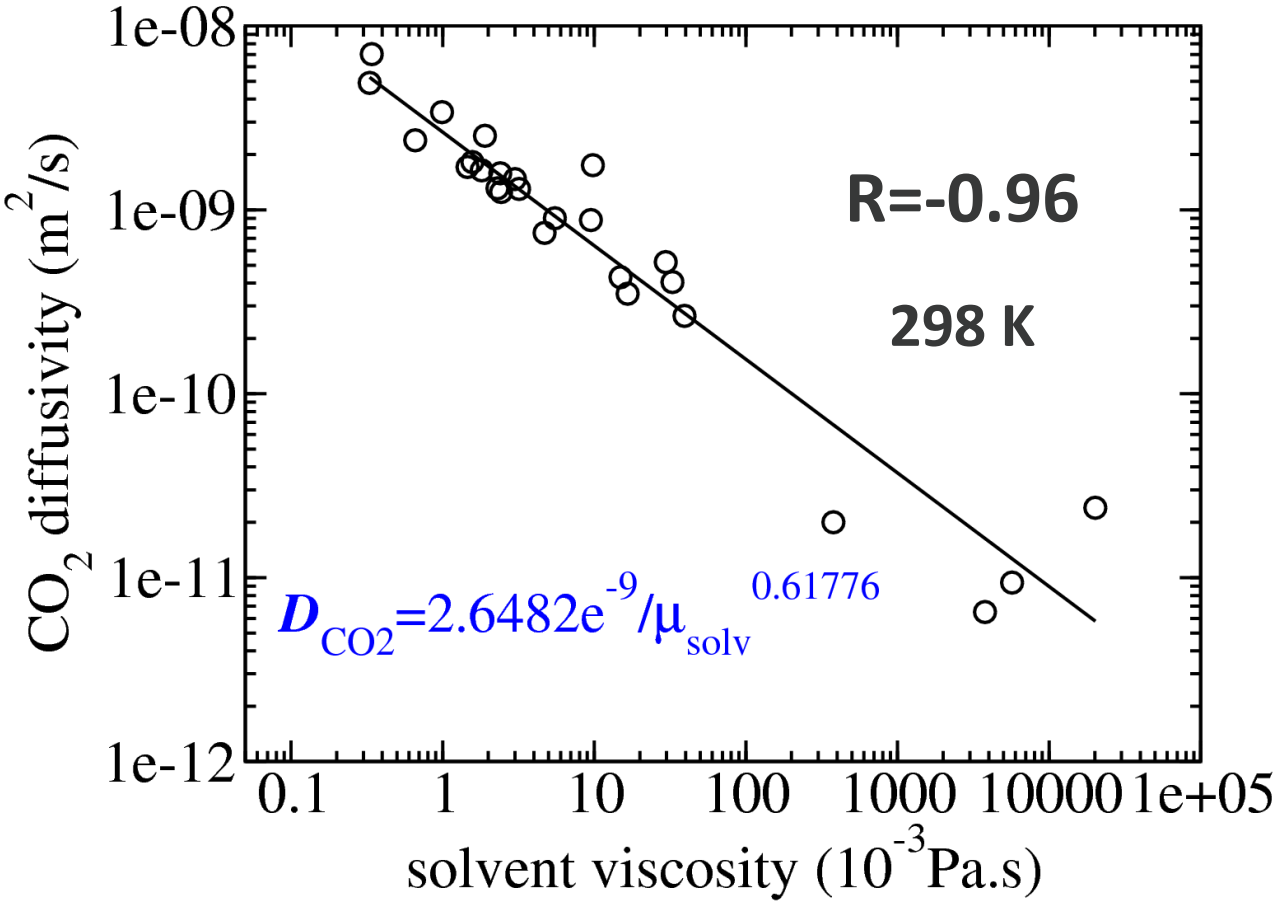
- H_2O competes for CO_2 interaction with solvent.
- Presence of water significantly & unfavorably decreases both CO_2 loading and CO_2/H_2 selectivity.

