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# Optimization of Amine-Based Solid Sorbent Chemistry for Post-Combustion Carbon Capture

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# Introduction

- **Background**
  - Amine impregnated mesoporous sorbent
  - Amine chemistry
  - $CO_2$ capture process
- **Simulation based optimization**
- **$CO_2$ capture system optimization**
- **Sorbent optimization**
  - Design targets for sorbent properties
  - Base sorbent vs Hypothetical sorbent
- **Conclusion**

# Amine-based Solid Sorbent

| | | |
|---|---|---|
| $H_2O_{(g)} \leftrightarrow H_2O_{(phys)}$ | (1) | Water Physisorption |
| $R_1R_2NH + CO_{2(g)} + H_2O_{(phys)} \leftrightarrow R_1R_2NH_2^+ + HCO_3^-$ | (2) | Bicarbonate Formation |
| $2R_1R_2NH + CO_{2(g)} \leftrightarrow R_1R_2NH_2^+ + R_1R_2NCO_2^-$ | (3) | Carbamate Formation |

$$\frac{da}{dt} = k_1\left[p_1 - \frac{a}{K_1}\right] - k_2\left[sap_2 - \frac{bw}{K_2}\right]$$

$$\frac{db}{dt} = k_2\left[sap_2 - \frac{bw}{K_2}\right]$$

$$\frac{dx}{dt} = k_3\left[s^2p_2 - \frac{xw}{K_3}\right]$$

$a$: adsorbed water concentration

$b$: bicarbonate concentration

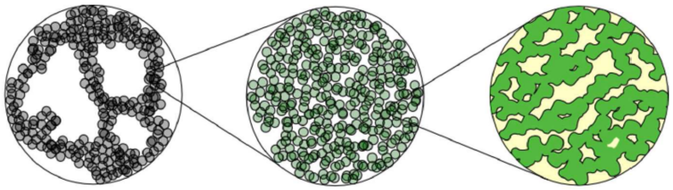
$x$: carbamate site fraction

$s$: free amine site fraction

$w$: protonated amine site fraction

$p_1$: $CO_2$ partial pressure

$p_2$: $H_2O$ partial pressure



$k_i$: rate constants

$K_i$: equilibrium constants



A. Lee, D. Mebane, D. J. Fauth and D. C. Miller, "A Model for the Adsorption Kinetics of CO2 on Amine-Impregnated Mesoporous Sorbents in the Presence of Water," Proceedings of the 28th International Pittsburgh Coal Conference, 2011.

# Amine Chemistry

### Equilibrium constant expression

$$K_i = \exp\left(-\frac{\Delta S_i}{R}\right)\exp\left(-\frac{\Delta H_i}{RT}\right)/P$$

### Rate constant expression

$$k_i = A_i T \exp\left(-\frac{E_i}{RT}\right)$$

### $R_1R_2NH$ Properties

| | |
|---|---|
| $\Delta H_i$ | reaction enthaply |
| $\Delta S_i$ | reaction entropy |
| $E_i$ | activation energy |
| $A_i$ | frequency factor |

