Thermodynamic Characterization of Reservoir Fluids and Process Analysis

Adidharma/Towler/Radosz

Department of Chemical and Petroleum Engineering, University of Wyoming

- The thermodynamic characterization of reservoir and injected fluids allows us to perform rigorous analyses of the oil recovery processes.
- A continuous program that will reveal important factors that are still unknown or not well understood and affecting the efficiency of oil recovery.
- A synthesis of theoretical and experimental components.
Achievement

Theoretical component:

- Developed a unified advanced model (SAFT) to predict the thermodynamic properties of reservoir fluids, including brine, at reservoir conditions.
- Developed unified advanced models (FT-SAFT/FV-SAFT) to predict the viscosity of gas/liquid/supercritical fluids for carbon dioxide and alkanes.
- Developed an advanced model (Multiple Mixing Cells model coupled with key tie line approach) to predict Minimum Miscibility Pressure (MMP) for model oils.

Refereed publications: 10
Submitted: 2
Achievement

Experimental component:

- Built a slim tube apparatus for Minimum Miscibility Pressure (MMP) measurements
- Measured MMP for model oils and Wyoming oils.
- Investigated the effects of injected gas composition on MMP.

Refereed publications: 2
Future Work
(2007-2008)

Theoretical component:
- Extend our model to predict the MMPs of systems with increasing degree of complexity.

Experimental component:
- Continue supporting the modeling work and measuring the MMPs of Wyoming oils.
- Study the effects of operating conditions, gas composition, and brine on oil recovery in CO$_2$ flooding.
Viscosity of pure $n$-alkanes at $P = 200$ bar; broken lines are calculated using our model (numbers $n$ are for $C_nH_{2n+2}$); circles: experimental data.
Injected gas: C1  
Model oil: 50% C4 + 50% C10  
T = 344 K, P = 16 MPa  
f_g = 1, GOR = 0.3
MMP Measurements for Wyoming Oil

(a) Oil recovery, % OOIP vs. PV of CO₂ injected at different pressures (1200 Psia, 1400 Psia, 1500 Psia, 1600 Psia, 1800 Psia).

(b) Oil recovery, % OOIP vs. Pressure (MPa) showing breakthrough at 1.2 PV.
Effects of $O_2$ and $N_2$ on MMP

- **Cottonwood Creek oil**
- **Model oil**

Effects of $O_2$ and $N_2$ on MMP.
Publications

Enhanced Oil Recovery Using CO$_2$

- There is a current supply shortage
- Other sources are the Exxon Shute Creek plant
- The Madden Gas Plant
- Big Supplies of CO$_2$ from the flue gas of several coal fired Power Plants in Wyoming
- Separation technology is critical
CO$_2$ Separation

- Key to economically viable CO$_2$-based enhanced oil recovery.
- Amine absorption process $\sim$ $40$/ton CO$_2$
- $2.25$/MCF CO$_2$
- CO$_2$-separation alone will add $18$ cost to each barrel of oil
Current Subprojects

- New CO$_2$ absorbents and adsorbents
  - Poly(ionic liquid) absorbents
  - Carbonaceous adsorbent
- New processes for CO$_2$ desorption
- New polymer membrane for CO$_2$ separation
  - Poly(ionic liquid) membrane
  - Nanocomposite membrane
CO$_2$ Sorbents

- To develop and test novel adsorbents and adsorption cycles or processes for capture of CO$_2$ using pressure or temperature-swing process.
- To determine the impact of process parameters (cycle time, cycle configuration, temperature) on CO$_2$ capture efficiency.
- To determine capital and power requirements by using simulation tools to scale up to appropriate size.
- To acquire sufficient process performance data for the adsorption processes developed so as to permit technical and economic assessment of the viability of adsorption technologies.
Example of CO2 PSA Process

100%N₂  100%CO₂

Step 1
Issues of Current CO$_2$ Sorbents

- High energy consumption
- Amine loss and degradation
- Equipment corrosion.
- Costly zeolites ($80,000/ton$)
Our Focus

Low heat capacity
Non-volatility
No-corrosion
Versatility
Tailored capacity/properties
Low cost
Our New CO2 absorbents and adsorbents

Poly(ionic liquid) absorbents - patent pending

Carbonaceous adsorbents - patent pending
Poly(ionic liquid)s for CO$_2$ separation

- Unexpectedly, we found that simply making the ionic liquids based on imidazolium into polymeric forms significantly increased the CO$_2$ absorption capacity compared with ionic liquids.

- With fast CO$_2$ absorption and desorption rate, reversible desorption and feasibility to fabrication, these polymers are very prospect as sorbent and membrane materials for CO$_2$ separation.
CO₂ absorption of the poly(ionic liquid) based on ammonium and imidazolium, their corresponding monomers and an ionic liquid as a function of time (592.3 mmHg CO₂, 22 °C).
Cycles of CO$_2$ sorption and desorption

Faster sorption and desorption
Reversible sorption

Ionic liquid
High CO$_2$/nitrogen selectivity
Carbonaceous Adsorbents

- Much lower cost
- High capacity
- Tested in lab
- Plan to test in the UW power plant
- Patent pending
New CO$_2$-desorption process

- Current approach - steam heating
  - Low efficiency
  - Deteriorate the sorbents, making the sorbents be used only for several cycles

Our New approach
- High Efficiency
- Do not affect the sorbents; sorbents can be numerous cycles
- Patent pending
New Polymer membranes
Ionic Liquid Polymer Membrane

Representative polymers
- P[MATMA][BF4]-g-PEG 2000
- P[VBTMA][BF4]-g-PEG 2000
- [emim][dca]

**Graph:**
- X-axis: CO$_2$ permeability (Barrer)
- Y-axis: CO$_2$/N$_2$ Permselectivity
- Symbols:
  - Blue diamonds: Representative polymers
  - Black circles: P[MATMA][BF4]-g-PEG 2000
  - Red triangles: P[VBTMA][BF4]-g-PEG 2000
  - Purple square: [emim][dca]
BPPO_{dp}/10 nm-silica nanocomposite membranes

- BPPO_{dp}/silica (10nm) composite membranes

![Graph showing CO\textsubscript{2}/N\textsubscript{2} permselectivity vs. CO\textsubscript{2} permeability for representative polymers and BPPO_{dp}/silica (10nm) composite membranes.](attachment:image.png)
Polymer-Carbon Nanotube Membranes

![Graph showing CO₂/N₂ permselectivity vs. CO₂ permeability (Barrer) for representative polymers and BPPOdp/SWNT composite membranes.]

- **Representative polymers**
- **BPPOdp/SWNT composite membranes**

Key points:
- 0%
- 5%
- 17%
- 9%
Refereed Journals

Refereed Preprints:

Academic Achievement: 10 refereed journal papers
6 refereed preprints
1 paper highlighted in Chemical and Engineering News
Proprietary Documents and Plans

1 patent is granted
4 patents are pending

Pilot testing scheduled in the UW Power Plant (this spring if the weather allows or summer)

1. To determine the impact of process parameters (cycle time, cycle configuration, temperature) on CO2 capture efficiency
2. To determine capital and power requirements from simulation to scale up
3. To acquire performance data to permit technical and economic assessment