Kinetics of the chemical looping reduction of CuO/bentonite by methane (CH_4)

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Objective

Extract kinetic parameters from experimental test data using Thermo-gravimetric Analysis (TGA) and Mass spectrometry (MS) on selected metal oxygen carrier (Cu-based and Fe-based/Bentonite) developed at the National Energy Technology Laboratory (NETL).

Thermo-gravimetric Analysis (TGA)

- Used to record the change in mass of ~40 mg samples over- time

Mass spectrometry (MS)

- Used to determining the elemental composition of a sample or molecule

Chemical Looping

Oxygen is removed from air stream and transported to a fuel reactor via a metal or other oxygen carrier. The metal must then be separated from ash once oxygen is freed in the reactor and returned to the air reactor

Fuel Reactor

$$4CuO + CH_4 \rightarrow 4Cu + CO_2 + 2H_2O$$

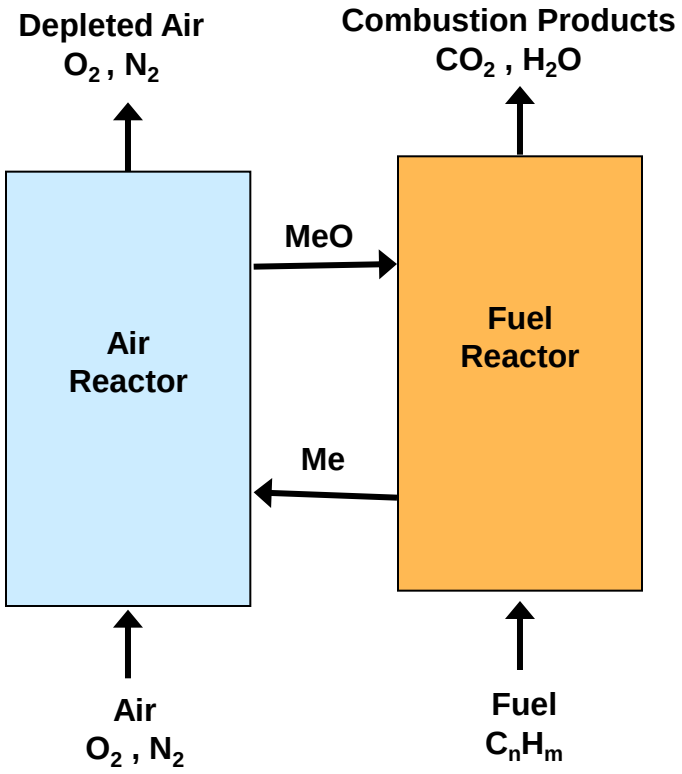
$\Delta G = -590$ kJ/mol, $\Delta H = -217$ kJ/mol

Air Reactor

$$2Cu + O_2 \rightarrow 2CuO$$

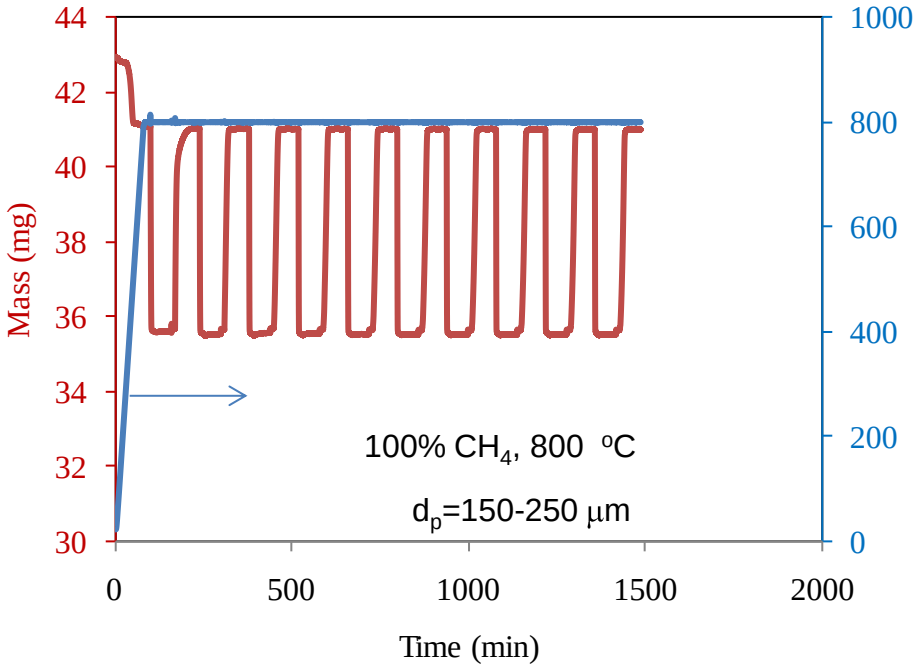
$$4Cu + O_2 \rightarrow 2Cu_2O$$

$$2Cu_2O + O_2 \rightarrow 4CuO$$

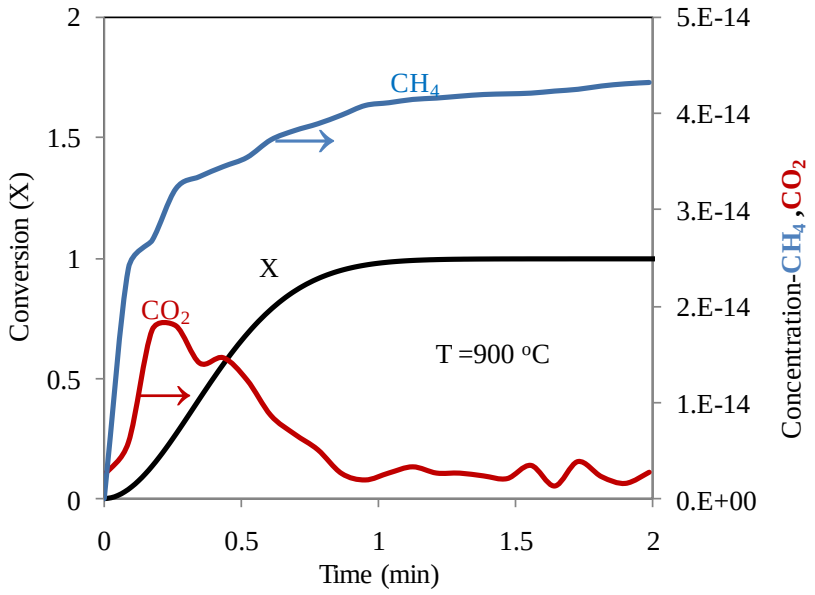


NETL TGA Data for Cu base sorbent

$$4CuO + CH_4 \rightarrow 4Cu + CO_2 + 2H_2O$$



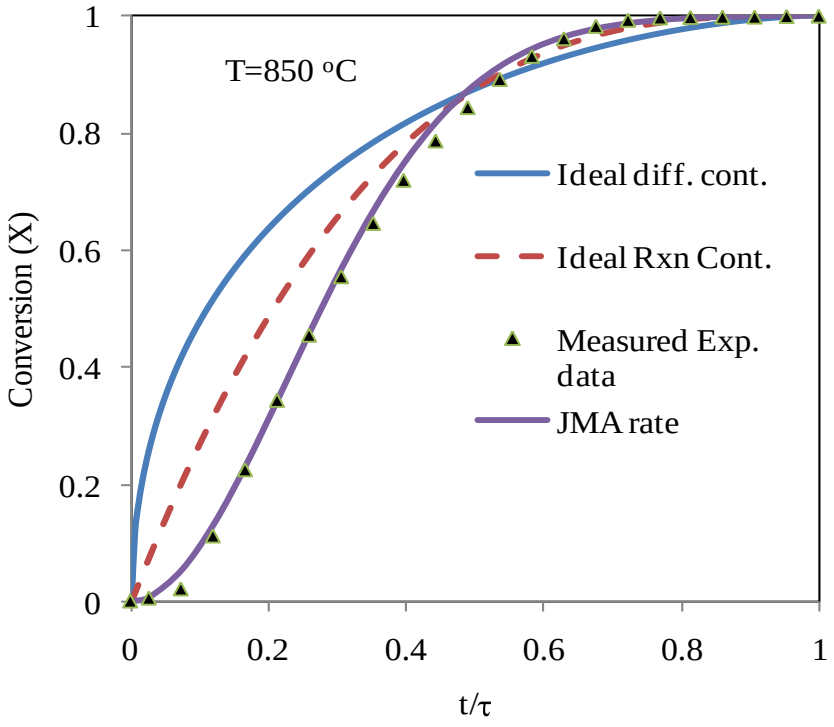
Typical mass and temperature measurement for CuO/bentonite particle and 100% CH_4 for reduction and air for oxidation reactions



Conversion, *X*, and outlet gas analysis of CH_4 and CO_2 for the reduction of copper oxide (CuO) with methane (100%CH_4)

$$X_r = 1 - \frac{m - m_r}{m_{ox} - m_r}$$

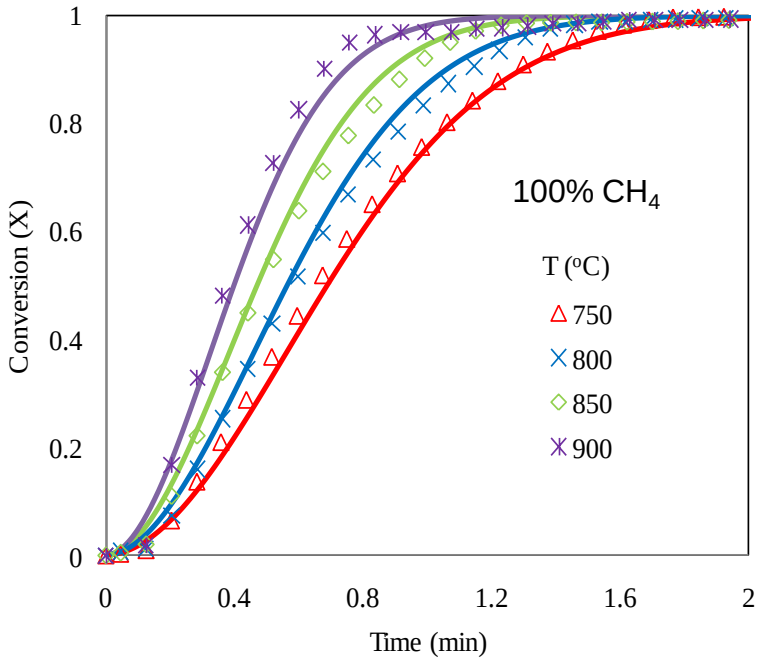
Rate Analysis (Cu-base Reduction)



Typical curve fitting of experimental reduction data using shrinking core model (diffusion and reaction control) and JMA rates for 100% methane and 850 °C.