Developing a Hydrophobic CO_2 Capture Solvent Is Challenging



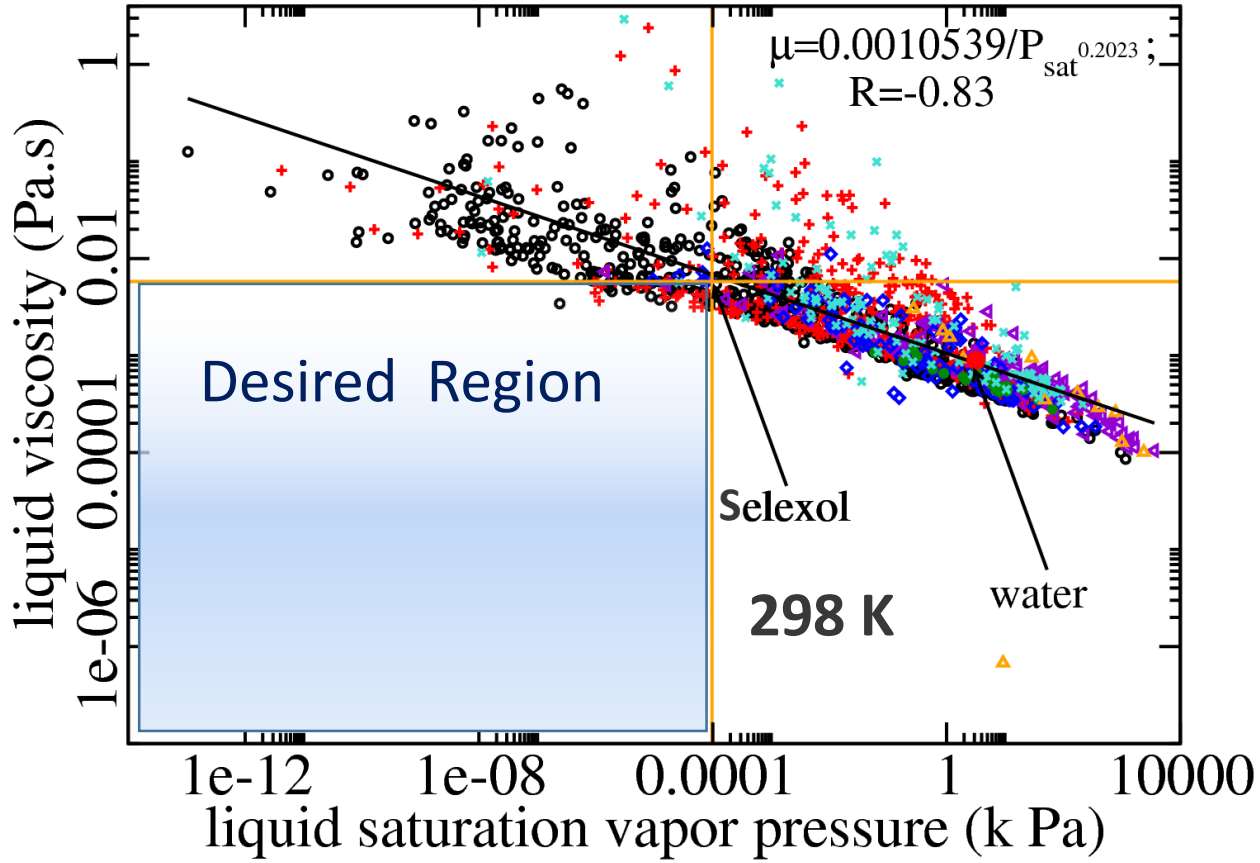
- Minimizing water absorption by adding functional groups could decrease CO_2 absorption

Why Low Solvent Viscosity is Desirable?



