Class 8

Simple Coal Devolatilization Models

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Outline

- 1-step
- 2-step
- DAEM
- Compare capabilities
- Blowing Factor
- Bateman video
- Discuss effects of blowing

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1-Step Model

$$\frac{dV}{dt} = k(V_\infty - V)$$

- V = % of coal that becomes volatiles
- V_∞ = "Ultimate" yield (yield at infinite time)
- k = Arrhenius rate constant {A exp(-E/RT)}

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Question 1

1. One step devolatilization models are of the form:

$$\frac{dV}{dt} = k(V_\infty - V)$$

where V is the fractional yield of volatiles (mass of volatiles per mass of daf coal), and V_∞ is the hypothetical ultimate yield. Assuming a V_∞ of 0.5, please integrate this expression at 10^4 K/s from 300 K to 1400 K for the following two rates:

(a) Badzioch & Hawksley (1970): $k = 3.12 \times 10^5 \exp[-8961/T]$

(b) Solomon, et al. (1976): $k = 4.3 \times 10^{14} \exp[-27{,}544/T]$

where T is in Kelvin and k is in seconds^{-1}. Plot V versus T. What is the time and corresponding temperature when the yield reaches V = 0.4? You will probably have to integrate this numerically.

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2-Competing Step Model

$$\text{Coal} \begin{cases} \nearrow (1\text{-}Y_1)\ Char_1 + Y_1V_1 \\ \searrow (1\text{-}Y_2)\ Char_2 + Y_2V_2 \end{cases}$$

$$\frac{dCoal}{dt} = -(k_1 + k_2)Coal$$

$$\frac{dV}{dt} = \frac{dV_1}{dt} + \frac{dV_2}{dt} = (Y_1k_1 + Y_2k_2)Coal$$

- Advantage: Heating rate effect on both rate and yield

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Ubhayaker Coefficients

(buried in a figure)

tion, with consequent rupturing of unsaturated = 0.

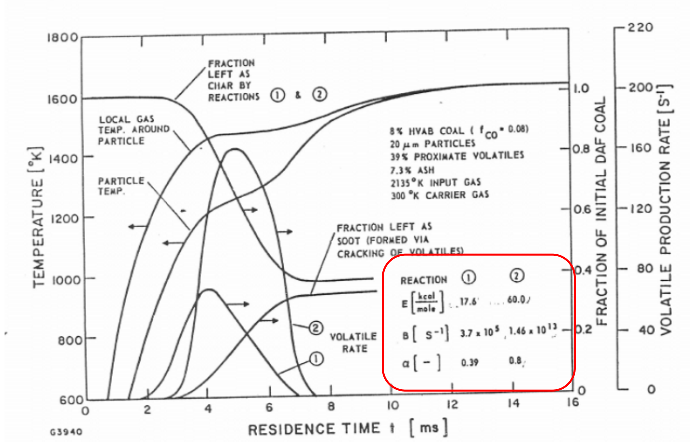

Fig. 2. Numerical solution to the analytical model evaluated for a monodisperse pulverized coal sample. The kinetic parameters were obtained by curve fitting the data of Kimber and Gray[3] and Badzioch and Hawksley.[4]

From Ubhayakar, et al., 16th Symp. (Intl.) on Comb. (1976), p. 480.

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Question 2

2. Repeat problem 1 for the 2-step competing model using the following rate constants:

	A_1 sec^{-1}	A_2 sec^{-1}	E_1 (kcal/mol)	E_2 (kcal/mol)	α_1	α_2
Kobayashi 2-step	2.0e5	1.3e7	25	40	0.3	1.0
Ubhayakar 2-step	3.7e5	1.46e13	17.6	60	0.39	0.80

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Distributed Activation Energy Model (DAEM)

$$\frac{V_\infty - V}{V_\infty} = \int_0^\infty e^{-\int_0^t k dt} F(E) dE$$

$$F(E) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(E-E_0)^2}{2\sigma^2}}$$

- Assumption: Volatiles can be released from bins of different activation energy in parallel
- Advantage: Heating rate effects on rate
- Derivative form available

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How do you solve the DAEM?

Gaussian quadrature!

$$\int_{-1}^{1} f(x)dx = \sum w_i\, f(x_i)$$

- Break up activation energies into 5 to 10 bins
- Quadrature theory tells what the weighting functions are
- Like 5 to 10 parallel reactions weighted appropriately

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Series Distributed Activation Energy

- Concept of an effective E
- E_{eff} changes according to the distribution function:

$$E_{eff} = f(V, V_{\infty}, \sigma)$$

- E_{eff} changes according to a Gaussian distribution based on extent of conversion

$$\frac{dV}{dt} = k_{eff}(V_{\infty} - V)$$

$$k_{eff} = Ae^{-\frac{E_{eff}}{RT}}$$

- MUCH faster with great results

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Question 3

3. Why was the distributed activation energy model (DAEM) developed (i.e., what was the underlying idea)? Please find the typos in Equation 3.7 in Smoot and Smith. Repeat Problem 1 for the DAEM model using the following coefficients:
   - $V_\infty = 0.5$
   - $k_0 = 1.67e13\ sec^{-1}$
   - $E_0 = 50.65$ kcal/mol
   - $\sigma = 7.01$ kcal/mol

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Question 4

4. Please compare the capabilities of the 3 simple models (1-step, 2-step, and DAEM) with respect to calculation of total volatiles yields as a function of time, temperature, heating rate, pressure, and coal type. You may want to look at the paper by Richards et al., *Fuel*, **185**, 171-180 (2016).