Eight different rate equations were indentified and examined, including shrinking core model (diffusion and reaction control), linear, parabolic and cubic rate laws, first and second order global reaction rate, and Jonson-Mehl-Avarmi (JMA) rate, to fit the TGA experimental data for CuO-bentonite/methane reduction reaction. None of the models gave satisfactory results over the range of 750-900 °C with the exception of JMA equation.

Rate Analysis (Cu-base Reduction)



Effect of reaction temperature and fitting of Jonson-Mehl-Avarmi (JMA) equation

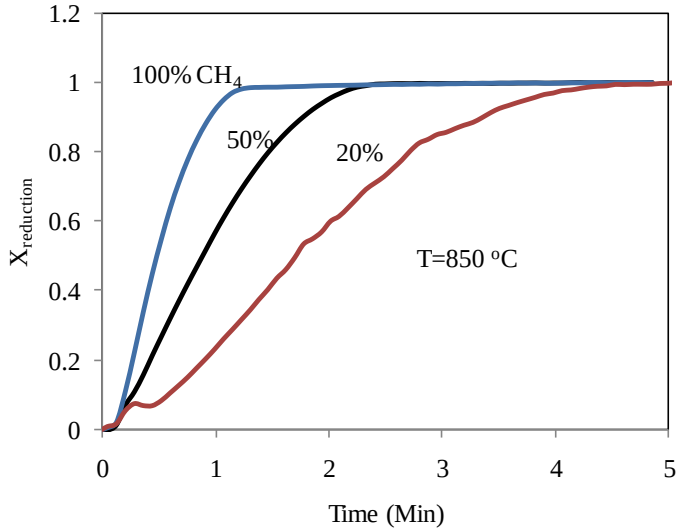
Jonson-Mehl-Avarmi (JMA) equation

$$X = (1 - e^{-(kt)^n})$$

n~kinetic exponent which depends on the mechanism of growth and the dimensionality of the crystal

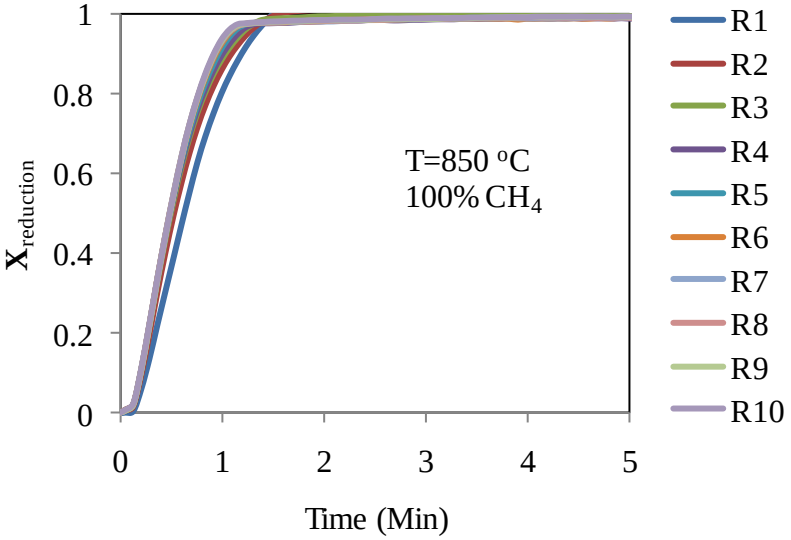
k ~reaction rate constant, whose temperature dependence is generally expressed by the Arrhenius equation ,

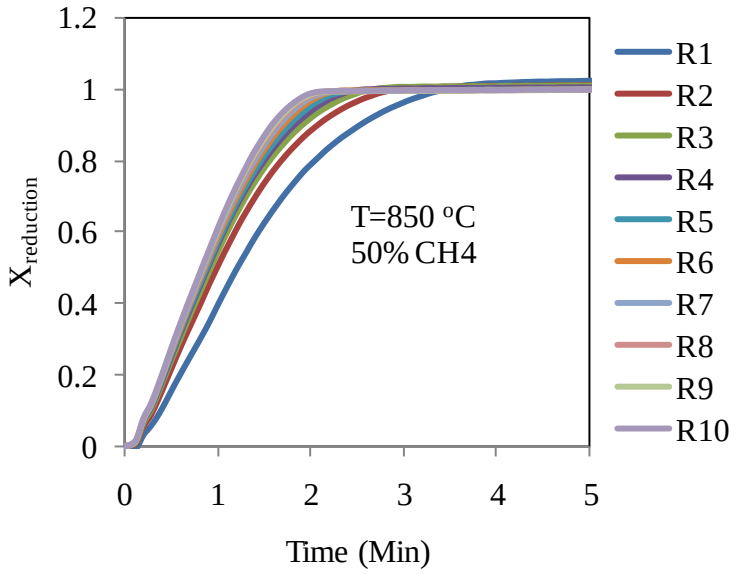
$$k = k_0 e^{-(E/RT)}$$

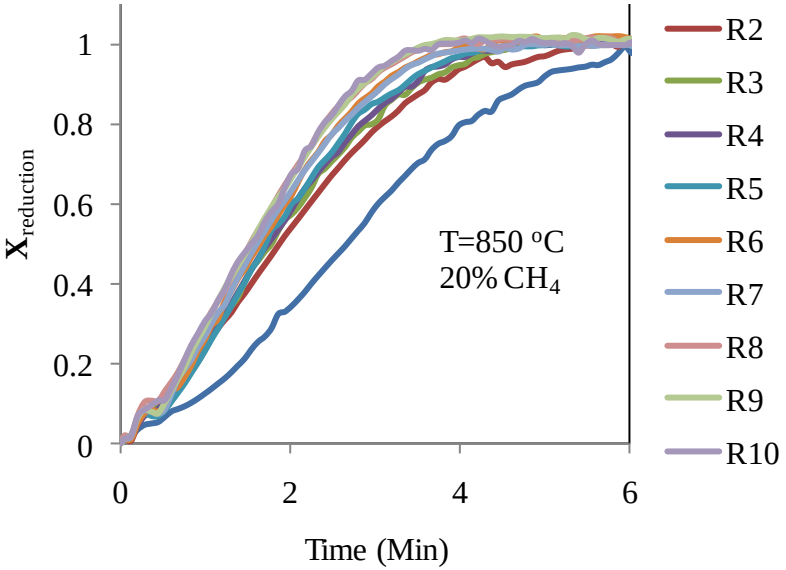


Effect of methane concentration on reduction for T=850 °C

Rate Analysis (Cu-base Oxidation)

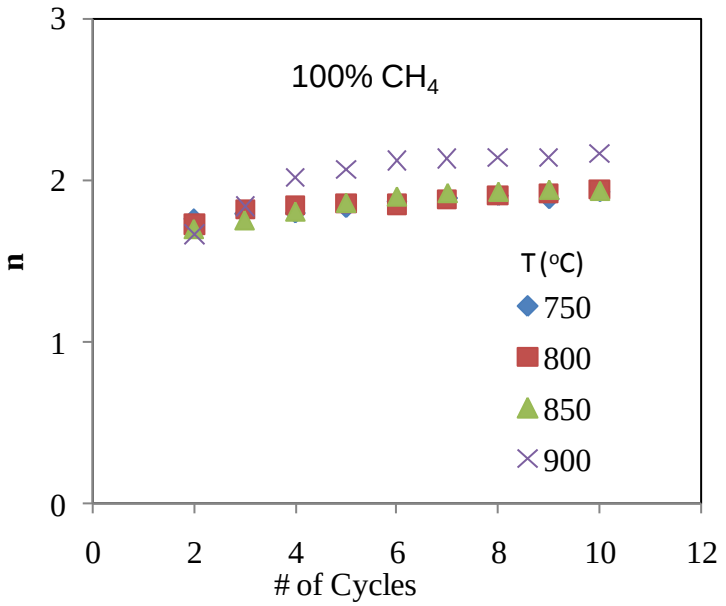


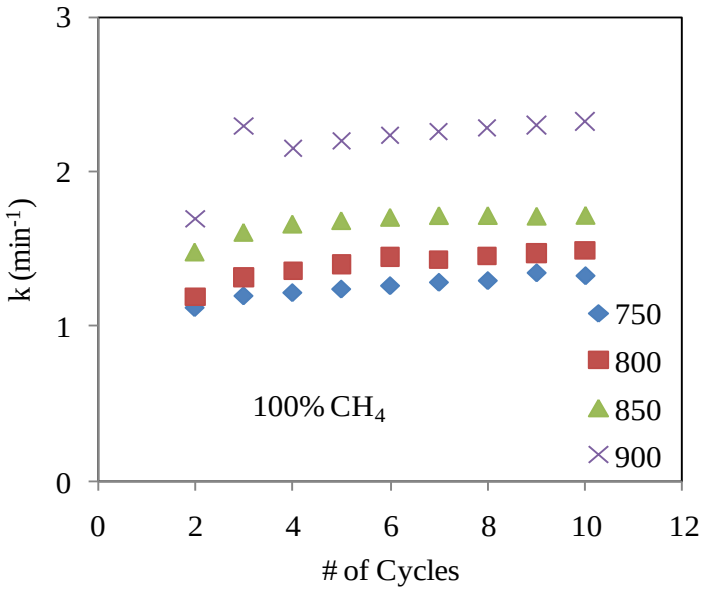




Reduction's conversion increases as cycle increased at given temperature

Effect of Cycles on n and k of JMA rate (CuO/CH4)