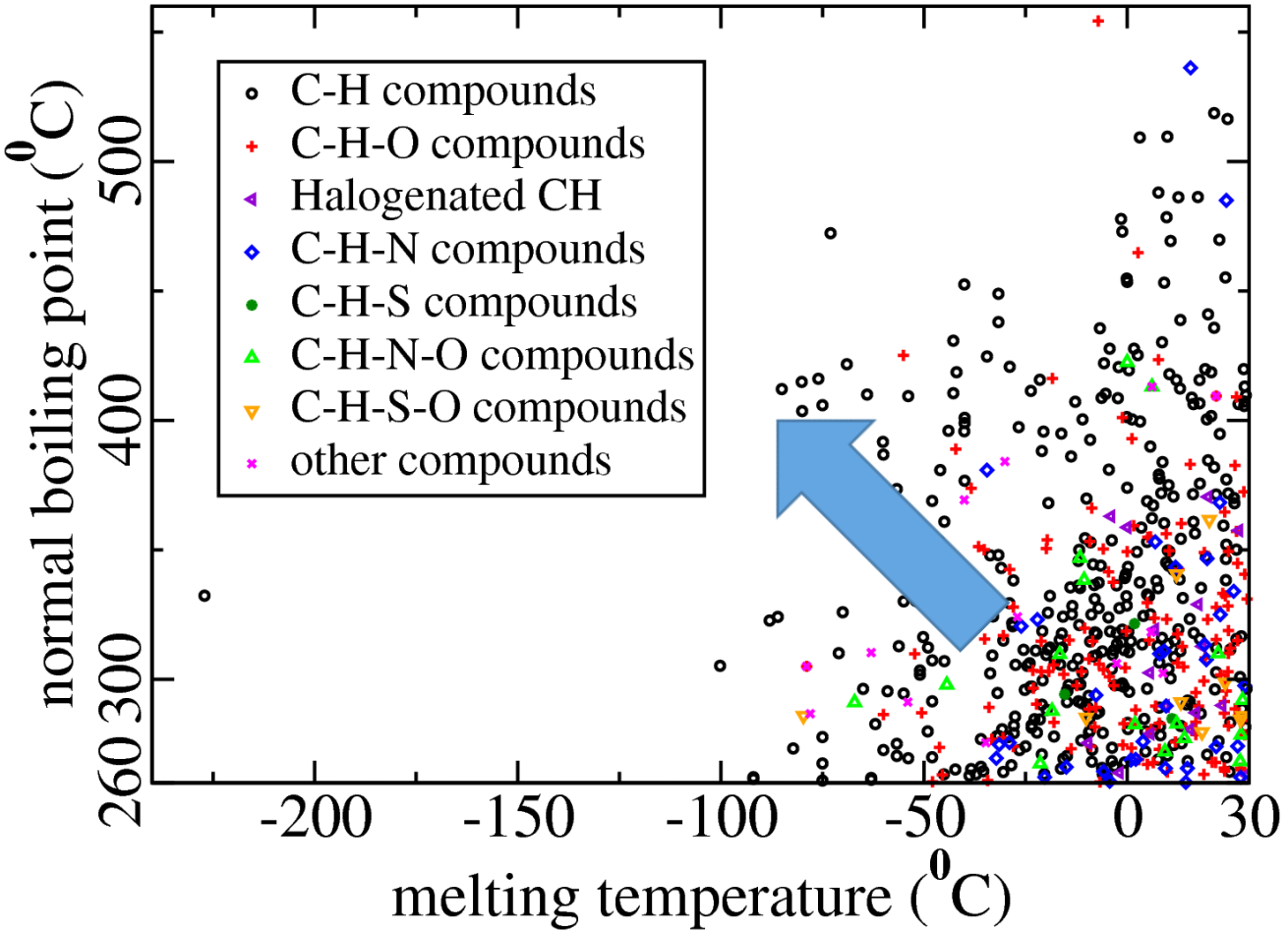
- **Low viscosity increases CO_2 diffusivity → faster absorption**
  - decrease capital cost

Compromise Between Solvent Viscosity and Vapor Pressure



- 53 solvents exhibit both smaller vapor pressure and smaller viscosity than Selexol

