Oil Shale Pyrolysis Modeling

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Overview

- Background
  - Pyrolysis process
  - Previous studies
- Model Description
- Results
- Conclusions

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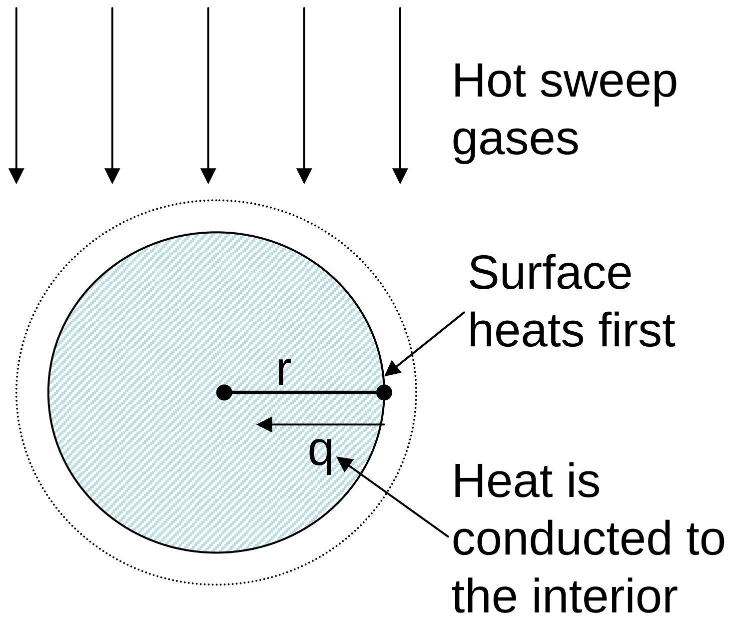
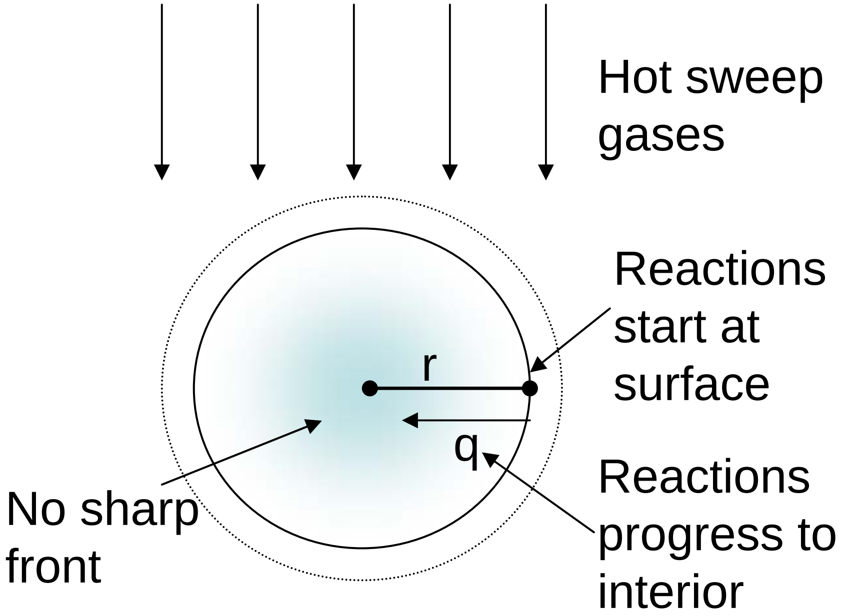
Background

Pyrolysis: (1) Heat Transfer



- Hot gases heat the surface of the particle
- Heat is conducted from the surface to the interior

Pyrolysis: (2) Chemical Reaction



- Temperature rise induces chemical reactions
- Endothermic reactions consume heat
- Rate of temperature rise slows
- Porosity is created as solid reactants form gaseous products

