Char Oxidation Concepts

1. χ
2. CO/CO_2 ratio
3. nth order
4. α
5. T dependence
6. d_p dependence
7. $CO \rightarrow CO_2$ in boundary layer (2-film model)
8. energy balance / iteration
9. Thiele modulus
10. Ian Smith reactivity correlation
11. TGA rate vs high T rate
12. Catalytic effects at low T
13. Pressure effects
14. Correlations vs. chemistry
15. Late burnout ideas
16. N-release during char oxidation

Reading Questions

1. One of the current industrial reasons for studying char combustion is to identify the causes of decreases in reactivity at late stages of burnout. In other words, a coal combustor may have excessive carbon in the fly ash, and therefore has to pay disposal costs. Please discuss possible causes for this decrease in reactivity in late stages of burnout given by Hurt, and how his model works.
2. Discuss the experimental and data reduction method to determine both the apparent reaction rate (at high temperature) and the CO/CO_2 product ratio?
3. The high pressure data shown in the book (Figs. 123-124, Table 77) were explained by changing the activation energy at each pressure. Usually, activation energies are thought to be independent of pressure. Please explain what could be wrong with the experiments or the data reduction method.
4. Please explain the approach of Hong, and explain his results.
5. Ca is thought to be a catalyst in char combustion. Why does it only cause significant effects at relatively low temperatures and for low rank coals?

RQ12.1

Possible causes for decreases in reactivity late in burnout

- Distribution of reactivities
  - Most reactive stuff burns out early
- Annealing
  - Chemical structure change at long t_{res} and high T_p
- Channeling
  - Large particles get through
- Ash encapsulation
  - Carbon sealed off from O_2

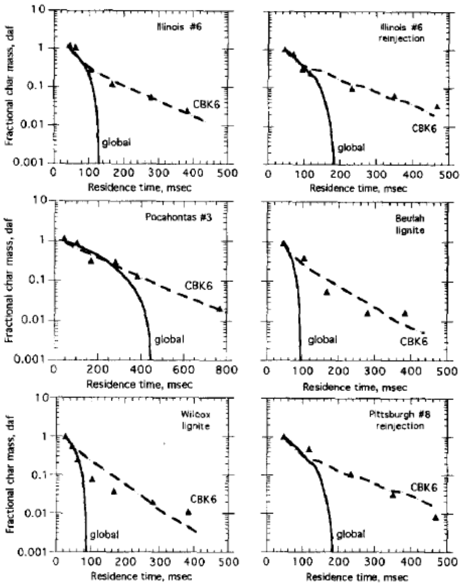


Fig. 1. Comparison of measured conversion profiles from one-dimensional laboratory reactors (points) with predictions of the simple, global model of Hurt and Mitchell, [12] (solid curves) and the CBK model (dashed curves).

Hurt et al.
Comb & Flame
(1998)

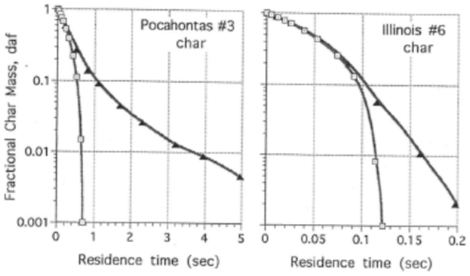


FIG. 5. Calculations showing the effect of distributed reactivity during combustion of size-classified coal particles. Initial particle diameters are 100 μm and oxygen concentration is constant at 7 mole-%. For Illinois #6 coal char, T_g = 1650 K and A_{mean} = 14.4 g-carbon/s-cm^2-atm$^{0.5}$. For the Pocahontas #3 coal char, T_g = 1450 K and A_{mean} = 8.0 g-carbon/s-cm^2-atm$^{0.5}$.

From Hurt, 26th Symposium, p. 3174

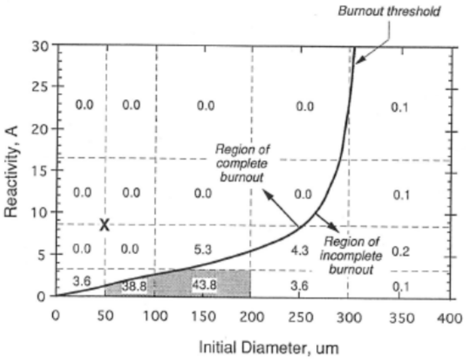


FIG. 6. The origin of unburned carbon in simulation Ib. The solid line divides the size-reactivity space into regions of complete and incomplete burnout. The cross, X, marks the position of the mean size and reactivity in the parent fuel. Sector entries are the percentages of the total unburned carbon that originate from the given size and reactivity bin in the parent fuel (sectors add to 100% of the total unburned carbon). The shaded region at low reactivity represents approximately 80% of the total unburned carbon.