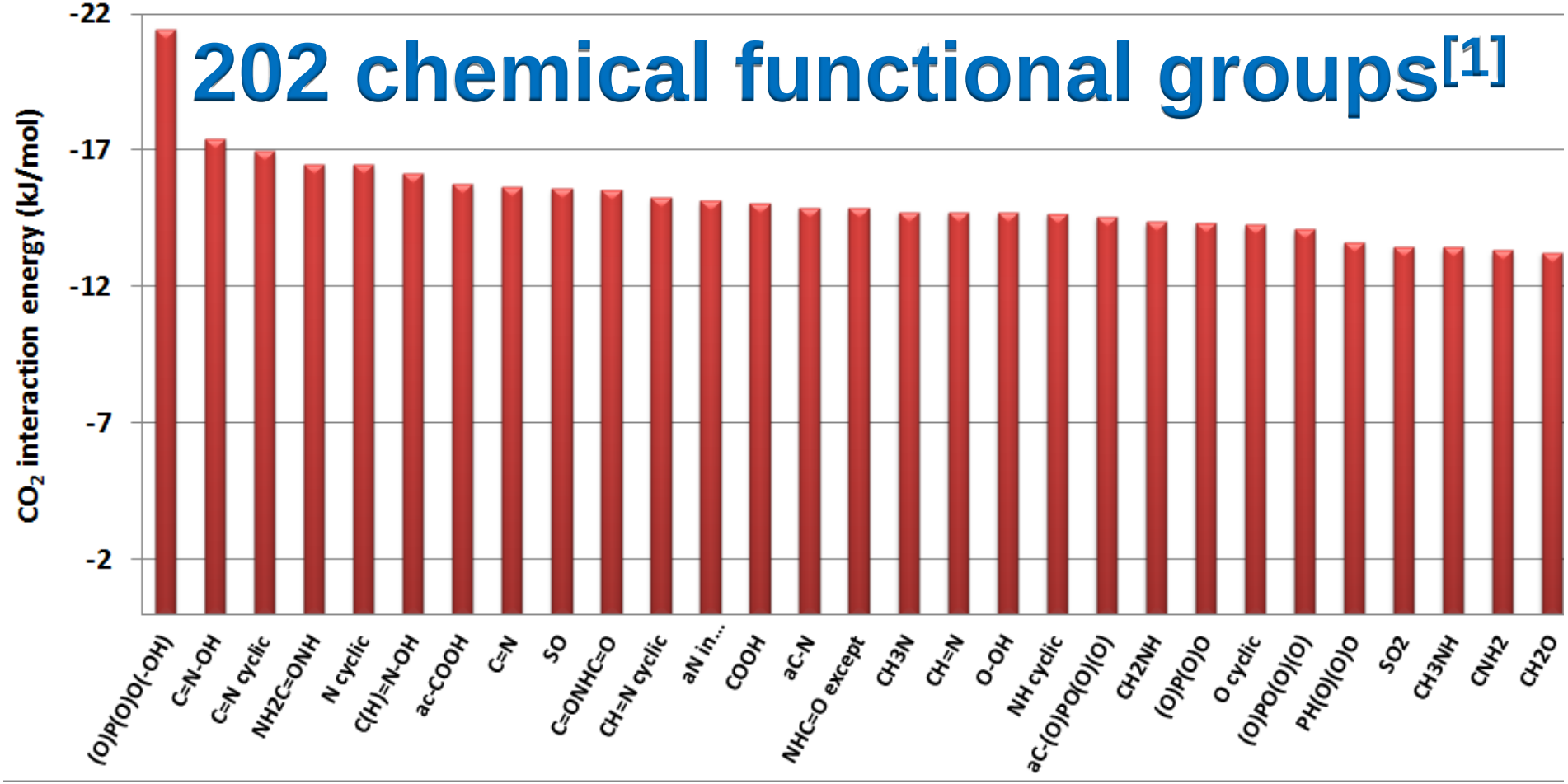
23,000→600 NIST Database Search



- ~600 compounds were found in NIST database with

$T_m < 30$ °C & $T_b > 260$ °C

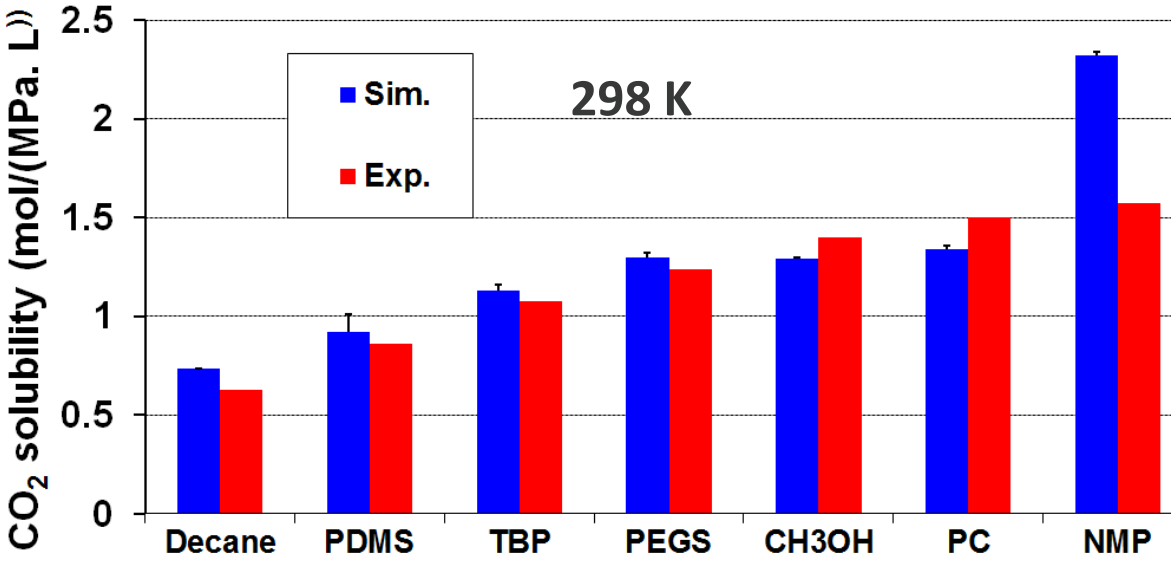
In-house Computation Database: Chemical Functional Group Interactions with CO_2



- 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)