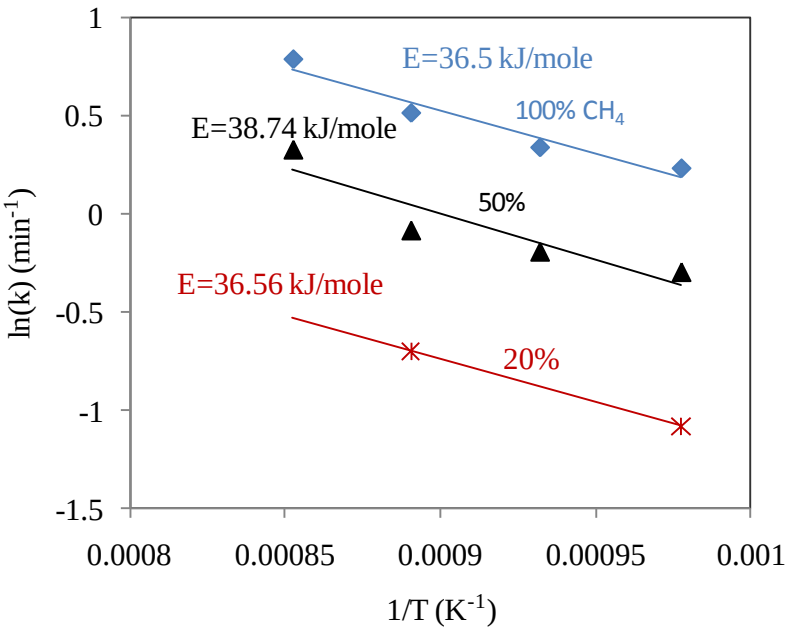


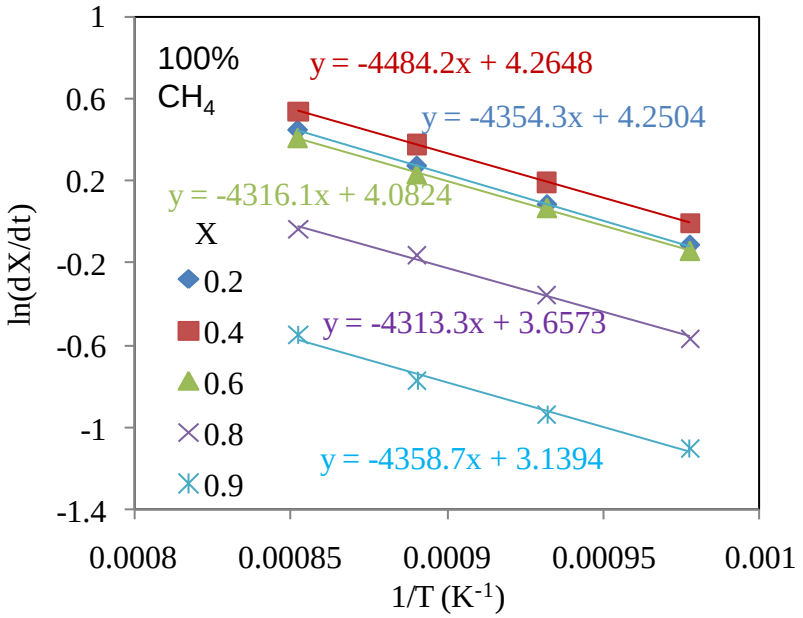


- **Diffusion controlled growth**
  - *All shapes growing from small dimensions*
  - Increasing nucleation rate >2.5
  - Constant nucleation rate 2.5
  - Decreasing nucleation rate 1.5-2.5
  - Zero nucleation rate 1.5

- 100% CH4-There is a slight increase (~10%) in n with increasing cycles @ T= 750, 800, and 850 °C (1.7-1.93) and about 30% increase for T=900 °C (1.6-2.1) average n=1.9.
- 50% CH4, n=1.6-1.74 for all T with average n=1.66)
- Rate constant, k, also increases (~20%) with increasing cycles @ T= 750, 800, and 850 °C and about 37% increase for T=900 °C.

Kinetics Parameters for Reduction of Cu-base Sorbent





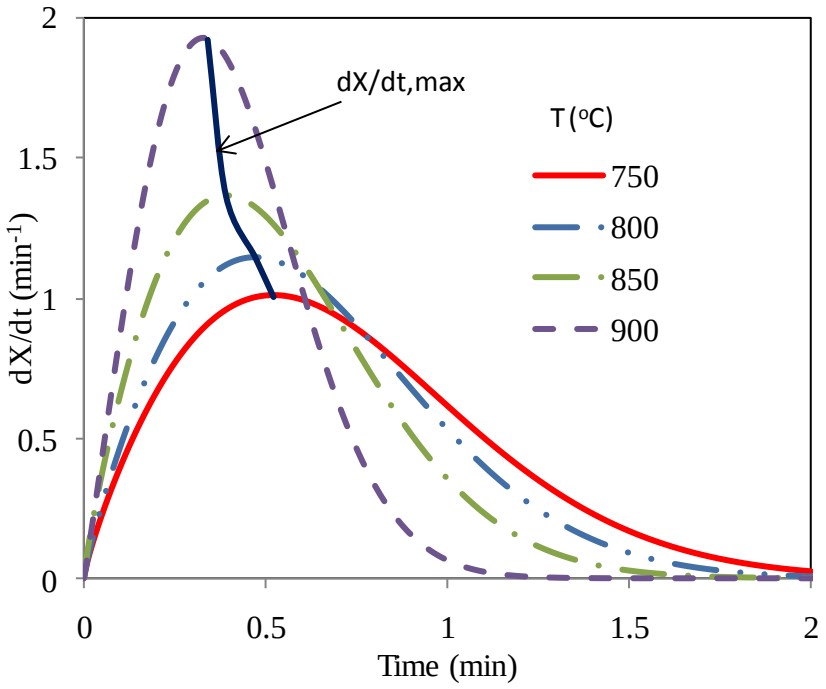
Temperature and CH4 concentration dependence of the rate constant, *k* (1/min.).

Plot of ln(dx/dt) vs 1/T shows that activation energy is uniform as a function of conversion

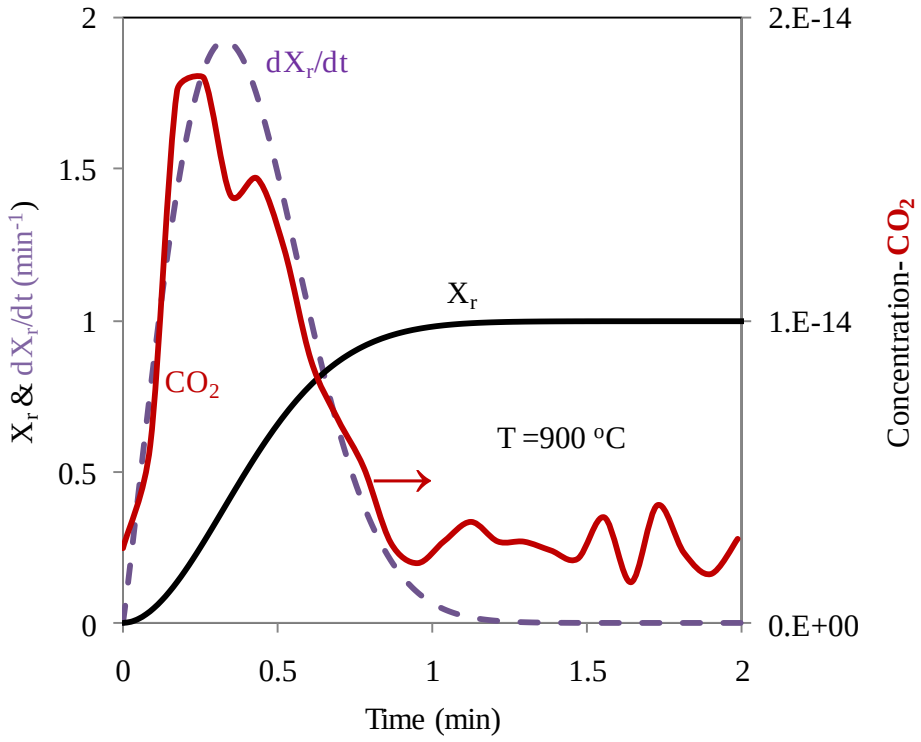
$$k(1/\min) = 91e^{(-4482.34/T)} y_{CH_4}^{0.654}$$

$$\ln\left(\frac{dX}{dt}\right) = \ln k_0 - \frac{E}{R}\frac{1}{T}$$

Rate Analysis (Cont.)



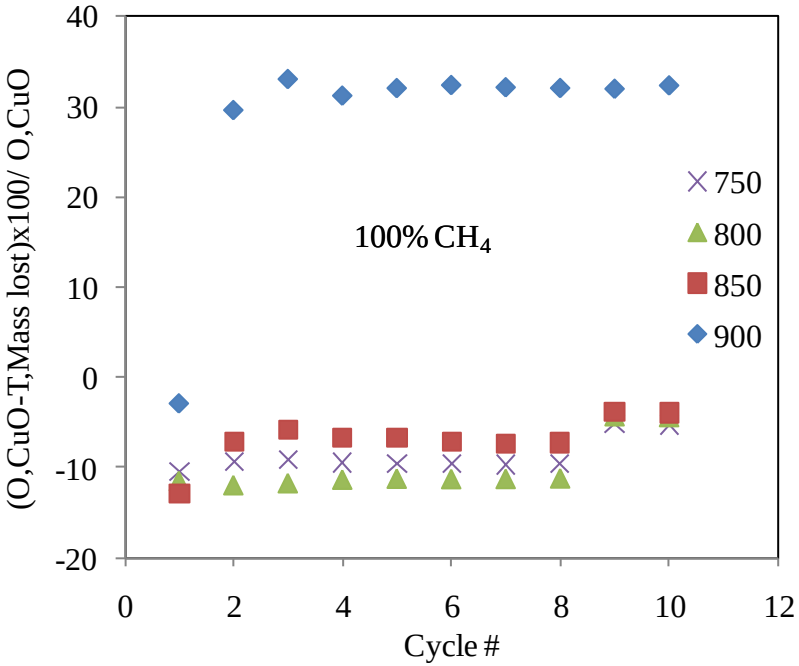
Effect of reaction temperature on the rate reduction of CuO/bentonite particle and CH_4 reaction