Annealing

- During heating & pyrolysis
  - Heating rate
  - Residence time
  - Peak temperature
- During char oxidation
  - Loss of heteroatoms
  - Carbon structure reordering
  - Ash fusion

RQ2:

CO/CO$_2$ Ratio Approach

1. Assume CO/CO$_2$ ratio (or ψ)
2. Using heat balance, get r_p/A (or q)

$$m\,C_p\,d\overset{\text{measured}}{T}_p/dt = q_{conv} + q_{rad} + \overset{\text{unknown}}{r_p}\;\overset{\text{specified by }\psi\text{ (unknown)}}{\Delta H_{rxn}}$$

3. Using continuity, calculate m_p from r_p

$$-dm/dt = r_p$$

4. Compare m/m_0 vs t calculations with measured values of m/m_0
5. Must know:
   - Mass release (m/m_0)
   - Residence time
   - T_g
   - y_{O2}
   - T_p

RQ3:

Monson data (effect of pressure on char oxidation)

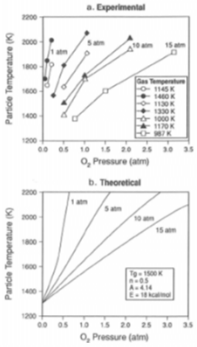


Figure 123. Measured and calculated effects of pressure on particle temperature during char oxidation as a function of the partial pressure of oxygen (a) measured by laser optical *in situ* method and (b) predicted based on the global reduction method of Hurt and Mitchell (1992) (Monson *et al.*, 1992).

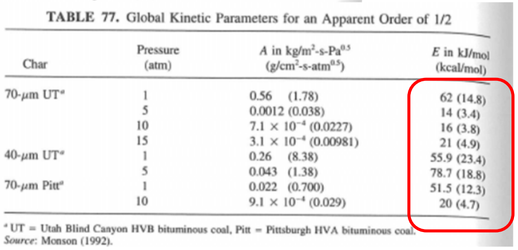


TABLE 77. Global Kinetic Parameters for an Apparent Order of 1/2

Char	Pressure (atm)	A in kg/m^2-s-Pa$^{0.5}$ (g/cm^2-s-atm$^{0.5}$)	E in kJ/mol (kcal/mol)
70-μm UT[a]	1	0.56 (1.78)	62 (14.8)
	5	0.0012 (0.038)	14 (3.4)
	10	7.1×10^{-4} (0.0227)	16 (3.8)
	15	3.1×10^{-4} (0.00981)	21 (4.9)
40-μm UT[a]	1	0.26 (8.38)	55.9 (23.4)
	5	0.043 (1.38)	78.7 (18.8)
70-μm Pitt[a]	1	0.022 (0.700)	51.5 (12.3)
	10	9.1×10^{-4} (0.029)	20 (4.7)

[a] UT = Utah Blind Canyon HVB bituminous coal, Pitt = Pittsburgh HVA bituminous coal.
Source: Monson (1992).

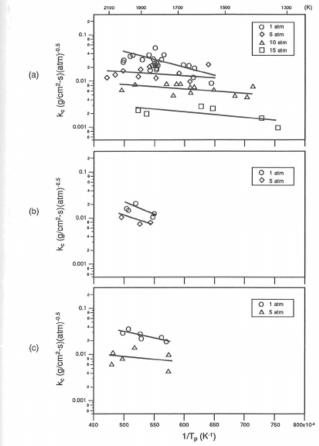


Figure 124. Reaction rate constants as a function of particle temperature and total pressure for the (a) 70-μm-diameter Utah bituminous coal char, (b) the 40-μm-diameter Utah bituminous coal char, and (c) the 70-μm-diameter Pittsburgh bituminous coal char (Monson *et al.*, 1992).

Different E for each condition?

Problems with Monson data

- Tried to measure T_p
- Most particles lower than temperature measurement threshold
- Only outlier T_p's measured
- Led to χ factors greater than 1!
- Activation energies are VERY low (4 kcal/mol)

RQ4:

Hong approach

I have too much stuff here

(Stop me when you are saturated)

Effectiveness Factor for the Langmuir Rate Equation

- Intrinsic Langmuir rate equation

$$r_{in}''' = \frac{k_1 C}{1 + KC}$$

apparent reaction order between 1 and 0

- Observed rate equation

$$r_{obs}''' = \eta \frac{k_1 C_s}{1 + KC_s}$$

- How can we calculate η?

General Asymptotic Solution of Effectiveness Factor (η)

- Thiele (1939); For spherical particles, first order reactions:

$$\eta = \frac{1}{M_T}\left(\frac{1}{\tanh(3M_T)} - \frac{1}{3M_T}\right) \qquad M_T = L\sqrt{\frac{\nu_0 k_1}{D_e}}$$

- Bischoff (1965); For all rate forms:

$$\eta = \frac{1}{M_T}\left(\frac{1}{\tanh(3M_T)} - \frac{1}{3M_T}\right)$$

$$M_T = \frac{L\nu_0 r_{in}'''(C_s)}{\sqrt{2}}\left[\int_0^{C_s} D_e(C)\nu_0 r_{in}'''(C)\,dC\right]^{0.5}$$

Method to get M_T for n ≠ 1

Generalized Thiele Moduli

- Standard:

$$M_T = L\sqrt{\frac{\nu_O k_1}{2D_e}\frac{KC_s}{1+KC_s}}[KC_s - \ln(1+KC_s)]^{-\frac{1}{2}}$$