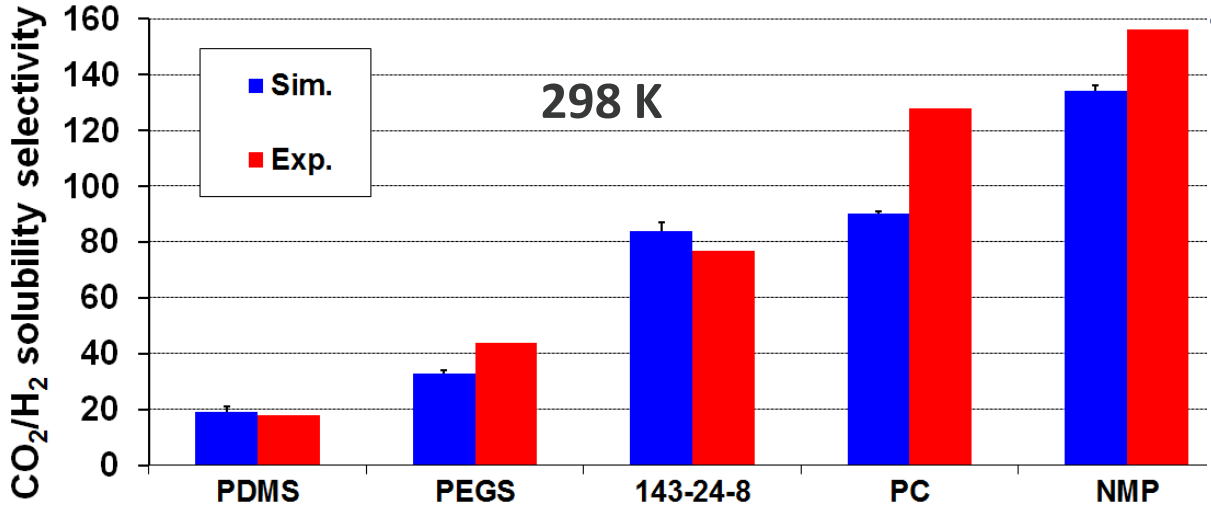
[1] Marrero, J.; Gani, R. *Fluid Phase Equilib.* **2001**, 183

Experimental Validation of Simulation



- CO_2 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]