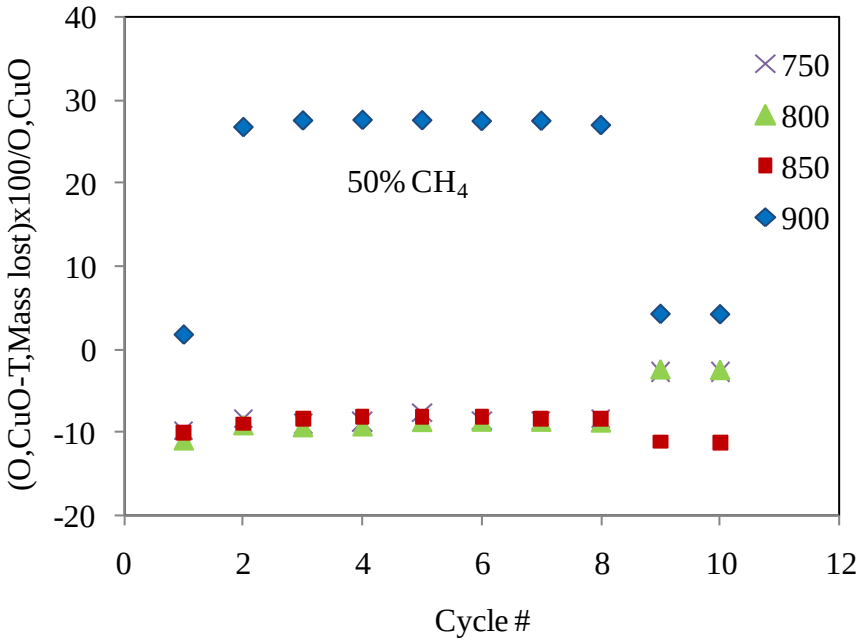


Rate reduction of CuO/bentonite particle and CO2 production

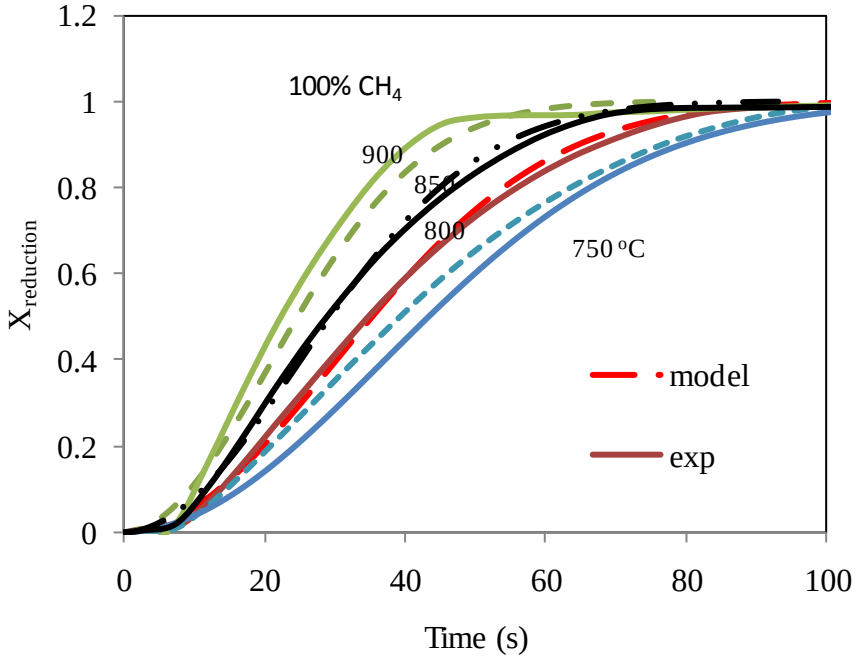
$$\frac{dX}{dt} = kn(1-X)[-\ln(1-X)]^{1-\frac{1}{n}}$$

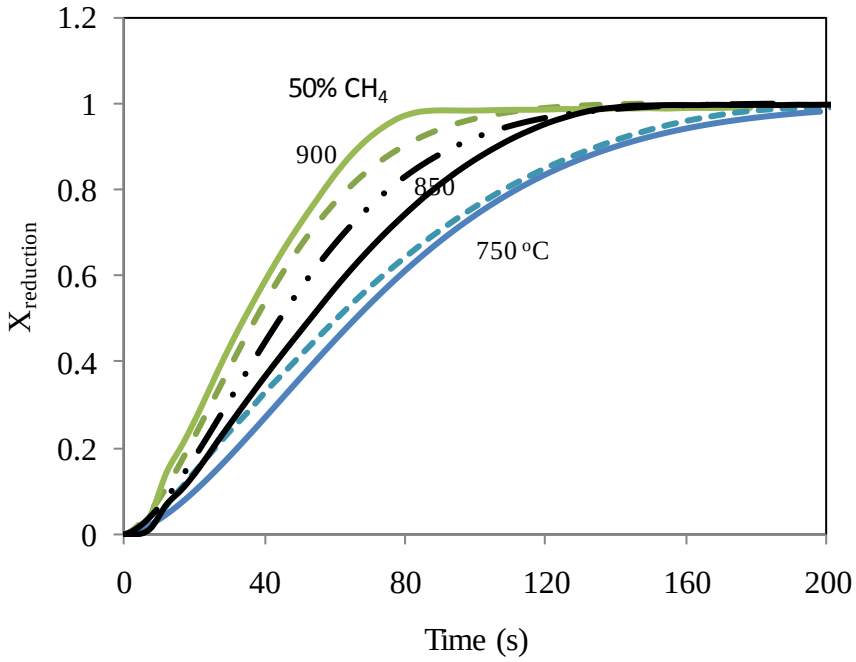
Mass balance during reduction of CuO with methane





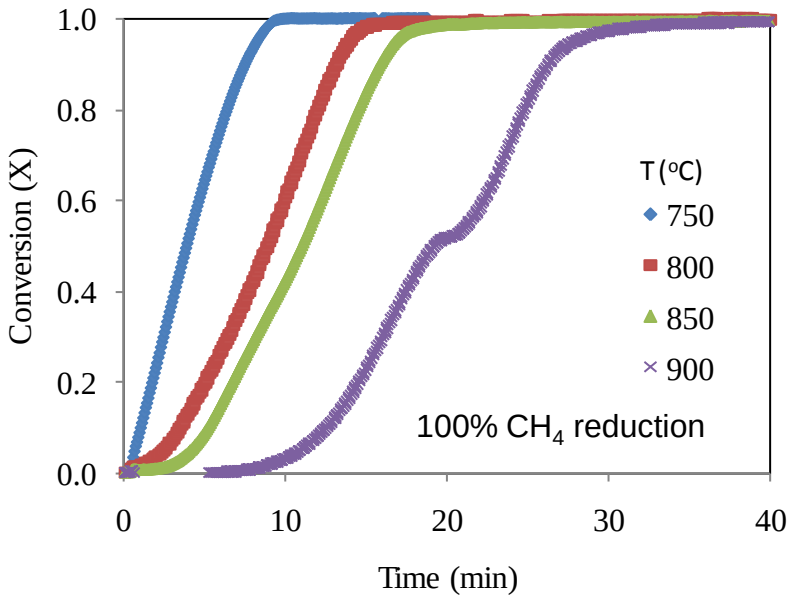
Reduction kinetics test

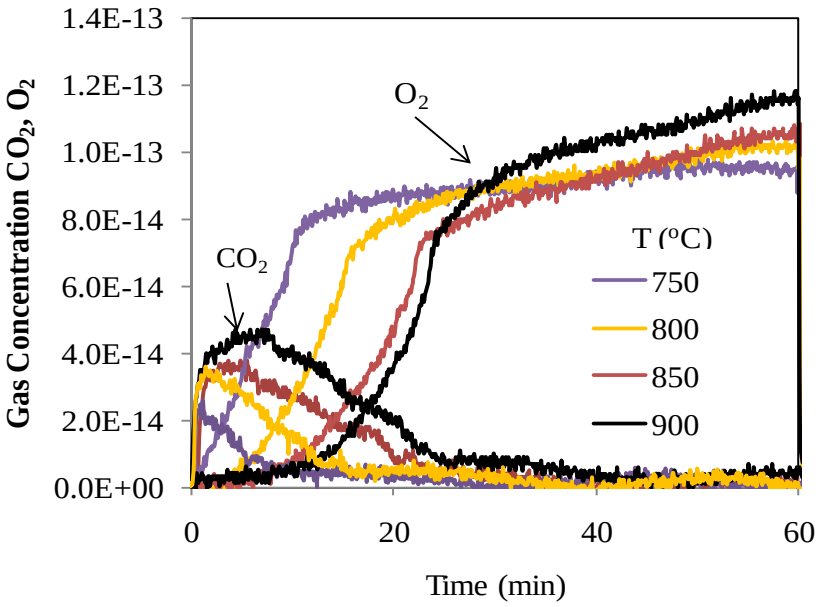




Comparison between kinetic model predictions and experimental data at several temperatures.

Rate Analysis (Cu-base Oxidation)





Effect of reaction temperature on oxidation conversion for Cycle #5

Effect of reaction temperature on CO_2 and O_2 gas concentration

$$X_{Oxd} = \frac{m - m_{rd}}{m_{oxd} - m_{rd}}$$

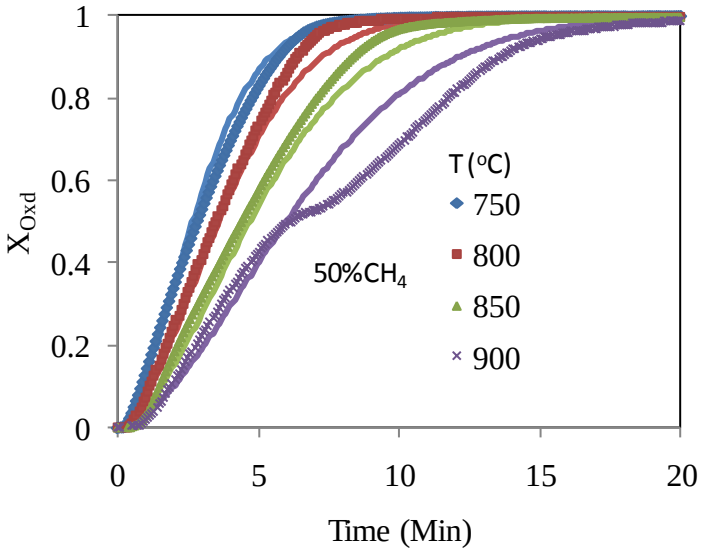
Conversion rate decreases as temperature increases