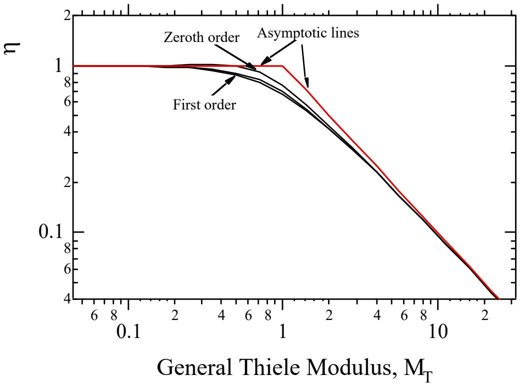
- Simpler:

$$M_T = L\sqrt{\frac{\nu_O k_1 / D_e}{2KC_s + \frac{1}{1+KC_s}}}$$

- The simpler modulus approximates the standard modulus with 0 ~ 5% error
- The simpler form is more robust in the limits. For example, when $KC_s = 0$, the standard modulus results in zero divided by zero.

Error in the Transition Zone

- Zone I: $\eta = 1$ (when $M_T < 0.2$)
- Zone II: $\eta = 1/M_T$ (when $M_T > 5$)



Error in the Transition Zone

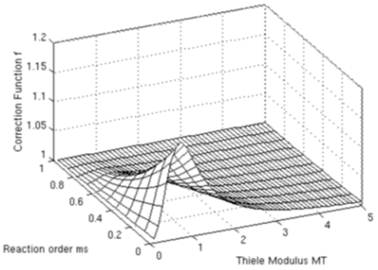
$1/(1+KC_s)$ M_T	1.00	0.75	0.50	0.25	0.00
0.125	0.019	-0.162	-0.342	-0.583	-0.925
0.25	0.016	-0.588	-1.282	-2.188	-3.560
0.5	-0.013	-1.639	-3.672	-6.557	-12.375
0.707	-0.076	-2.162	-4.802	-8.618	-16.081
1	-0.215	-2.274	-4.756	-8.000	-12.392
2	-0.491	-1.584	-2.813	-4.277	-6.018
4	-0.679	-1.191	-1.774	-2.472	-3.156
8	-0.933	-1.186	-1.473	-1.821	-2.274

Correction Function

- A correction function was developed for η:

$$\eta = f\frac{1}{M_T}\left(\frac{1}{\tanh(3M_T)} - \frac{1}{3M_T}\right)$$

$$f = \left(1 + \frac{\sqrt{1/2}}{\frac{1}{2M_T^2} + 2M_T^2}\right)^{\frac{1}{2}\left(1-\frac{1}{1+KC_s}\right)^2}$$



- Reduces error in transition zone from 17% to 2%.

Reaction Order in Zone I & II

- Zone 1:

$$m_{obs} = \frac{d\ln\left(\frac{k_1C_s}{1+KC_s}\right)}{d\ln(C_s)} = \frac{1}{1+KC_s}$$

- Zone II:

$$n_{obs} = \frac{d\ln\left(\eta\frac{k_1C_s}{1+KC_s}\right)}{d\ln(C_s)} = \frac{d\ln\left(\frac{1}{M_T}\frac{k_1C_s}{1+KC_s}\right)}{d\ln(C_s)}$$

$$= \frac{1}{2}\frac{KC_s}{[KC_s - \ln(1+KC_s)]}\frac{1}{1+KC_s}$$

What was the point of the Hong approach?

- Method to use the Thiele modulus for more complex model forms than 1st order

HP-CBK vs. CBK

- CBK **(Hurt)**
  - Global
  - n-th order rate
  - Atmospheric
  - Small particles

- HP-CBK **(Hong)**
  - Intrinsic
  - Langmuir rate equation
  - Arbitrary pressure
  - Arbitrary size

New Components in HP-CBK

- Pore structure model (Wakao and Smith, 1964)
- Effective diffusivity
  - Knudsen diffusion
  - Molecular diffusion
- General asymptotic solution of the effectiveness factor with correction
- General correlations for Sherwood and Nusselt numbers.

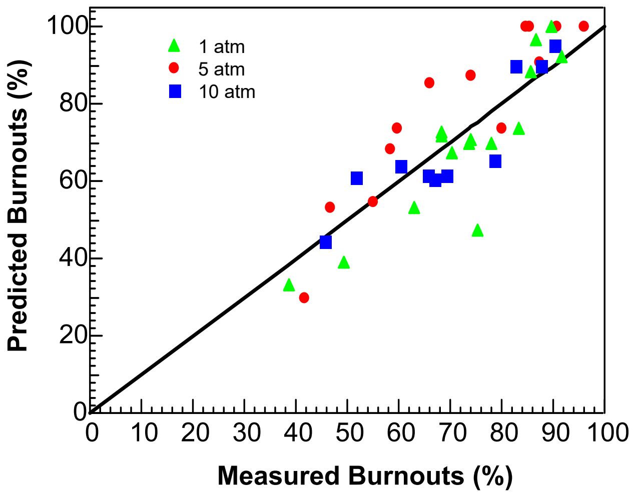
Model Evaluation

- Comparison with 5 cases (**3 shown here**)
  - graphite oxidation (Ranish and Walker)
  - large particle data (Mathias)
  - small particle data (Monson)
  - rough sphere combustion (Banin et al.)
  - FFB and TGA data (BYU, 1999)