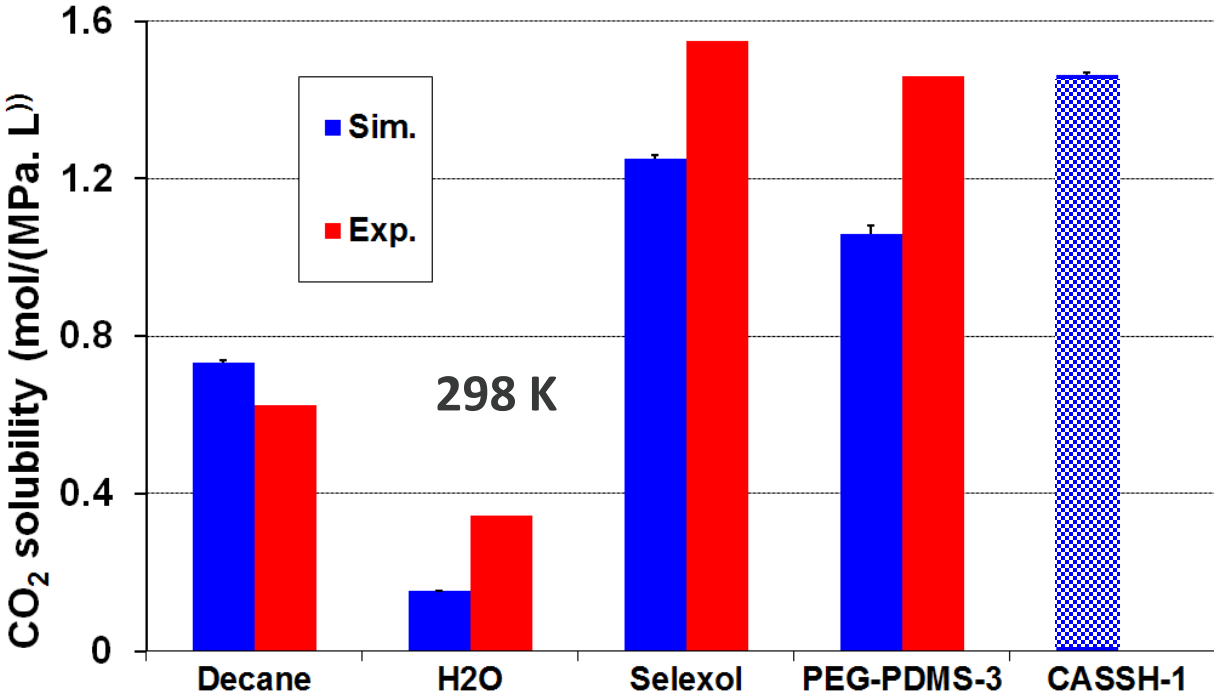


- CO_2/H_2 selectivity values agree (17.3% difference)
  - Same trends

CAS 143-24-8: Selexol surrogate

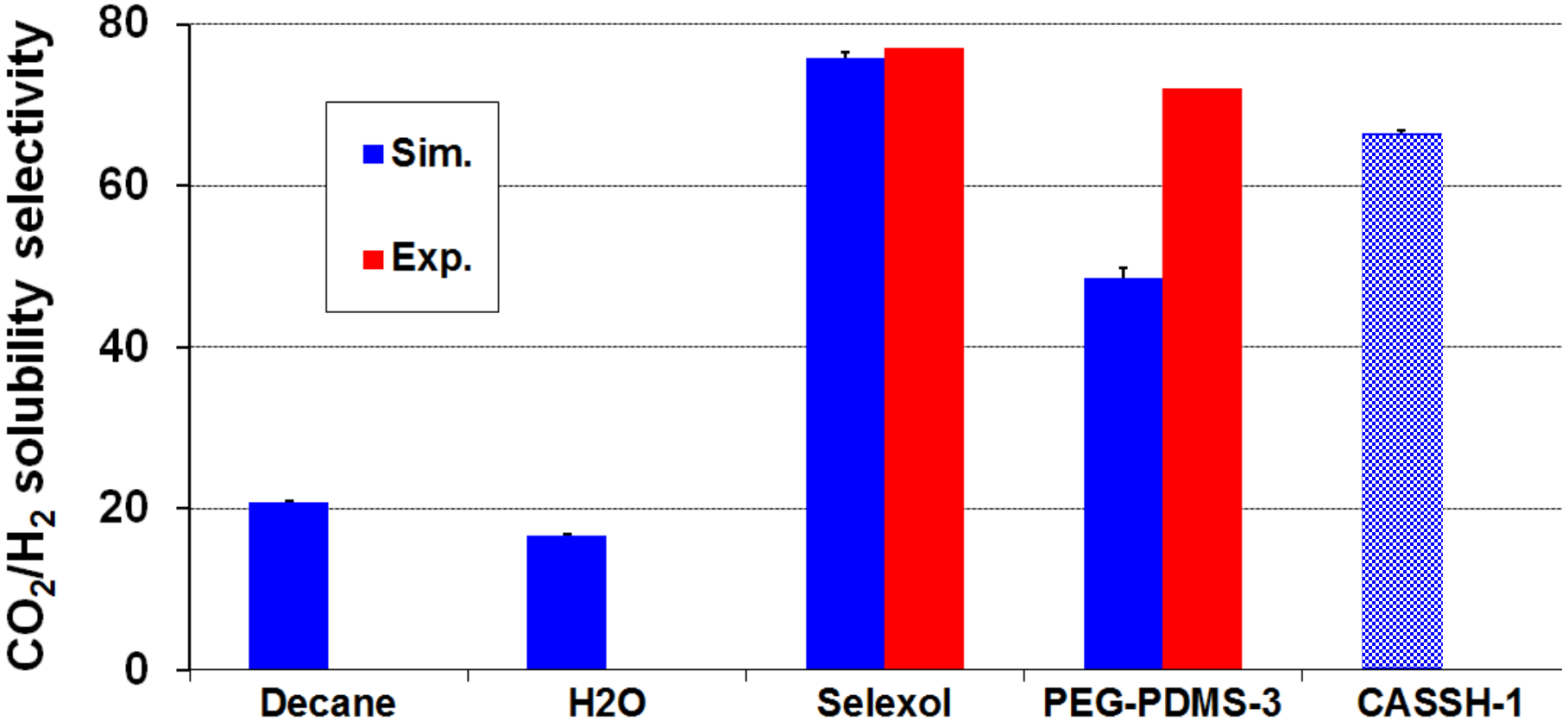
[1] Shi, W. et al., *J. Phys. Chem. C* **2015**, 19253
[2] Shi, W. et al., *J. Phys. Chem. C* **2016**, 20158
[3] Burr, B. et al. *Hydrocarbon Processing* **2009**, 43

Simulated CO_2 Solubility Values in ~30 Solvents: Identify One of the Best



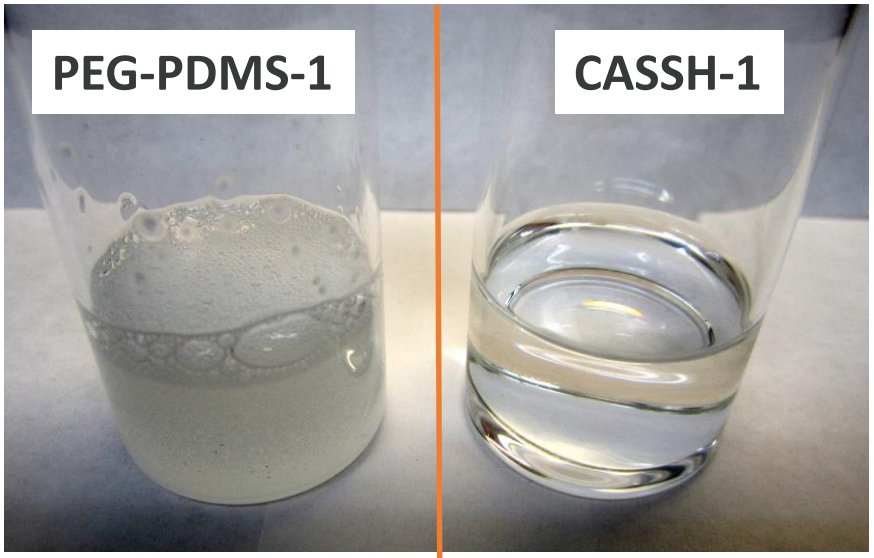
- **One of the best solvents, CASSH-1, was identified from the computational screening.**
- **Similar CO_2 solubility trend**
  - —Sim.: CASSH-1 > Selexol > PEG-PDMS-3 > decane > H_2O
  - —Exp.: Selexol ~ CASSH-1 ~> PEG-PDMS-3 > decane > H_2O