### NETL -32D (Base Sorbent) Properties

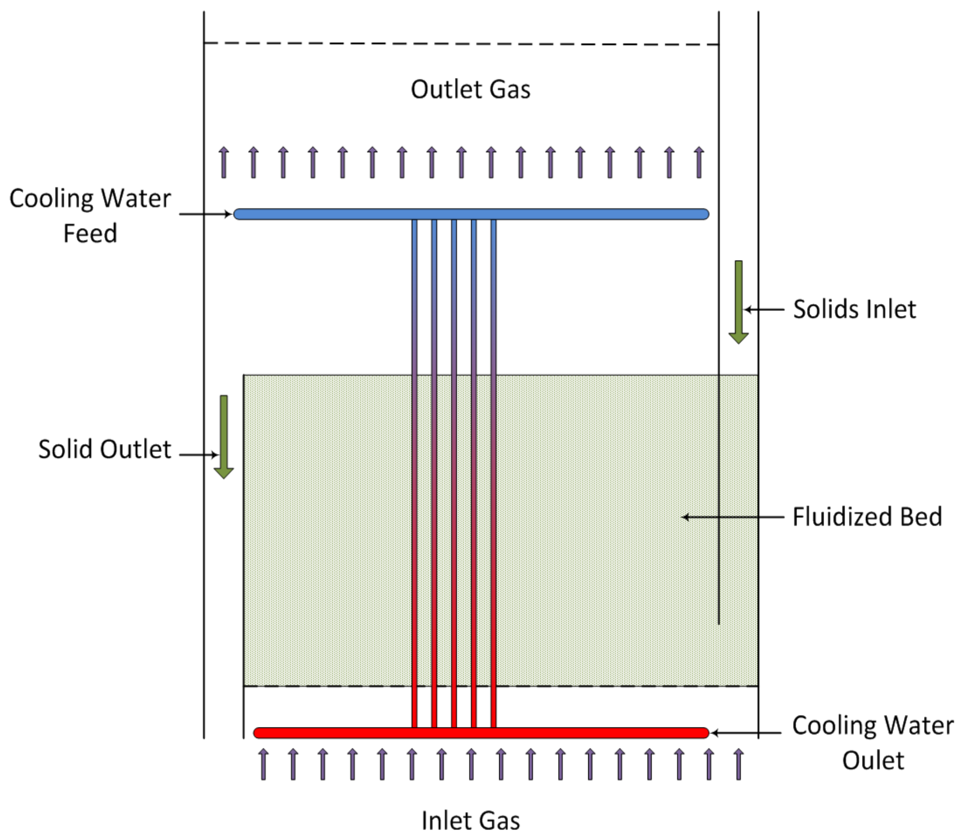
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\Delta H_1$ | -72,580 | $\Delta S_1$ | -141.4 | $E_1$ | 29,623 | $A_1$ | 0.1758 |
| $\Delta H_2$ | -79,079 | $\Delta S_2$ | -216.2 | $E_2$ | 83,174 | $A_2$ | 0.091098 |
| $\Delta H_3$ | -109,691 | $\Delta S_3$ | -281.3 | $E_3$ | 27,523 | $A_3$ | 141.994 |

($\Delta H_i$ : J/mol $\Delta S_i$ : J/mol/K $E_i$: J/mol)



A. Lee, D. Mebane, D. J. Fauth and D. C. Miller, "A Model for the Adsorption Kinetics of CO2 on Amine-Impregnated Mesoporous Sorbents in the Presence of Water," Proceedings of the 28th International Pittsburgh Coal Conference, 2011.