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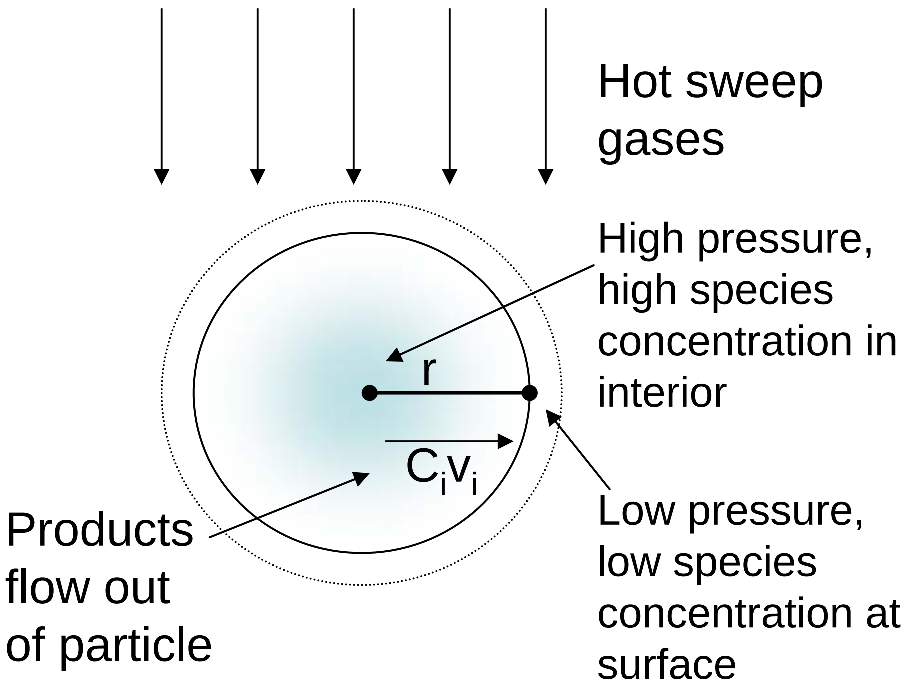
Pyrolysis:
(3) Mass & Momentum Transfer



- Momentum Transfer
  - Pressure buildup inside particle causes gas to flow out
- Mass Transfer
  - Concentration gradients cause products to diffuse out of particle
  - Sweep gases diffuse into particle
  - Thermal diffusion causes heavier molecules to diffuse toward cooler regions

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Previous Studies

- Experimental Studies
  - Kerogen Pyrolysis
    - Campbell et al. [1978]
  - Gas Evolution
    - Campbell et al. [1980] (2)
    - Huss & Burnham [1982]
  - Oil Coking
    - Campbell et al. [1977]
  - Oil Cracking
    - Bissell et al. [1983]
  - Char Gasification
    - Burnham [1979] (3)
    - Thomson et al. [1983]
  - Carbonate Minerals
    - Campbell [1978]
- Modeling Studies
  - Particle
    - Johnson et al. [1975]
    - Campbell et al. [1977]
    - Shih & Sohn [1978]
    - Gregg et al. [1981]
    - Burnham & Braun [1985]
    - Wang & Lee [1986]
  - Retort
    - Braun & Chin [1977/1981]
    - Tyner & Hommert [1978]
    - Crowl et al. [1979]
    - Parker & Zhang [2006]

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Model Description

All models are wrong,
some are useful.

~ George Box

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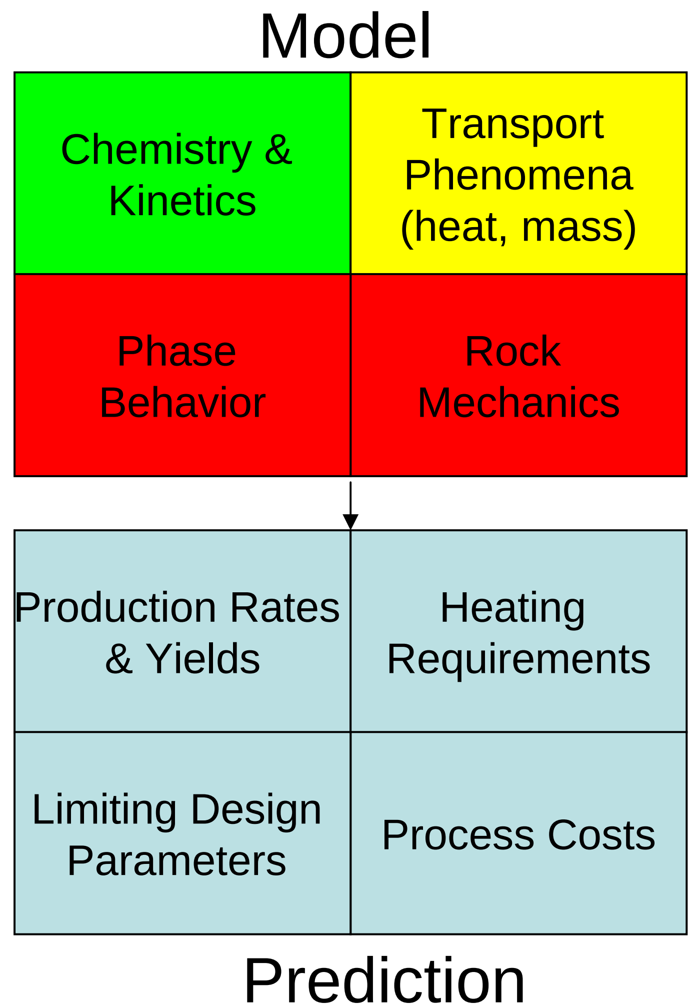
Objective