Example: Comparison with Monson Data

- C. R. Monson, Ph.D., ME dept. BYU, 1992
- Conditions
  - total pressure: 1, 5, 10, 15 atm
  - oxygen mole fraction: 5 - 21%
  - gas temperature: 1000 - 1500 K
- Utah coal char
- Diameter: 67 μm

Hong Predictions of Monson Data



Adjustable Parameters

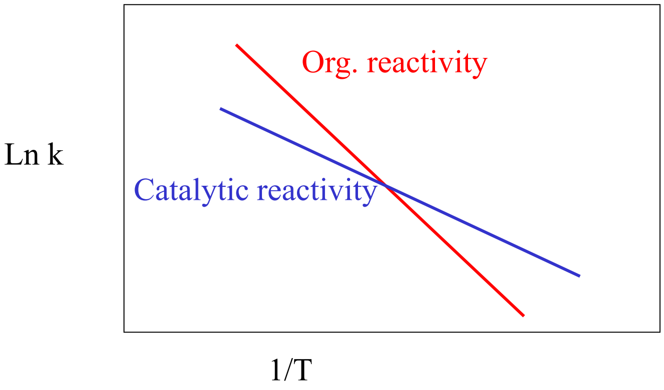
- Maximum number of parameters in HP-CBK Model:
  A_1, E_1, A, E , ε_M, r_{p1}, r_{p2} (7)

	# of constants used
• Graphite flake: A_1, E_1, A, E	4
• Large particle: A_0, E_0, ε_M	3
• Small particle: A_0, E_0, r_{p1}	3

⇒ The Mathias and Monson data were correlated with a zero-order Langmuir rate equation!

RQ#5
Catalytic Effects

- Ca is a known catalyst
  - Organically associated
  - Changes activation energy

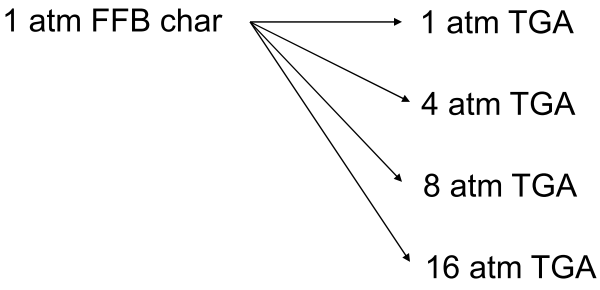


Effect of Pressure on Char Reactivity to O_2

High Pressure TGA

- DMT high pressure TGA
  - – Capable of pressures to 100 bar
  - – Sample sizes of 2 mg of char used
  - – Base temperature conditions were coal-dependent
    - ~375°C for lignite
    - ~475°C for bituminous coal
  - – He/O_2 used to prevent mass transfer effects
  - – Flow rates adjusted to eliminate mass transfer effects