# Bubbling Fluidized Bed (BFB)

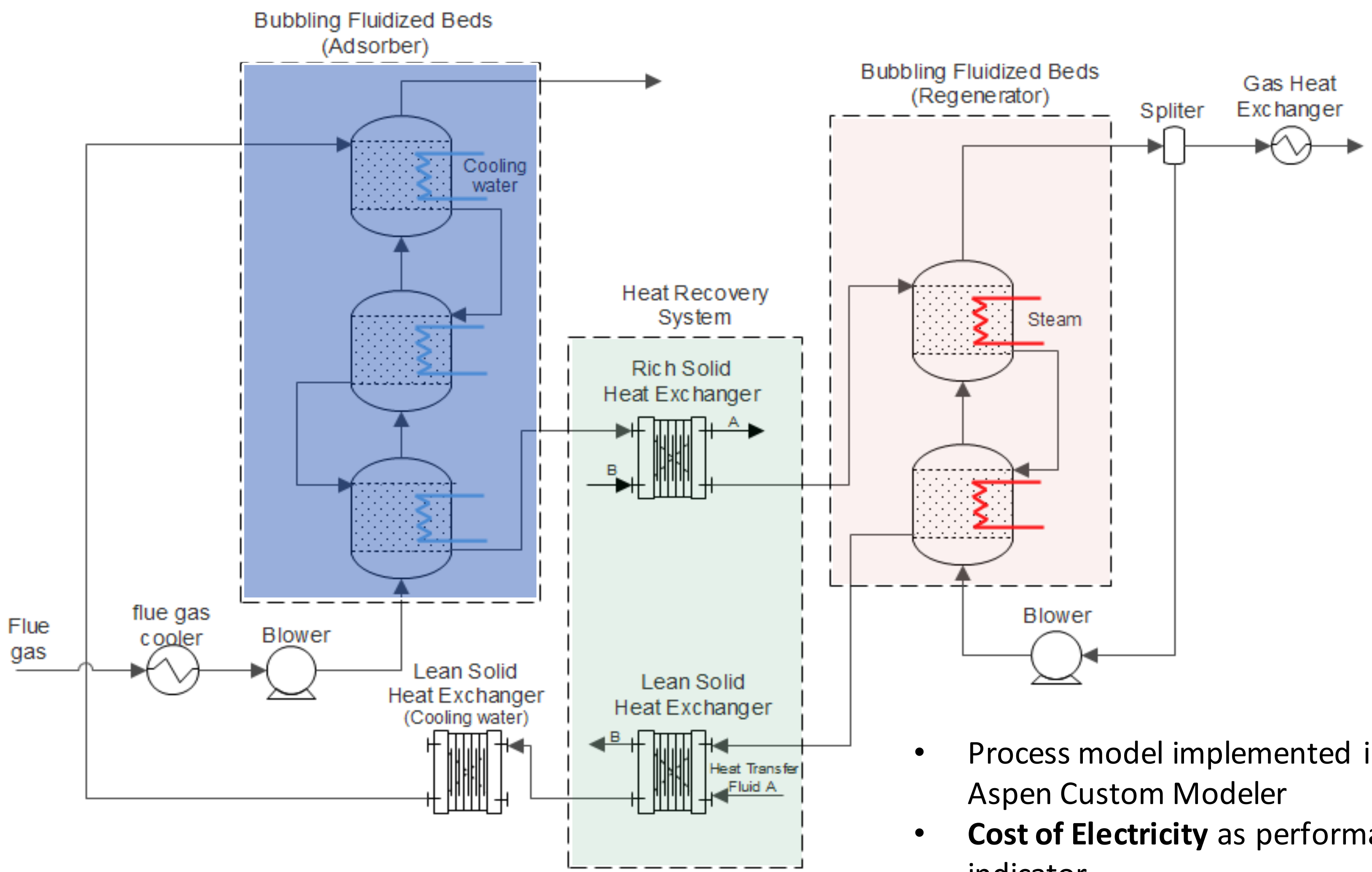



- **1-D, two-phase, pressure driven and non-isothermal models**
- **Flexible configurations**
  - Adsorber or regenerator
  - Under/overflow
  - Integrated heat exchanger for heating or cooling
- **Supports complex reaction kinetics**



*A. Lee and D. C. Miller, "A one-dimensional (1-D) three-region model for a bubbling fluidized-bed adsorber," Ind. Eng. Chem. Res.,* ***2013****, 52, 469-484.*