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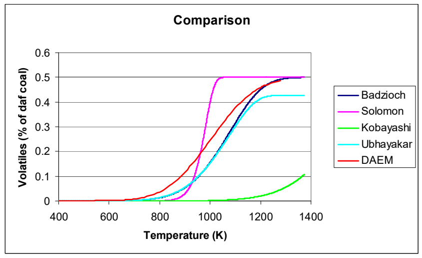
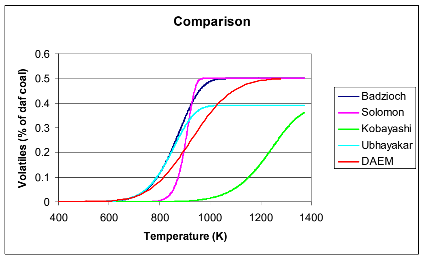
Comparison of Coal Devolatilization Models



(10^4 K/s)



(10^3 K/s)

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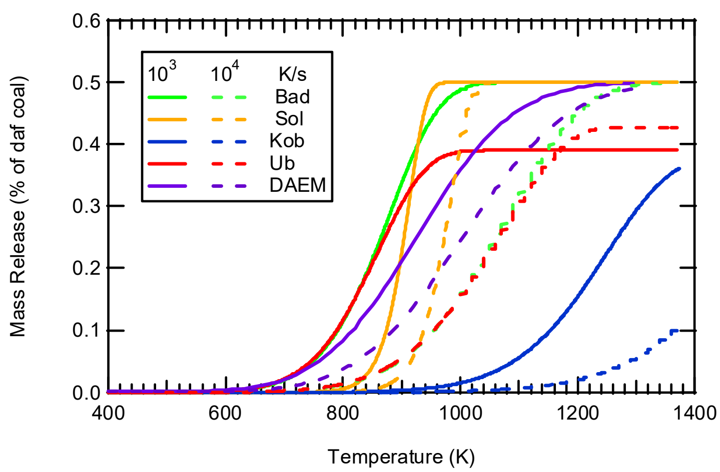
Effect of Heating Rate



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Model Comparison

	# of constants	Yield = *f*(heating rate)?	Pressure effects?	T effect?	Coal type?
1-Step	A,E,V*			X	
2-step	A1,E1,Y1 A2,E2,Y2	x		X	
DAEM	A,E0,Sigm a,V*			X	

Industrial practice: Use 2-step,
Y_1 = ASTM volatiles yield,
$Y_2 = 2Y_1$

Result: works OK but not great

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Coal Video

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Question 5

5. Please discuss what the blowing factor is in relation to coal devolatilization. You may want to look at the paper by Fletcher, *Combustion Science and Technology* **63**, 89 (1989).

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Blowing Factor

See MS Word Handout

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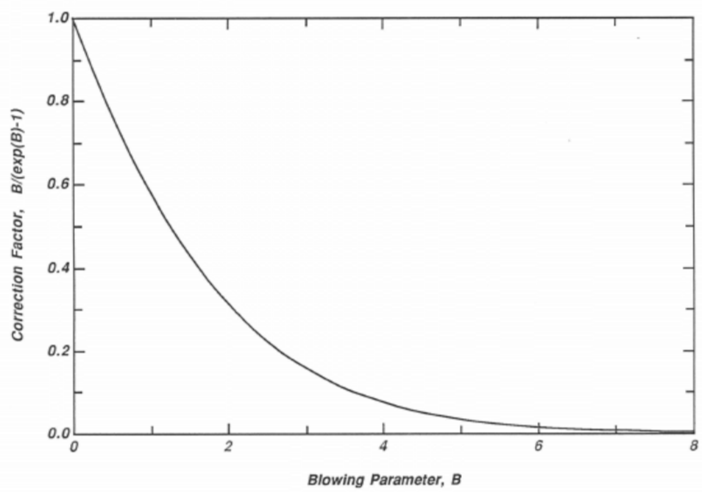
Effect of the Blowing Factor



$$B = \frac{\left(-\frac{dm_p}{dt}\right) C_{p,g}}{2 \pi d_p k_g}$$

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Question 6

6. If the coal ignites heterogeneously before devolatilization, why will the heterogeneous reaction quickly quit and then restart at a later time?

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