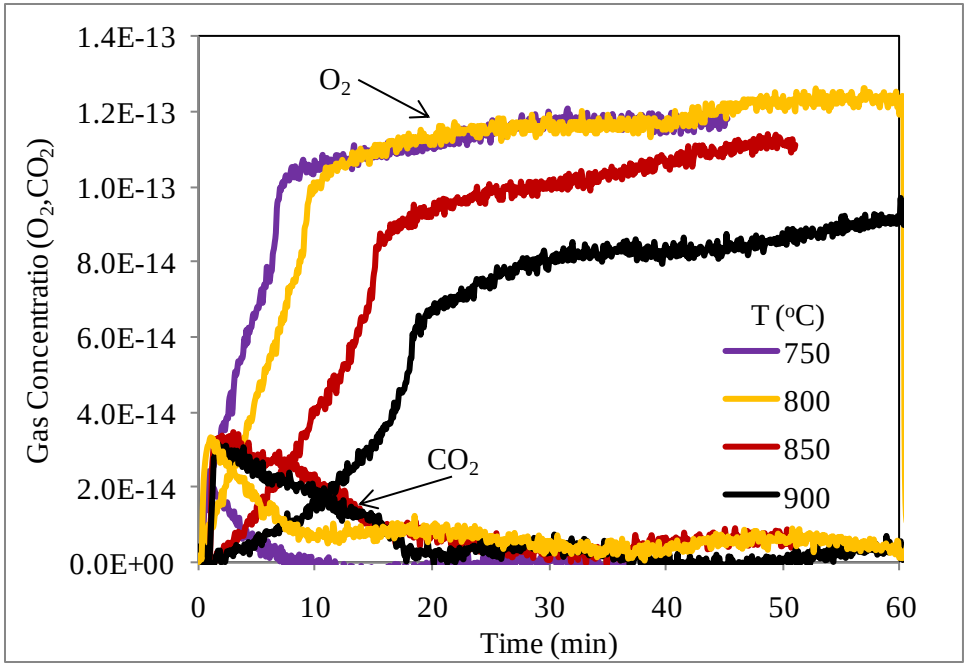
$$2Cu + O_2 \rightarrow 2CuO$$

$$4Cu + O_2 \rightarrow 2Cu_2O$$

$$2Cu_2O + O_2 \rightarrow 4CuO$$

Rate Analysis (Cu-base Oxidation)





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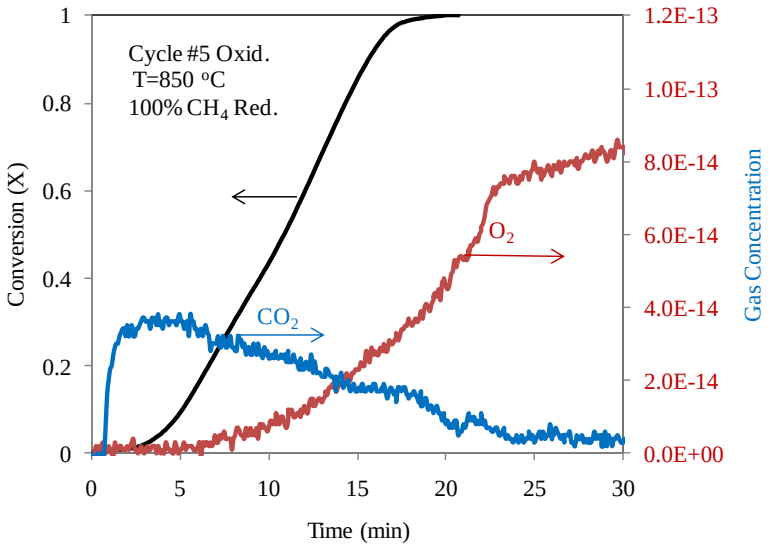
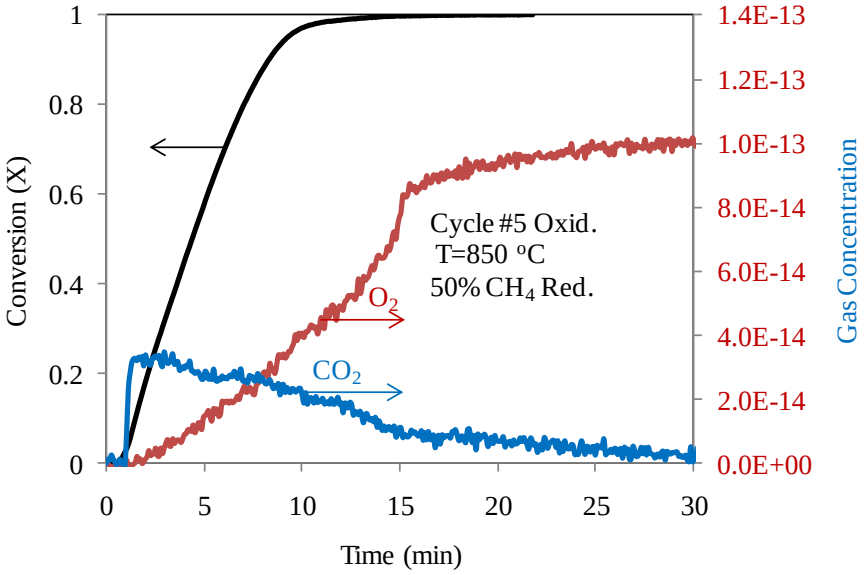
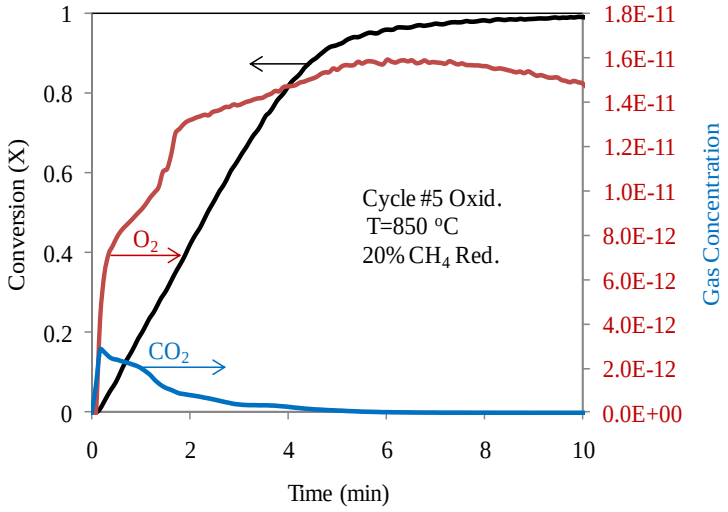
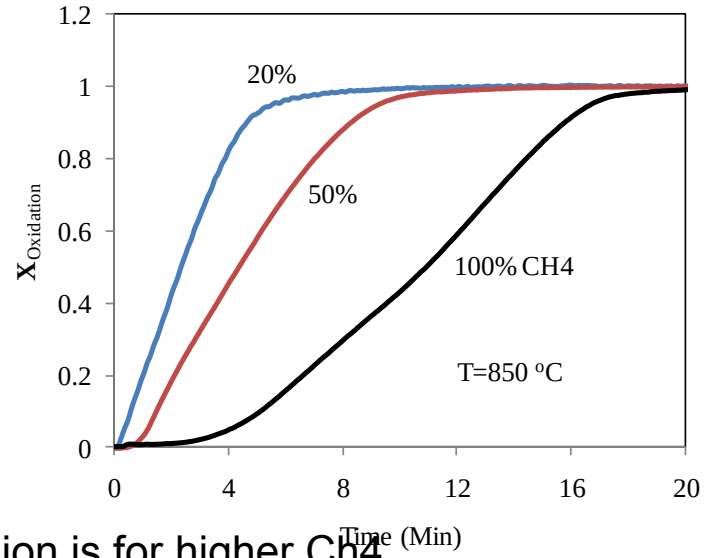
Effect of methane concentration during reduction process on oxidation of Cu



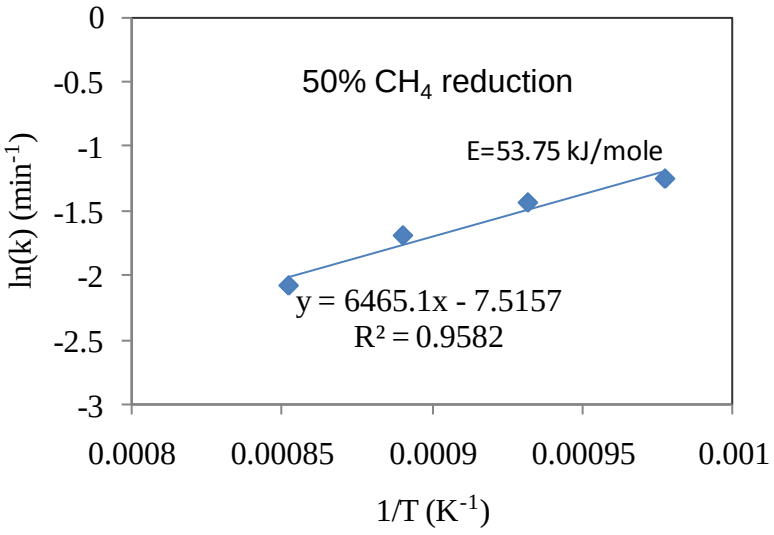


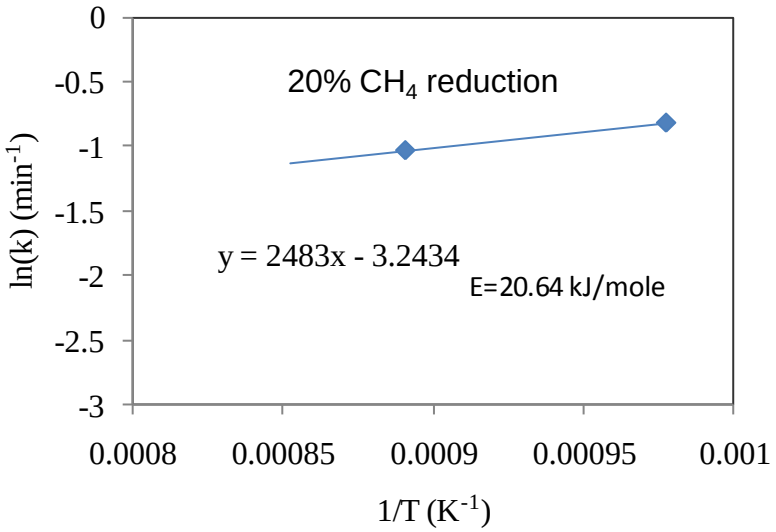




Oxidation's conversion is for higher CH4 concentration during reduction

Rate Analysis (Cu-base Oxidation)





Fuel Reactor Analysis

For reaction aA(g) +bB(s)=cR(g)+dS(s)

$$CH_4 + 4CuO \rightarrow 4Cu + CO_2 + 2H_2O$$

Gas phase mass transport

$$\varepsilon_g \frac{d\dot{m}''_{CH4}}{dy} = -a\dot{R}''$$

Where "a" is contact area between solid and gas per unit volume of bed

$$a = \frac{6(1-\varepsilon)}{d_p}$$

Solid phase mass transport

$$(1-\varepsilon_g)\frac{d\dot{m}''_{CuO,mix}}{dy} = -ab\dot{R}''$$

$$\dot{R}''_A = \frac{1}{A_s}\frac{dm_A}{dt} = \frac{(m_r - m_o)}{A_s}\frac{dX}{dt} = \left(\frac{0.6 * MW_{oxy}}{MW_{CuO}}\right)\frac{\rho_s R_o}{3}\frac{dX}{dt}$$

Summary

Completed kinetics rate CuO/bentonite sorbent{1}

-Rate of reaction increases as temperature increased.