# Solid Sorbent-based $CO_2$ Capture Process

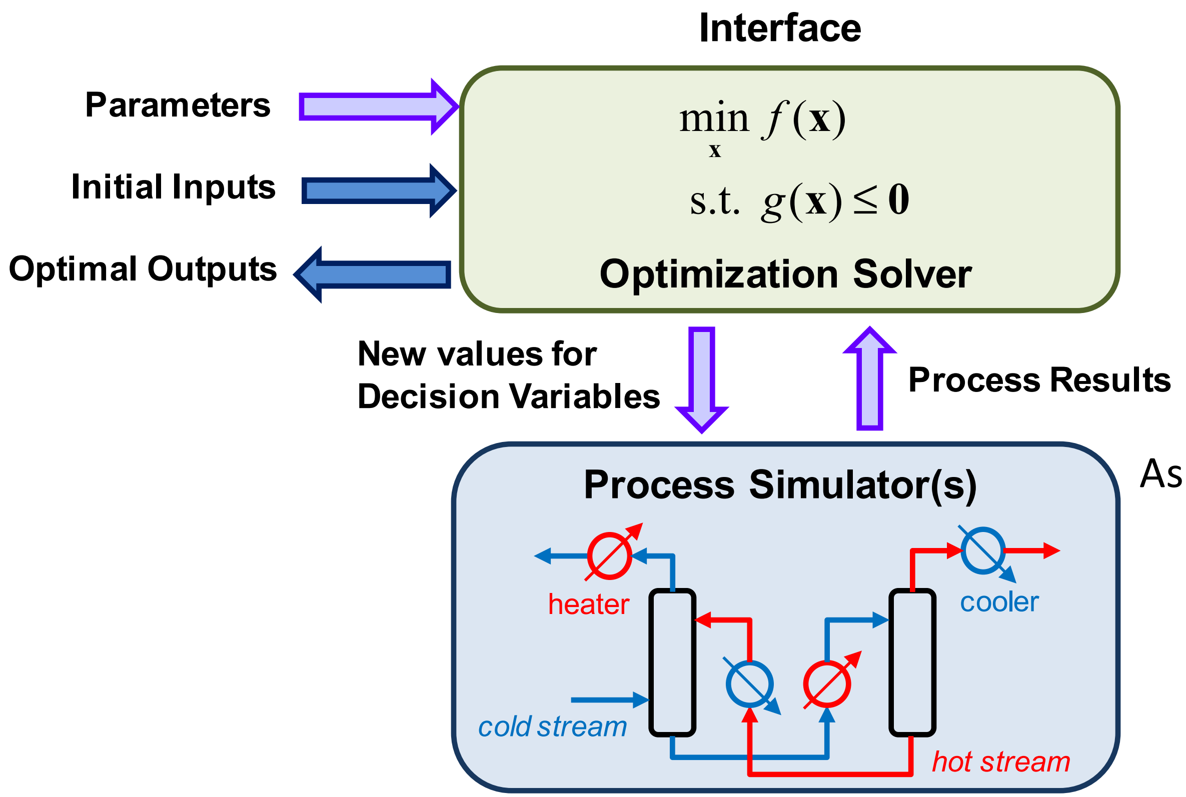



- Process model implemented in Aspen Custom Modeler
- **Cost of Electricity** as performance indicator



*Sahinidis, N. V., A. Cozad, D. C. Miller and Z. Wilson, "Extending the Scope of Algebraic MINLP Solvers to Black- and Grey-box Optimization", AIChE Annual Meeting, Atlanta, GA, 2014.*

# Simulation Based Optimization




Aspen Custom Modeler

D.C. Miller, B. Ng, J.C. Eslick, C. Tong, Y. Chen, "Advanced Computational Tools for Optimization and Uncertainty Quantification of Carbon Capture Processes," Proceedings of the 8th Foundations of Computer Aided Process Design Conference – FOCAPD 2014, M.R. Eden, J.D. Siirola , G.P. Towler (Eds.) , Elsevier, 2014.

# $CO_2$ Capture Process Optimization

- **Objective**

***min*** Cost of Electricity (COE)

- **Decision Variables**

$\boldsymbol{x}$ **:** Design and Operating variables

- **Constraints**

The $CO_2$ capture system model (Aspen Custom Modeler)

Cost Calculation (Spreadsheet or ACM)

$CO_2$ capture rate ≥ 90%

$$\boldsymbol{x}_{min} \leq \boldsymbol{x} \leq \boldsymbol{x}_{max}$$

# Decision Variables $x$

- **Design variables**
  - BFB dimensions
    - bed depth, diameter
    - Immersed heat exchanger tube diameter and spacing in adsorbers and regenerators
  - Solid Heat Exchanger dimensions
  - Flue gas cooler dimension
- **Operating variables**
  - Total sorbent circulation rate
  - Regeneration section recirculation gas split fraction
  - Temperature of the cooled flue gas
  - Temperature of solid sorbent into the absorber and regenerator

# Design Target for Sorbent Properties

$$R_1R_2NH + CO_{2(g)} + H_2O_{(phys)} \leftrightarrow R_1R_2NH_2^+ + HCO_3^-$$

$$2R_1R_2NH + CO_{2(g)} \leftrightarrow R_1R_2NH_2^+ + R_1R_2NCO_2^-$$

**Equilibrium constant expression**

*Carbamate formation*

$$\kappa_3 = \frac{\exp\left(-\frac{\Delta S_3}{R}\right)\exp\left(-\frac{\Delta H_3}{R\boldsymbol{T}}\right)}{P}$$

*Bicarbonate formation*

$$\kappa_2 = \frac{\exp\left(-\frac{\Delta S_2}{R}\right)\exp\left(-\frac{\Delta H_2}{R\boldsymbol{T}}\right)}{P}$$

**Rate constant expression**

*Carbamate formation*

$$k_2 = A_2 T \exp\left(-\frac{E_2}{RT}\right)$$

*Bicarbonate formation*

$$k_3 = A_3 T \exp\left(-\frac{E_3}{RT}\right)$$

**$R_1R_2NH$ Properties**

| | |
|---|---|
| $\Delta S_i$ | reaction entropy |
| $\Delta H_i$ | reaction enthaply |
| $E_i$ | activation energy |
| $A_i$ | frequency factor |

- **Substituted amines**
- **Mixtures of amines**
- **Structure of solid sorbents**

# Heat of Reaction $\Delta H_i$

- **High heat of adsorption**
  - Higher working capacity

$$K_i = \frac{\exp\left(\frac{\Delta S_i}{R}\right)\exp\left(\frac{-\Delta H_i}{R\boldsymbol{T}}\right)}{P}$$

- **Low heat of adsorption**
  - Reduced energy requirement

- **Focus on sorbents with either a high or low heat of adsorption is not sufficient.**
  - The operating parameters of the process and the interaction with the power plant should be taken into account.