Simulated High CO_2/H_2 Solubility Selectivity in CASSH-1

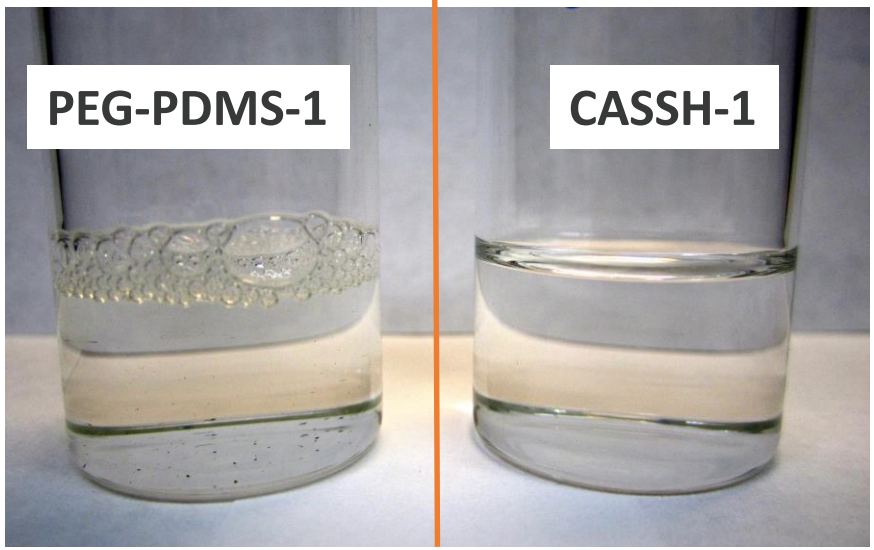


- **CASSH-1 exhibits high CO_2/H_2 selectivity**
  - –needs experimental validation