Analyzed kinetics rate Fe-based/bentonite sorbent

Publications

1. Esmail R. Monazam[1,2], Ranjani Siriwardane, Lawrence J. Shadle, George Richard, Hanjing Tian[2] , David E. Huckaby, and Stephen Carpenter[2] ‘‘Kinetics of the chemical looping reduction of CuO/bentonite by methane (CH_4) “ submitted for internal review

Performance and Kinetics of a Solid Amine Sorbent for Carbon Dioxide Removal

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Objective

To characterize a solid supported amine CO_2 sorbent (Amine/Bentonite , and PEI/Silica) developed at the National Energy Technology Laboratory (NETL).

- Investigate the kinetics of the CO_2 uptake from experimental data using thermo-gravimetric analyzer (TGA) and volumetric adsorption apparatus on selected solid supported amine.

Thermo-gravimetric Analysis (TGA)

–Used to record the change in mass of ~60 mg samples of (amine/bentonite) over time

Volumetric Adsorption Apparatus- equilibrium absorption

- Pressure measurements before and after the exposure of the sample chamber to CO_2

Reaction of CO_2 + Amine (R_1R_2NH),

Formation of zwitterion;

$$R_1R_2NH + CO_2 \underset{k_{-1}}{\overset{K_1,k_1}{\rightleftharpoons}} R_1R_2NH^+COO^-(zwitterion) \qquad (1)$$

Proton removal step of the zwitterion by amine;

$$R_1R_2NH^+COO^- + R_1R_2NH \underset{k_{-2}}{\overset{K_2,k_2}{\rightleftharpoons}} R_1R_2NCOO^-(carbamate) + R_1R_2NH_2^+$$

(2)

Combining Eqs (1) and (2) resulted;

$$2R_1R_2NH + CO_2 \underset{\frac{k_1k_2}{k_{-1}k_{-2}}}{\overset{K_3=K_1K_2}{\rightleftharpoons}} R_1R_2NH_2^+ + R_1R_2NCOO^-$$

(3)

(R_1=CH_2CH_2OH=C_2H_4OH) R_2=H for MEA, R_2=R_1 for DEA

Reaction of CO_2 + Amine (R_1R_2NH),

$$r_{CO_2,zwit} = k_1[CO_2][R_1R_2NH] - k_{-1}[Z]$$

$$r_{CO_2} = \frac{R_1R_2NH \quad CO_2 - CO_2 \; _e}{\frac{1}{k_1} + \frac{k_{-1}}{k_1k_2 \; R_1R_2NH}}$$

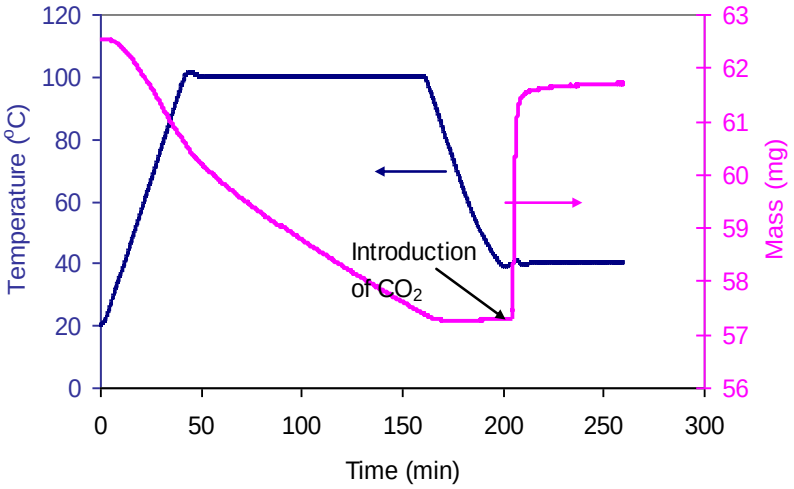
$$k_{app} = \frac{1}{\frac{1}{k_1} + \frac{k_{-1}}{k_1k_2[R_1R_2NH]}}$$

k_{app}=apparent rate coefficient for the reaction between CO_2 and amine (m^3/kmol.s)

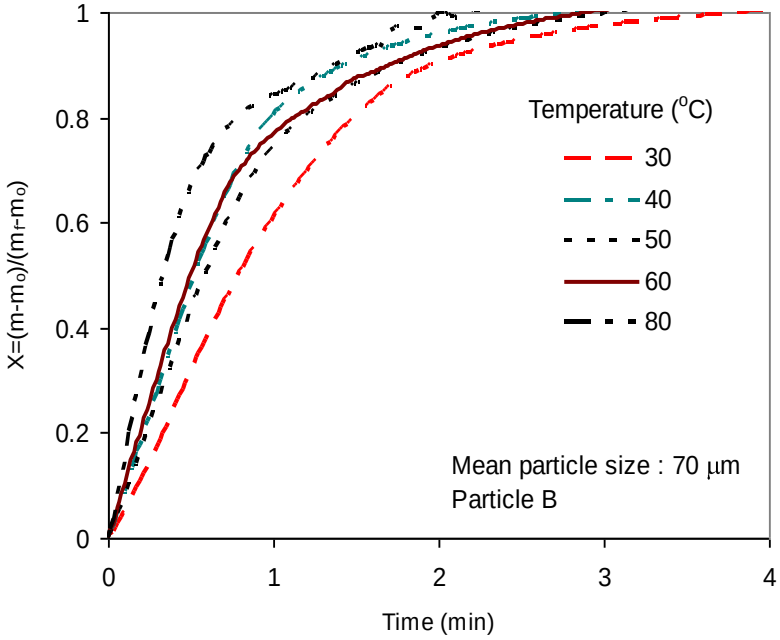
$$r_{CO_2} = k_{app} \; R_1R_2NH \quad CO_2 - CO_2 \; _e$$

Overall reaction rate (kmole/m^3.s)

Experimental data:Amine/bentonite (TGA)



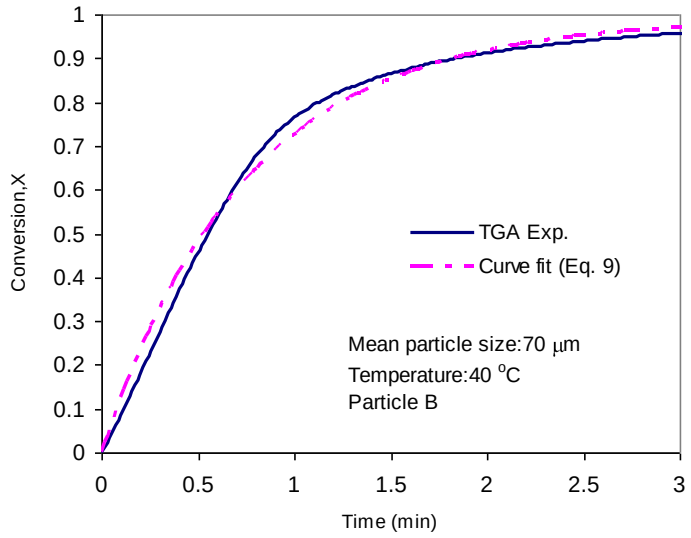
Typical temperature and mass measurements during TGA experiment



Effect of reaction temperature on Amine/bentonite particle and CO_2 reaction

Rate of reaction increases as temperature increases

Curve fitting to experimental data to obtain *k* and *n*

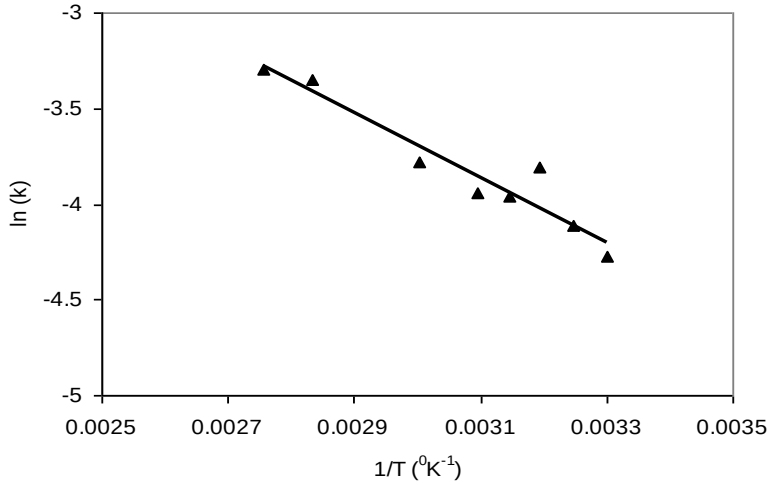


$$X = \frac{(m(t) - m_o)}{(m_f - m_o)}$$

$$\frac{dX}{dt} = k(1 - X)^n$$

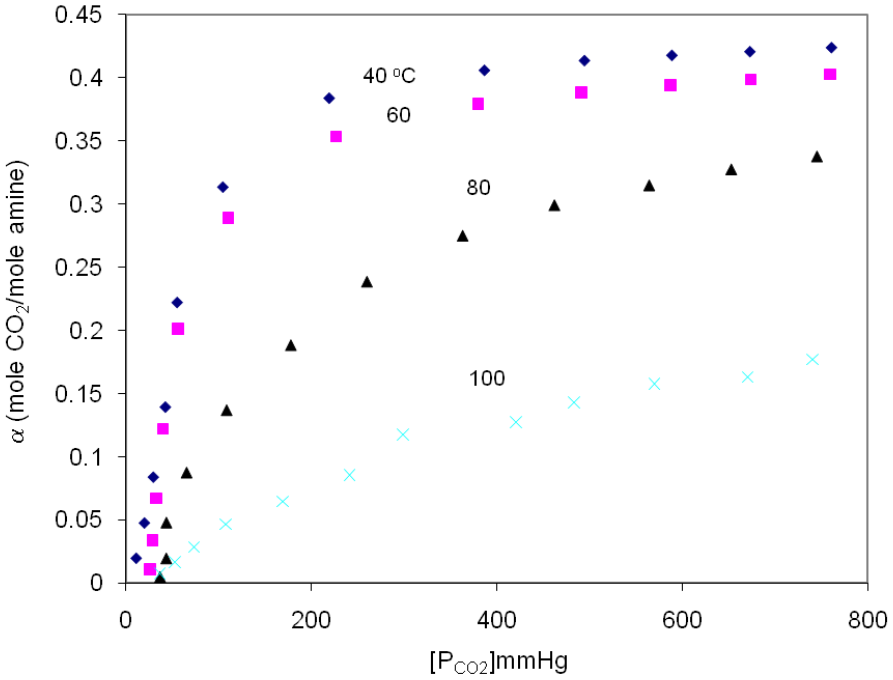
$$X = 1 - \left[1 - kt(1-n)\right]^{\frac{1}{1-n}}$$