J. Oexmann and A. Kather, Minimising the regeneration heat duty of post-combustion CO2 capture by wet chemical absorption: The misguided focus on low heat of absorption solvents," **International Journal of Greenhouse Gas Control,** 2010, 4, 36-43

# Interactions between Reactivity Parameters

- These parameters have nonlinear interactions since the reactions are linked. Sensitivity analysis on single parameter is not enough to provide comprehensive optimization.

$$R_1R_2NH + CO_{2(g)} + H_2O_{(phys)} \leftrightarrow R_1R_2NH_2^+ + HCO_3^-$$

$$2R_1R_2NH + CO_{2(g)} \leftrightarrow R_1R_2NH_2^+ + R_1R_2NCO_2^-$$

$$K_i = \frac{\exp\left(\frac{\Delta S_i}{R}\right)\exp\left(\frac{-\Delta H_i}{R\boldsymbol{T}}\right)}{P}$$

- Reaction parameters are optimized simultaneously

# Sorbent Optimization

- **Objective**

***min*** Cost of Electricity (COE)

- **Decision Variables**

Design and Operating variables + Reactivity Variables $\boldsymbol{x}'$

- **Constraints**

The $CO_2$ capture system model (Aspen Custom Modeler)

Cost Calculation (Spreadsheet or ACM)

$CO_2$ capture rate ≥ 90%

$$\boldsymbol{x}'_{min} \leq \boldsymbol{x}' \leq \boldsymbol{x}'_{max}$$

# NETL-32D vs Hypothetical Sorbent

| Reactivity Variables | Unit | NETL-32D | Hypothetical Sorbent 1 | Hypothetical Sorbent 2 |
|---|---|---|---|---|
| $\Delta H_2$ (Heat of reaction in bicarbonate formation) | J/mol | -79,079 | -74,710 | -62,368 |
| $\Delta H_3$ (Heat of reaction in carbamate formation) | J/mol | -109,691 | -73,192 | -85,940 |
| $\Delta S_2$ (Reaction entropy of bicarbonate formation) | J/mol/K | -216.24 | -233.18 | -147.13 |
| $\Delta S_3$ (Reaction entropy of carbamate formation) | J/mol/K | -281.26 | -198.97 | -235* |
| $E_2$ (Activation energy of bicarbonate formation) | J/mol | 83,174 | 83,174 | 28,000* |

| | | | | |
|---|---|---|---|---|
| Steam usage for regeneration | $10^2$ tonne/hr | 6.88 | 5.24 | 5.73 |
| Bicarbonate delta loading | mol/kg | 0.00 | 0.00 | 0.59 |
| Carbamate delta loading | mol/kg | 1.44 | 1.21 | 1.07 |
| Total delta loading (Working capacity) | mol/kg | 1.44 | 1.21 | 1.66 |
| Total sorbent circulation rate | $10^3$ tonne/hr | 7.41 | 8.81 | 6.43 |

| | | | | |
|---|---|---|---|---|
| Decrease in Cost of Electricity from base case | % | Base case | 5.5 | 8.4 |

* The value is on the lower bound of this decision variable.

# Conclusion

- **A balance between bicarbonate and carbamate formation is required.**
  - Reason: higher working capacity → lower capital costs
  - Current challenge: improve the kinetics of bicarbonate formation

- **Heats of reaction are vital in balancing regeneration energies and sorbent loading.**
  - High heats of reaction result in increase in working capacity.
  - Low heats of reaction lead to reduction in regeneration energies.
  - Optimal values vary and depend on other decision variables subject to practical limitations.

- **Future work**
  - More sorbent properties taken into consideration: particle diameter, particle density, etc.
  - Collaborate with experimental sorbent developers to tune reactivity

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