Hecker Strategy



1 atm FFB char

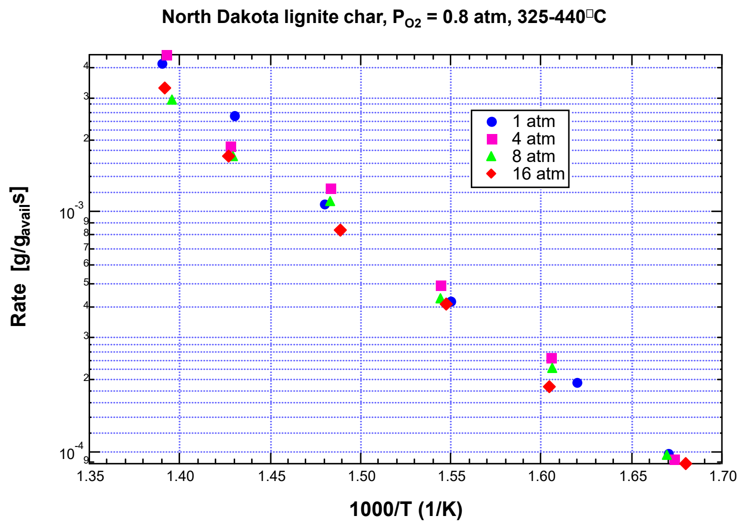
1 atm TGA

4 atm TGA

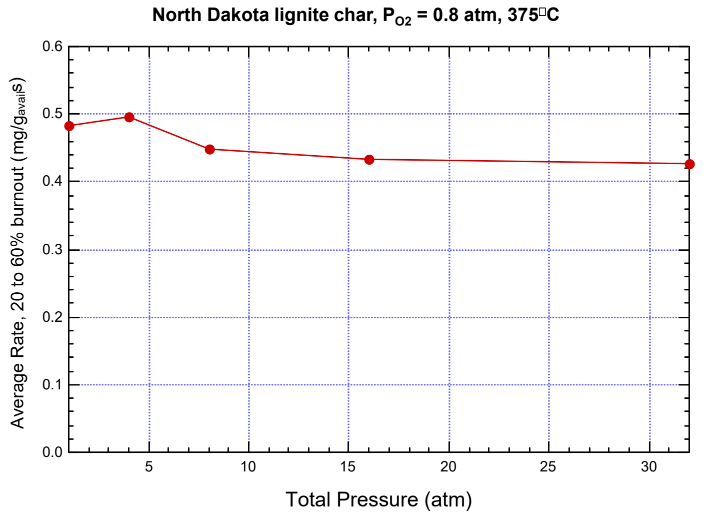
8 atm TGA

16 atm TGA

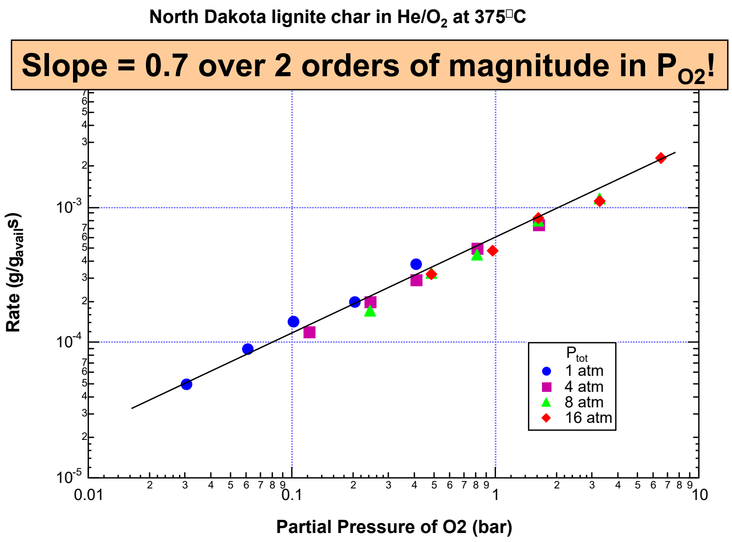
Activation Energy



Effect of Total Pressure on Rate

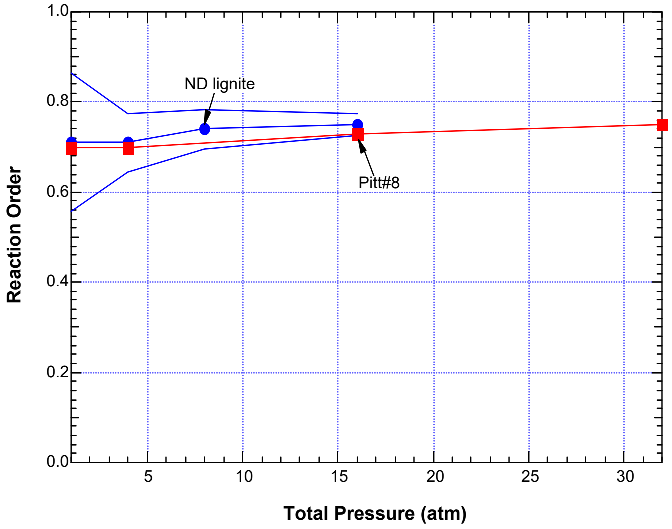


Reaction Order Determination


North Dakota lignite char in He/O$_2$ at 375°C

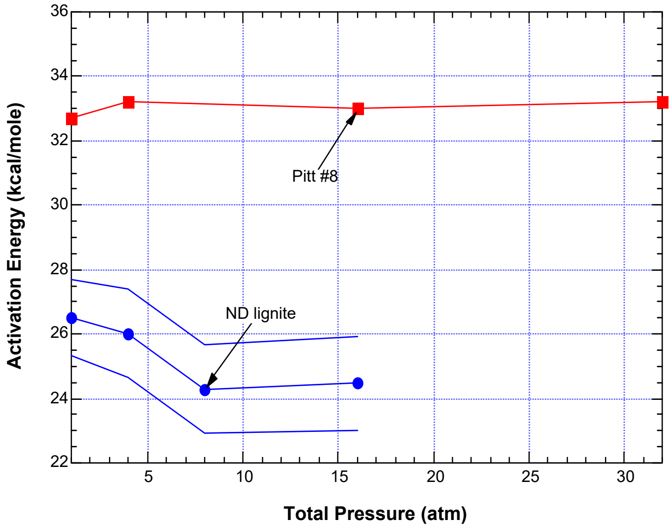
Slope = 0.7 over 2 orders of magnitude in P_{O2}!

Summary of Reaction Order Data



- TGA data indicate little (if any) change in order with P_{tot}

Summary of Activation Energy Data



- Changes in E_a with P_{tot} are small, based on TGA data

Hecker Conclusion

- Activation energy is not a function of pressure

Dong Zeng Strategy

1 atm drop tube char ⟶ 1 atm TGA

4 atm drop tube char ⟶ 4 atm TGA

8 atm drop tube char ⟶ 8 atm TGA

16 atm drop tube char ⟶ 16 atm TGA

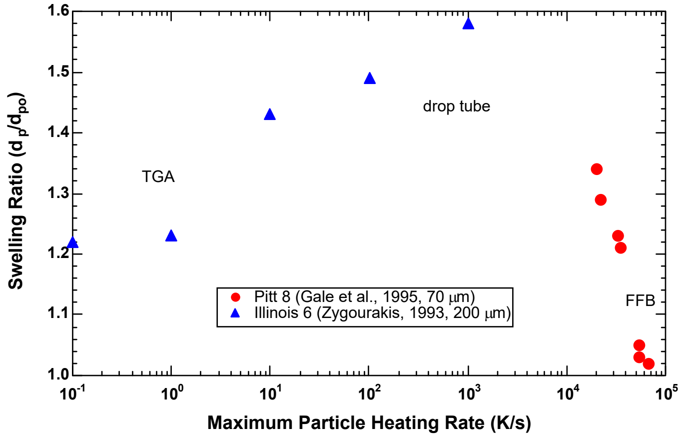
Why?