$$\ln k = 1.37 - \frac{1687.6}{T}$$

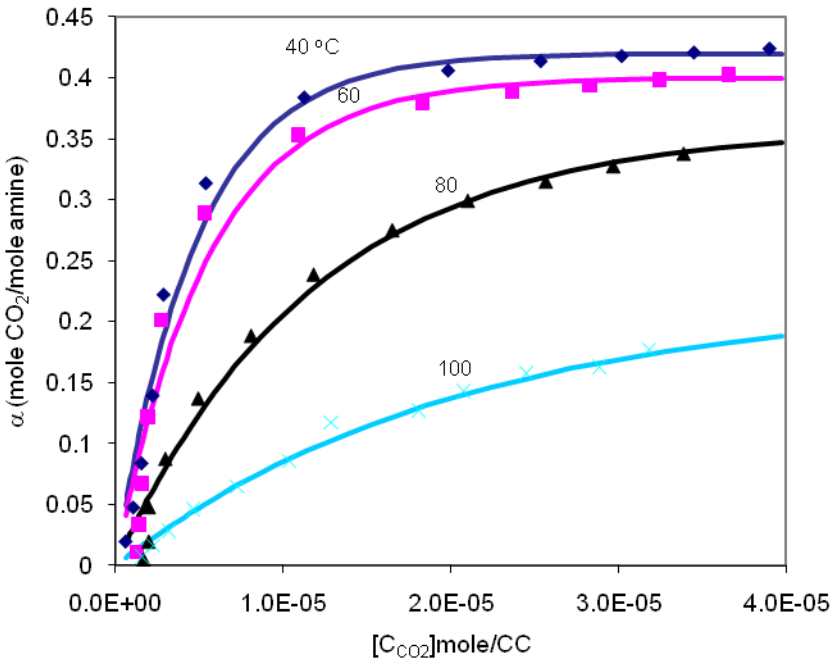


T (K)	k (s^{-1})	n
303	0.014	0.88
308	0.016	0.88
313	0.022	1.01
318	0.019	0.99
323	0.019	1.05
333	0.023	1.17
353	0.035	1.48
363	0.037	1.41

Volumetric Adsorption data- Adsorption Equilibrium



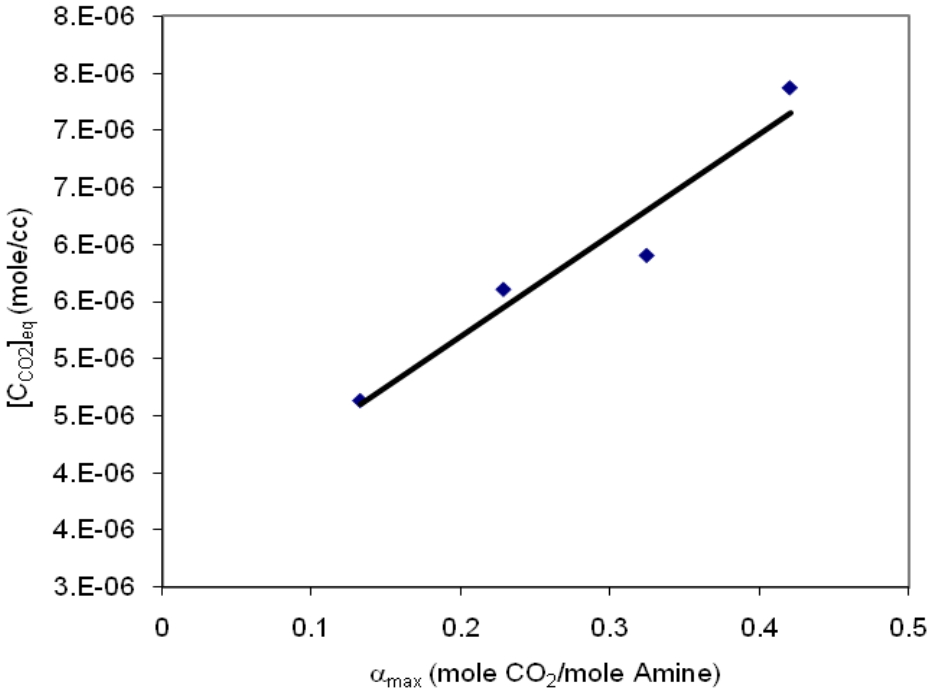
Experimental variation of CO_2 loading with equilibrium partial pressure

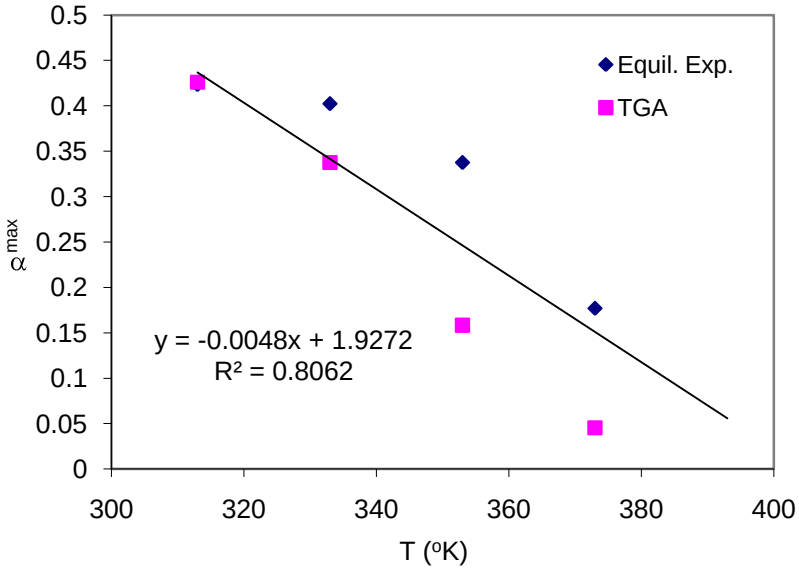


Curve fitting of experimental data to obtain K_{eq}

$$\frac{d\alpha_{CO_2}}{dC_{CO_2}} = -K_{eq}(\alpha_{CO_2} - \alpha_{\max})$$

$$\alpha_{CO_2} = \alpha_{\max}\ 1 - e^{-K_{eq}C_{CO_2}}$$





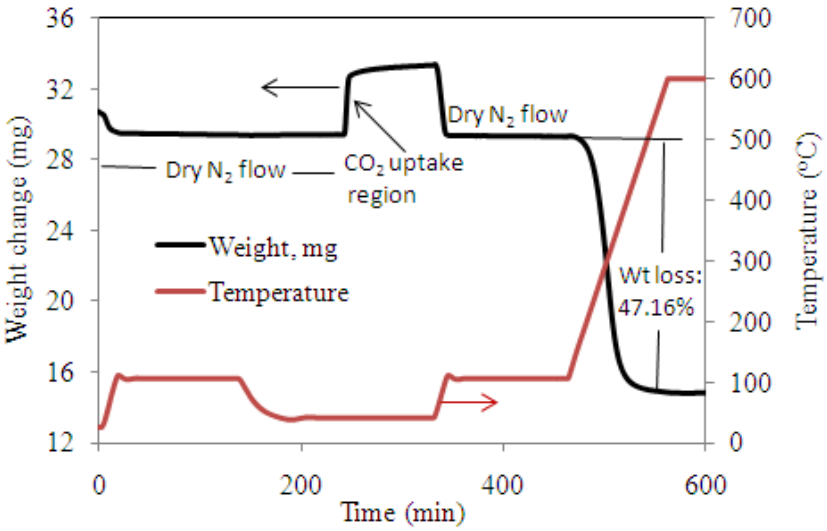
Variations of CO_2 concentration with CO_2 loading

$$CO_{2\ eq} = \frac{1}{K_{eq}}\left(\frac{\alpha_{\max}}{1-2\alpha_{\max}}\right)$$

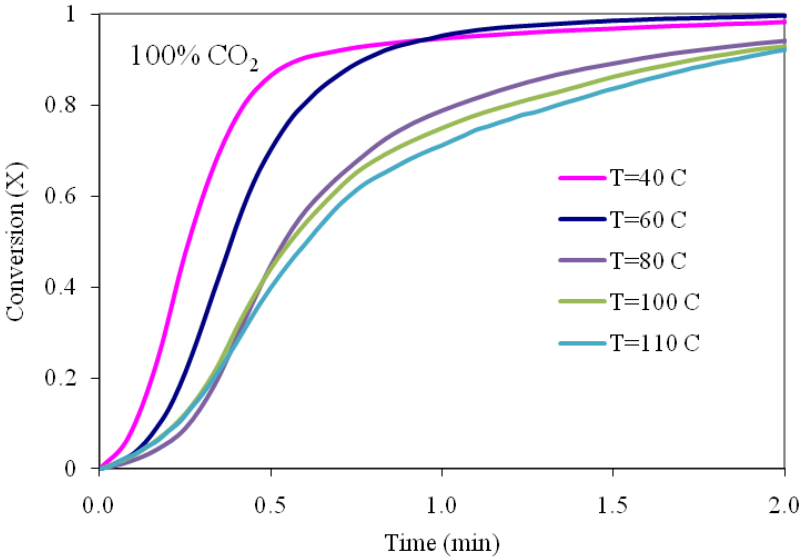
$$\alpha_{\max} = 1.923 - .0048T$$

(Alatiqi et al., 1994)

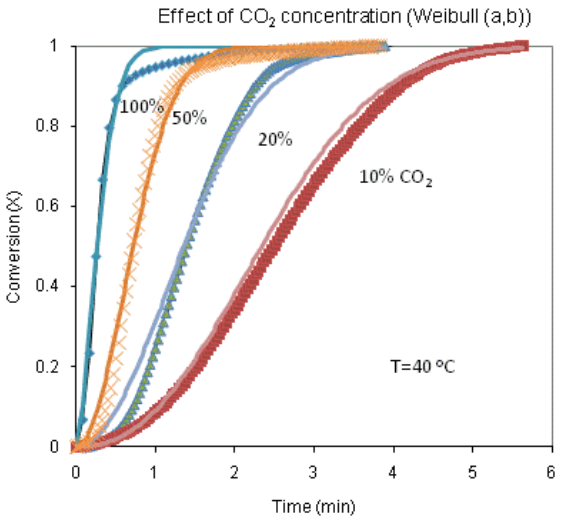
Experimental data:PEI/silica, 196C (TGA)



Typical temperature and mass measurements during TGA experiment (10%CO_2, 40 ºC)



Effect of reaction temperature on PEI/silica particle with CO_2 reaction



Rate of reaction decreases as temperature increased.