CASSH-1 is non-foaming



Hand shaken for 1 min., then photographed immediately

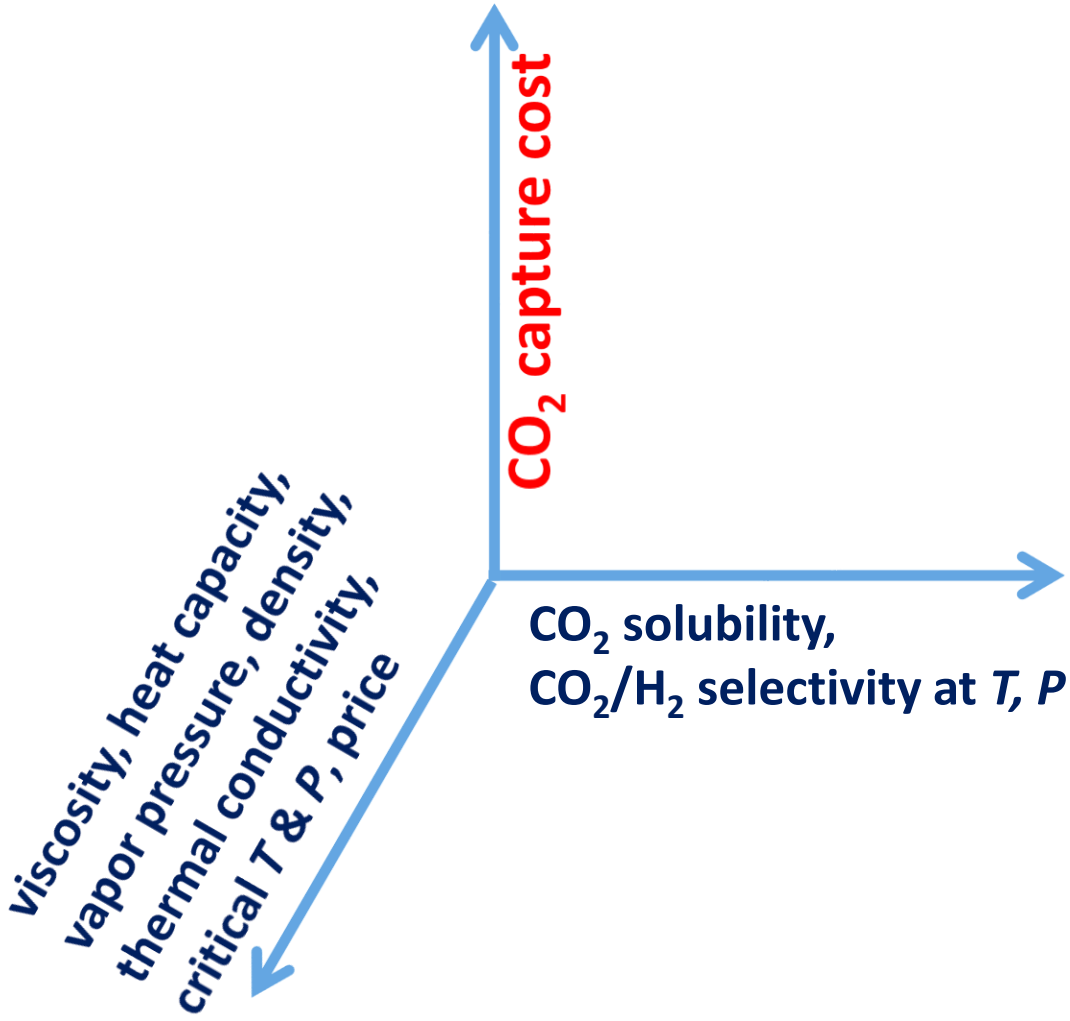


Hand shaken for 1 min., then photographed after 1 min.

Physical Properties at 298 K

Solvent	Selexol	PEG-PDMS-3	CASSH-1
Viscosity (cP)	5.8	12.2	5.1
Density (g/cm^3)	1.030	0.9847	0.960
Molecular weight (g/mol)	280	620	260
Vapor pressure (mmHg)	7.3×10^{-4}	small	1/100 of Selexol
Freezing point (°C)	-28		0
Normal boiling point (°C)	275	high	300
Hydrophobicity	Very hydrophilic	hydrophobic	Very hydrophobic
Foaming	No	No	No
Safety, health, environment	No	No	No

Future Work: TEA Analysis for ~30 Solvents



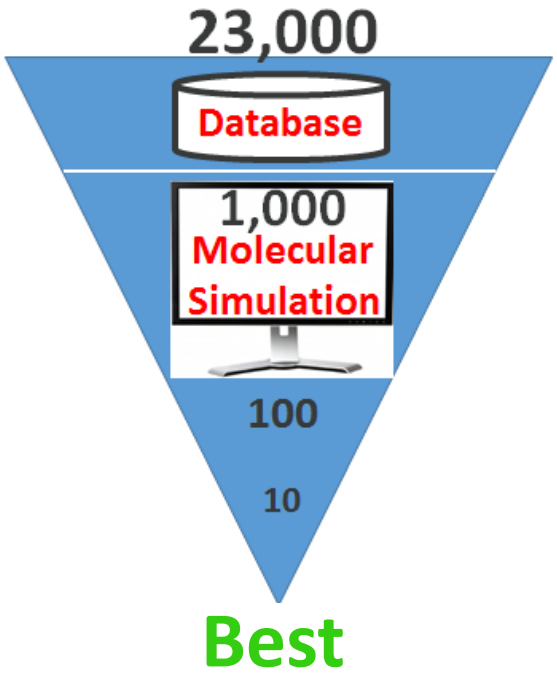
Extending the Same Approach to Polymer Screening for CO_2 Capture Membrane (New Project)

- **Polymer database**
  - **Over 800 organic polymers involving 9 species (C, H, O, N, S, F, Cl, Br, I)** [1]
  - **Experimental database development**
    - √ CO_2, CH_4, H_2O, N_2, O_2 and H_2 permeability, solubility, and diffusivity in polymers
    - √ Glass transition temperature, melting point, mechanic properties
    - √ Data for ~50 polymers collected so far
  - **Computational polymer database development**
    - √ CO_2 interactions with dimer built from monomer functional groups
    - √ 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**

[1] Kim C.; et al. *J. Phys. Chem. C* **2018**, DOI: 10.1021/acs.jpcc.8b02913

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



Acknowledgements

- **NETL Internal Collaborators**
  - —Robert Thompson, Megan Macala, Jeffrey Culp, Hong Lei, Surendar Venna
  - —Surya Tiwari, Samir Budhathoki, Jan Steckel, Dan Sorescu
  - —Nicholas Siefert, Kevin Resnik
  - —David Hopkinson
  - —CO_2 Capture team
  - —Computational materials group
  - —HPCEE super computer cluster
  - —Michael Matuszewski, Bryan Morreale
- **NETL external contacts**
  - —Rafiqul Gani @ Technical University of Denmark, Kevin Joback @ moleculardknowledge.com
  - —Edward Maginn @ University of Notre Dame
  - —Karl Johnson and Badie Morsi @ University of Pittsburgh

This technical effort was performed in support of the National Energy Technology Laboratory's ongoing research under the RES contract DE-FE0004000.

This project was funded by the Department of Energy, National Energy Technology Laboratory, an agency of the United States Government, through a support contract with AECOM. Neither the United States Government nor any agency thereof, nor any of their employees, nor AECOM, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.