char density = f(P_{tot}, heating rate)

intrinsic char reactivity = f($T_{final, heating rate}$)

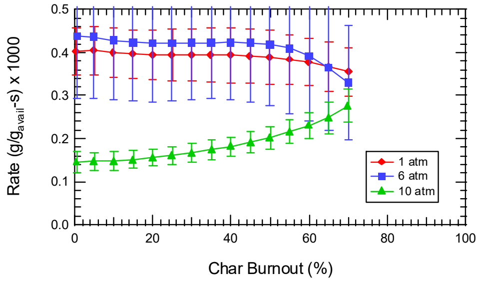
Challenges

Heating rate significantly affects swelling properties during pyrolysis of bituminous coals at atmospheric pressure (Gale et al., Comb. Flame, 1995)



Pitt #8 TGA Reactivity Data

(3-5 mg samples, P_{tot} = char formation pressure)



- Pitt # 8 char (P_{O2} = 0.32 atm; T = 715 K)
- TGA (intrinsic) reactivity relatively constant until 60% burnout
- Only late burnout reactivity changes for high pressure char

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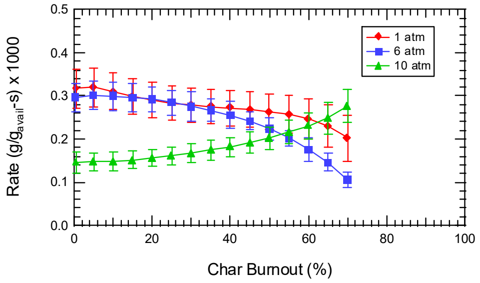
Lignite TGA Reactivity Data

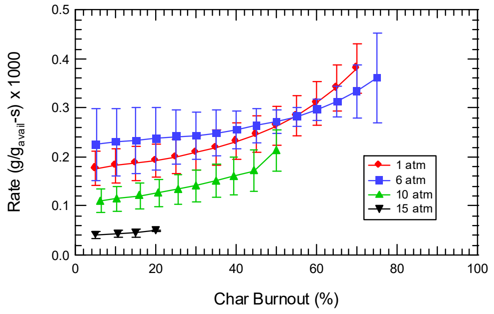
(3-5 mg samples P_{tot} = char formation pressure)



- Lignite reactivity much higher than Pitt #8, so TGA temperature lowered to get intrinsic rates
- Knife River lignite char (P_{O2}=0.28 atm; T=615 K)
- TGA (intrinsic) reactivity not constant like the Pitt #8 char
- High pressure char has 15% lower reactivity at these conditions

Illinois #6 TGA Reactivity Data

(3-5 mg samples P_{tot} = char formation pressure)

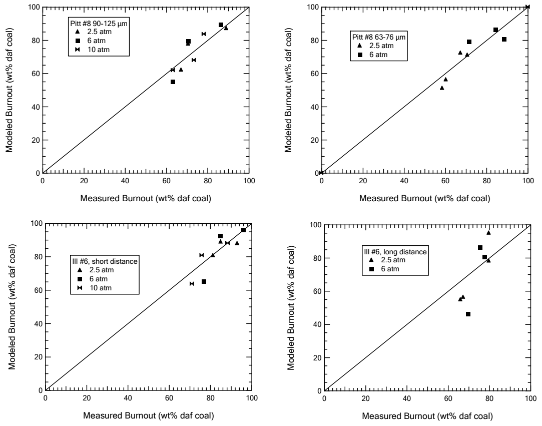


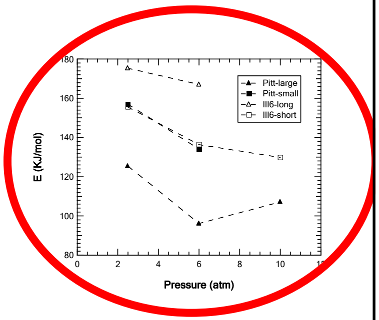
- Illinois #6 reactivity comparable to Pitt #8, so similar conditions used
- Illinois #6 (P_{O2}=0.40 atm; T=693 K)
- Char reactivity appears to decrease with increasing char formation pressure

Different conclusion than Hecker

Modeling Results of N-th Order Kinetics

(High T reactivity)





- Activation energy (E) was used as a fitting parameter for the nth-order kinetic model (CBK8)
- Char reactivity increases with increasing total pressure and constant O_2 molar fraction