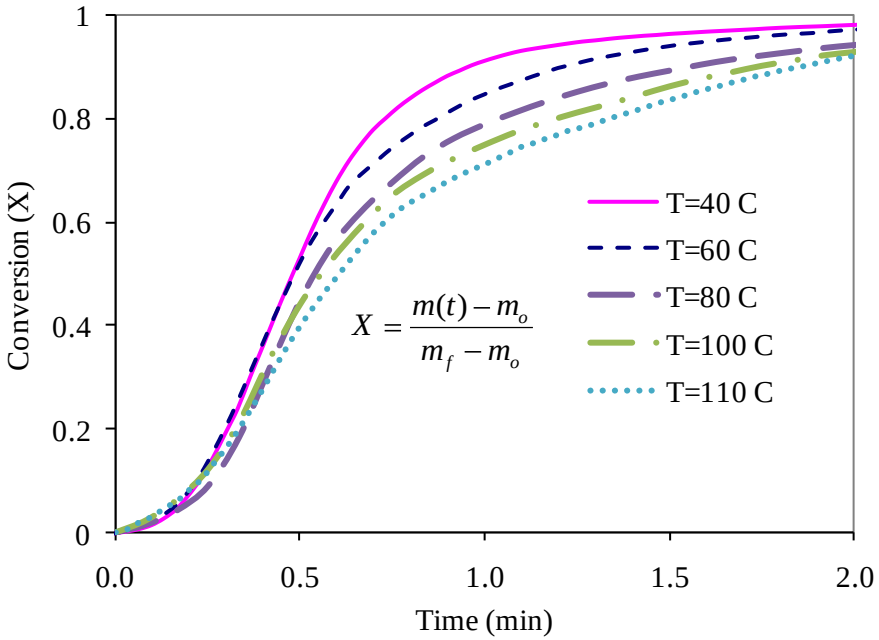
Weibull distribution function

$$X = 1 - e^{-at^b}$$

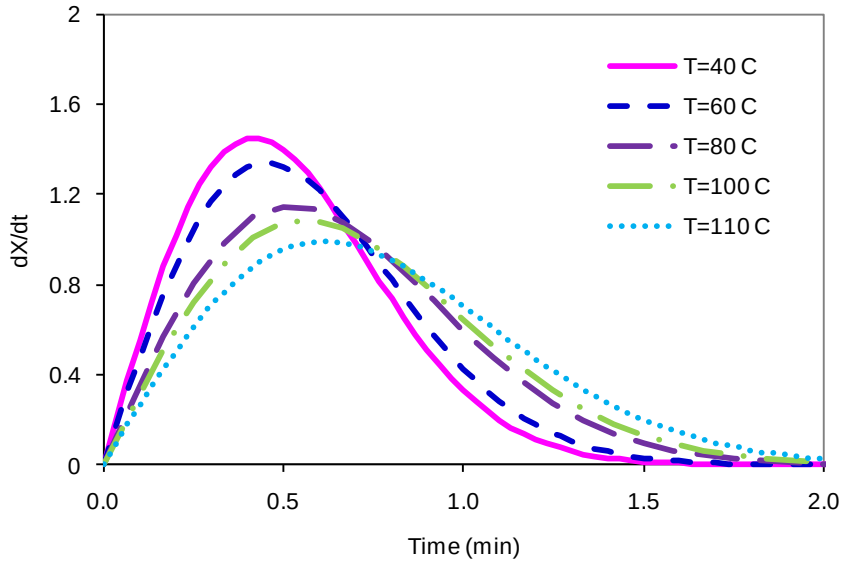
a~scale parameter

b~shape parameter

Rate Analysis



Effect of reaction temperature on immobilized PEI sorbent particle and CO_2 reaction using 100% CO_2



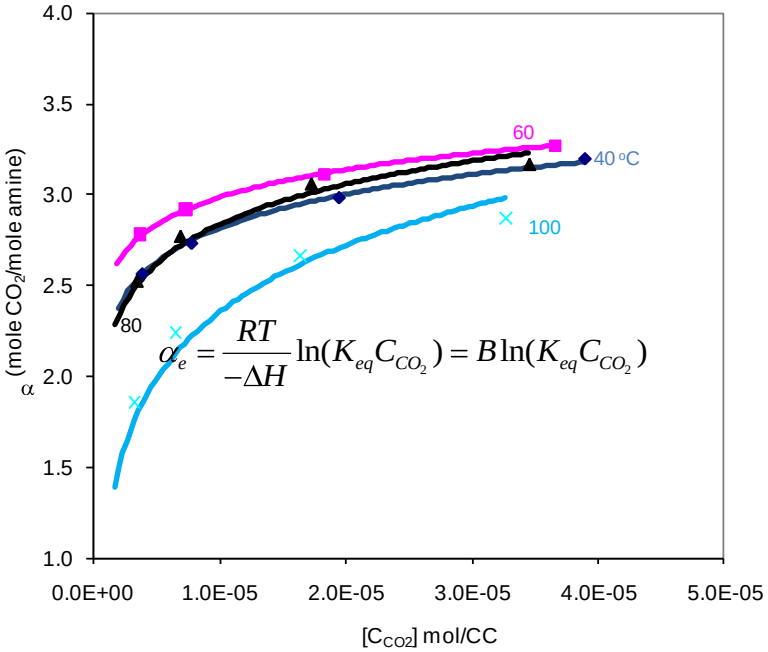
Effect of temperature on reaction rate

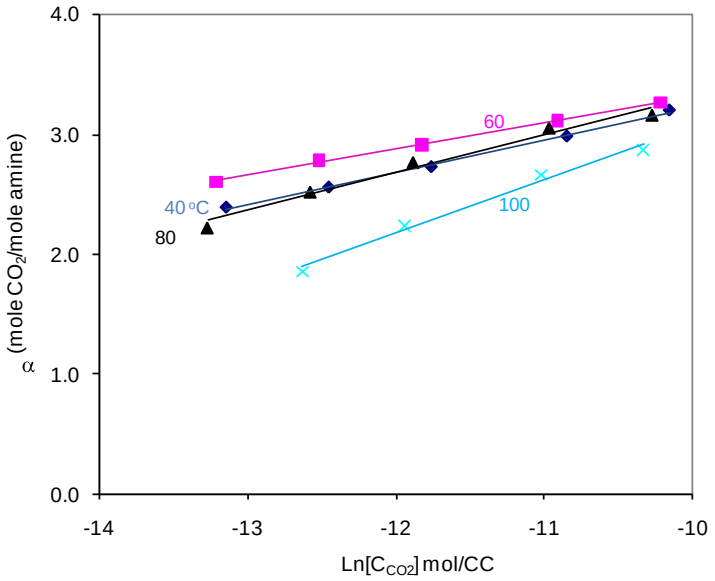
$$\frac{dX}{dt} = 0.42e^{\frac{662}{T}} y_{CO_2}^{0.693}(1-X)\sqrt{-\ln(1-X)}$$

$$X = (1 - e^{-at^b})$$

For b=2

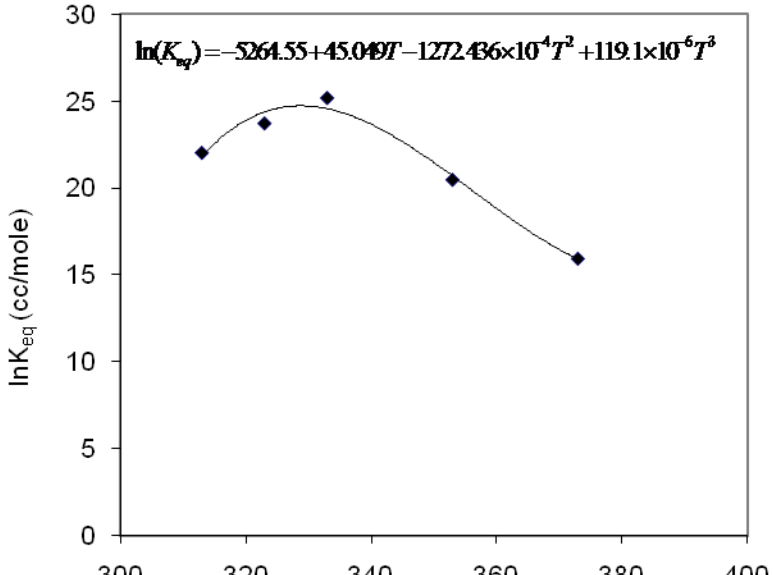
Adsorption Equilibrium-TGA data





$$\alpha_e = B\ln(K_{eq}) + B\ln(C_{CO_2})$$

Temkin's model assumes that the heat of adsorption of all molecules in the layer would decrease linearly with coverage



Summary

Completed kinetics rate Amine/bentonite sorbent (1, 2)

-Rate of reaction increases as temperature increased.

Completed kinetics rate PEI/silica sorbent (3)

-Rate of reaction appear to be faster at lower temperatures (apparent negative activation energy)

Publications

Esmail R. Monazam, Lawrence J. Shadle, and Ranjani Siriwardane "Equilibrium and Absorption Kinetics of Carbon Dioxide by Solid Supported Amine Sorbent "***AIChE J***. **2011**, DOI 10.1002,

Esmail R. Monazam, Lawrence J. Shadle, and Ranjani Siriwardane "Performance and Kinetics of a Solid Amine Sorbent for Carbon Dioxide Removal**"** Accepted for publication **Ind. & Eng. Chem. Res. (July 2011)** ie-2011-01214q

Esmail R. Monazam, Lawrence J. Shadle, Daniel Fauth, James S. Hoffman, McMahan L. Gray, and Henry Pennline "Kinetics Analysis of Carbon Dioxide Capture on Immobilized Amine on Meso-Porous Silica" ***AIChE J***. **2011,** submitted.