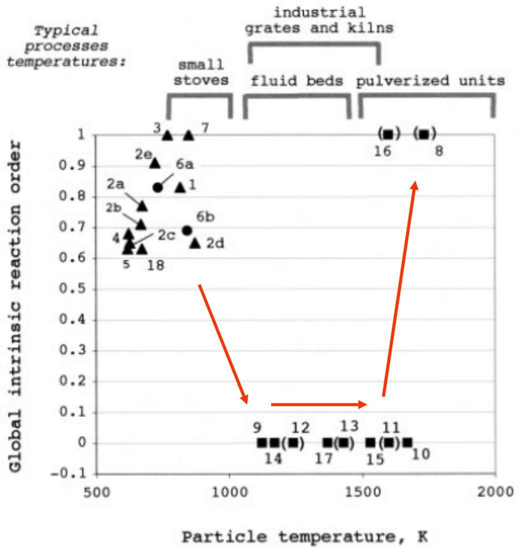
$$C + O_2 \rightarrow CO \text{ or } CO_2$$

$$r_{gas} = kP_{O_2}^n = A\exp(-E/RT)P_{O_2}^n$$

Principal Conclusions (Zeng)

- **TGA reactivity on a gram per gram available basis decreased with increasing char formation pressure**
  - The normalized reactivity was found to be relatively constant with increasing pressure for both the N_2 and CO_2 normalizations
  - Reactivity normalized by N_2 surface area shows less dependence on pressure than that normalized by CO_2 surface area
- **At high temperature in FFB, char oxidation rate constant increased with increasing total pressure**
  - A different value of E or A_{30} for nth order or 3-step kinetic models was necessary for each pressure condition for each coal
  - A one-point calibration would be necessary for every condition before CBK would be capable of predicting char burnout at elevated pressure

Observed Reaction Orders Change vs. Temperature



From Hurt and Calo, C&F, 125, 1138-1149 (2001)

Idea from Hurt and Calo

- Postulate a surface mechanism that allows for changing effective reaction order
  - One part of mechanism controls at low temperature
  - One part controls at intermediate temperatures
  - One part controls at high temperatures

CBK-E

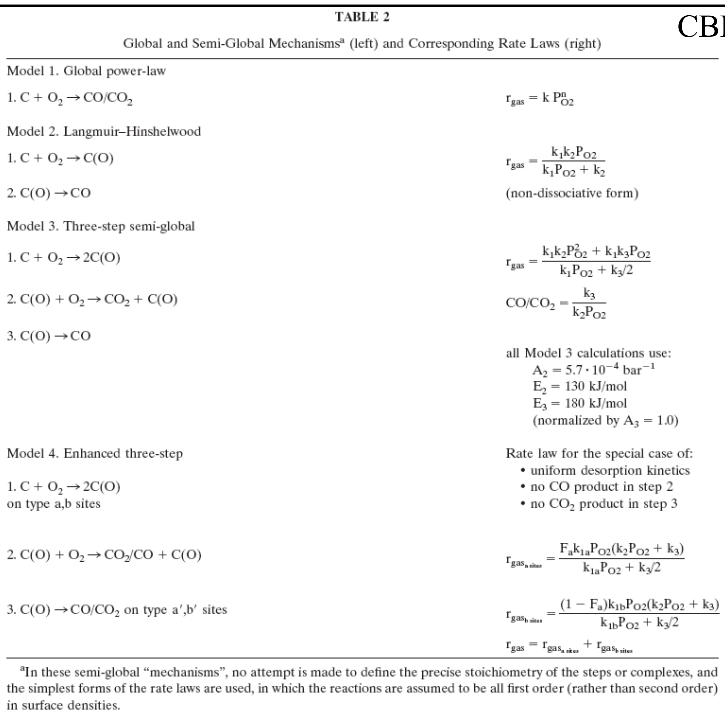


TABLE 2

Global and Semi-Global Mechanisms[a] (left) and Corresponding Rate Laws (right)

Model 1. Global power-law	
1. $C + O_2 \rightarrow CO/CO_2$	$r_{gas} = k\,P_{O2}^{n}$
Model 2. Langmuir–Hinshelwood	
1. $C + O_2 \rightarrow C(O)$	$r_{gas} = \dfrac{k_1 k_2 P_{O2}}{k_1 P_{O2} + k_2}$
2. $C(O) \rightarrow CO$	(non-dissociative form)
Model 3. Three-step semi-global	
1. $C + O_2 \rightarrow 2C(O)$	$r_{gas} = \dfrac{k_1 k_2 P_{O2}^2 + k_1 k_3 P_{O2}}{k_1 P_{O2} + k_3/2}$
2. $C(O) + O_2 \rightarrow CO_2 + C(O)$	$CO/CO_2 = \dfrac{k_3}{k_2 P_{O2}}$
3. $C(O) \rightarrow CO$	
	all Model 3 calculations use: $A_2 = 5.7 \cdot 10^{-4}\ \mathrm{bar}^{-1}$ $E_2 = 130$ kJ/mol $E_3 = 180$ kJ/mol (normalized by $A_3 = 1.0$)
Model 4. Enhanced three-step	Rate law for the special case of: • uniform desorption kinetics • no CO product in step 2 • no CO_2 product in step 3
1. $C + O_2 \rightarrow 2C(O)$ on type a,b sites	
2. $C(O) + O_2 \rightarrow CO_2/CO + C(O)$	$r_{gas_{a\ sites}} = \dfrac{F_a k_{1a} P_{O2}(k_2 P_{O2} + k_3)}{k_{1a} P_{O2} + k_3/2}$
3. $C(O) \rightarrow CO/CO_2$ on type a′,b′ sites	$r_{gas_{b\ sites}} = \dfrac{(1 - F_a) k_{1b} P_{O2}(k_2 P_{O2} + k_3)}{k_{1b} P_{O2} + k_3/2}$
	$r_{gas} = r_{gas_{a\ sites}} + r_{gas_{b\ sites}}$

[a] In these semi-global "mechanisms", no attempt is made to define the precise stoichiometry of the steps or complexes, and the simplest forms of the rate laws are used, in which the reactions are assumed to be all first order (rather than second order) in surface densities.

From Hurt and Calo, C&F, 125, 1138-1149 (2001)

Gasification

$C + H_2O \rightarrow CO + H_2$

$C + CO_2 \rightarrow 2CO$

Gasifiers:
- 30 to 50 atm total pressure
- Air-blown vs O_2-blown

Oxyfuel
- O_2-blown with recycled exhaust
- Atmospheric pressure

Simplest Model

1st Order

- Goetz (Comb. Eng.)
- Drop tube data
- HP-FFB data (Lewis et al., 2015)

Advanced Model

CBK-G

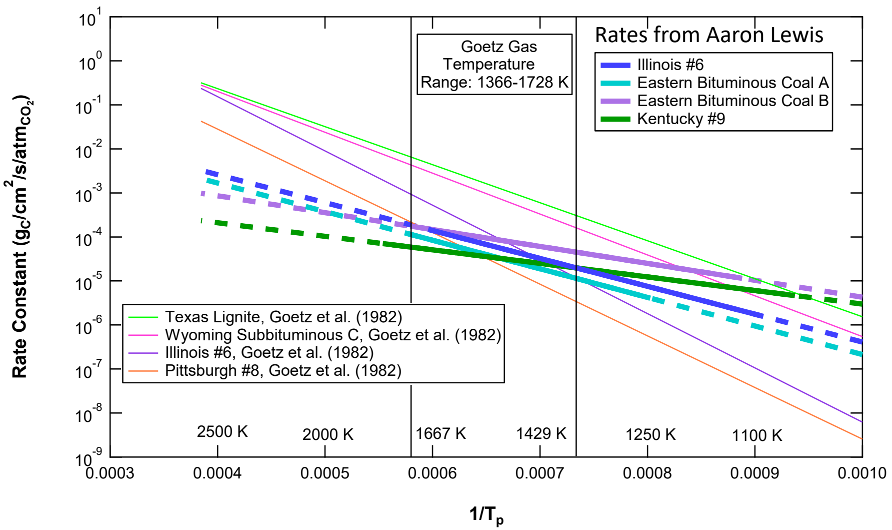
- Liu and Niksa, PECS
- Hard to follow
  - poorly written
- Surface mechanism
- Annealing, etc.
- $$$$

Improved Model

CCK and CCK^N

- Shurtz (2011)
- Data from PFFB
- Oxidation + gasification
- Rate coefficients for CO_2 gasification
- 1st order version available

1st-Order Rate Constant Comparison



Lewis, et al., "Steam Gasification Rates of Three Bituminous Coal Chars in an Entrained-Flow Reactor at Pressurized Conditions," *Energy and Fuels*, **29**, 1479–1493 (2015).

Sensitivity Analysis of CCK Model in Oxy-Fuel Conditions

(excluding main kinetic parameters)

Variable	Importance
Annealing Activation Energy (E_A)	0.74
Effective order of reaction (N)	0.51
Particle swelling (d/d_0) Ω	0.27
Mode of burning parameter (α)	0.20
Size of ash grains in the char particle (microns) (g_d)	0.20
Standard deviation of E_A (σ)	0.18
Char particle residence time (t_r)	0.14

New annealing model, accounting for t_{res} and T_p:
Holland, et al., "Modeling Effects of Annealing on Coal Char Reactivity to O_2 and CO_2 Based on Preparation Conditions," *Energy and Fuels*, **31**, 10727-10744 (2017).

Char Conversion Summary

1. **Atmospheric Char Oxidation (by O_2)**
   - Use Hurt's data/correlation (global) or advanced model (CCK)
   - Correct for high mass transfer
   - Approaches film diffusion limit at high T (2000 K)
   - Must correct for late burnout effects (Hurt --- CBK)
2. **Gasification**
   - Recent data at high temperature and pressure
   - Old correlations by Goetz reported in Smoot & Smith book
   - Summary in dissertation by Guisu Liu, U. Newcastle (2000)
   - These are 3-5 orders of magnitude slower than the C-O_2 reaction for coal (but maybe not for biomass)
   - New models
     - CBK-G
     - CCK & CCK^N (Shurtz dissertation, BYU, 2011)

Char Oxidation Summary (cont)

3. **Catalytic Effects**
   - Generally small at high T
   - Only significant in low rank coals
4. **High Pressure C-O_2**
   - Entrained flow data
     - Monson
     - Zeng (form char at same pressure as oxidation experiment)
     - other high T data sets SRI (Ripu), Australia (Harris)
   - n^{th} order seems to work for TGA's, but not at higher temperatures
   - Get char reactivity at same pressure at which char was formed
   - Simple Langmuir rate equation with effectiveness factor correction seems to work

Remainder of Class

- NO_x/So_x/Hg (Wed)
- Industrial Processes (Fri)
- Review (Mon)
- Final Exam
  - Wed (6/15)