- Review previous studies
- Develop unified kinetic model
- Validate model with experimental data



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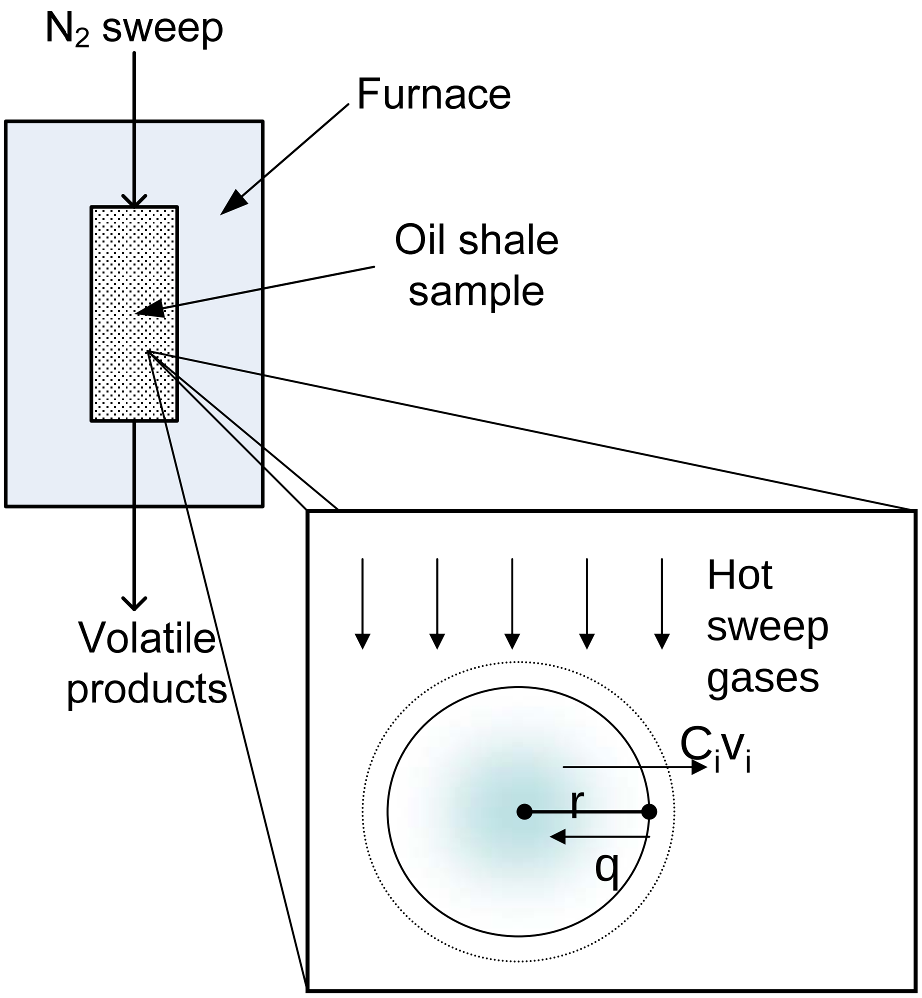
Physical Model

- Physical Model
  - Oil shale is heated in a furnace
  - Constant flow of inert gas sweeps through reactor
  - Volatile products flow out of reactor
  - Assume reactor is spatially uniform
- Chemistry (adapted from LLNL studies)
  - Kerogen pyrolysis
  - Oil Coking, Cracking
  - Char pyrolysis
  - Char gasification, WGS
  - Carbonate decomposition



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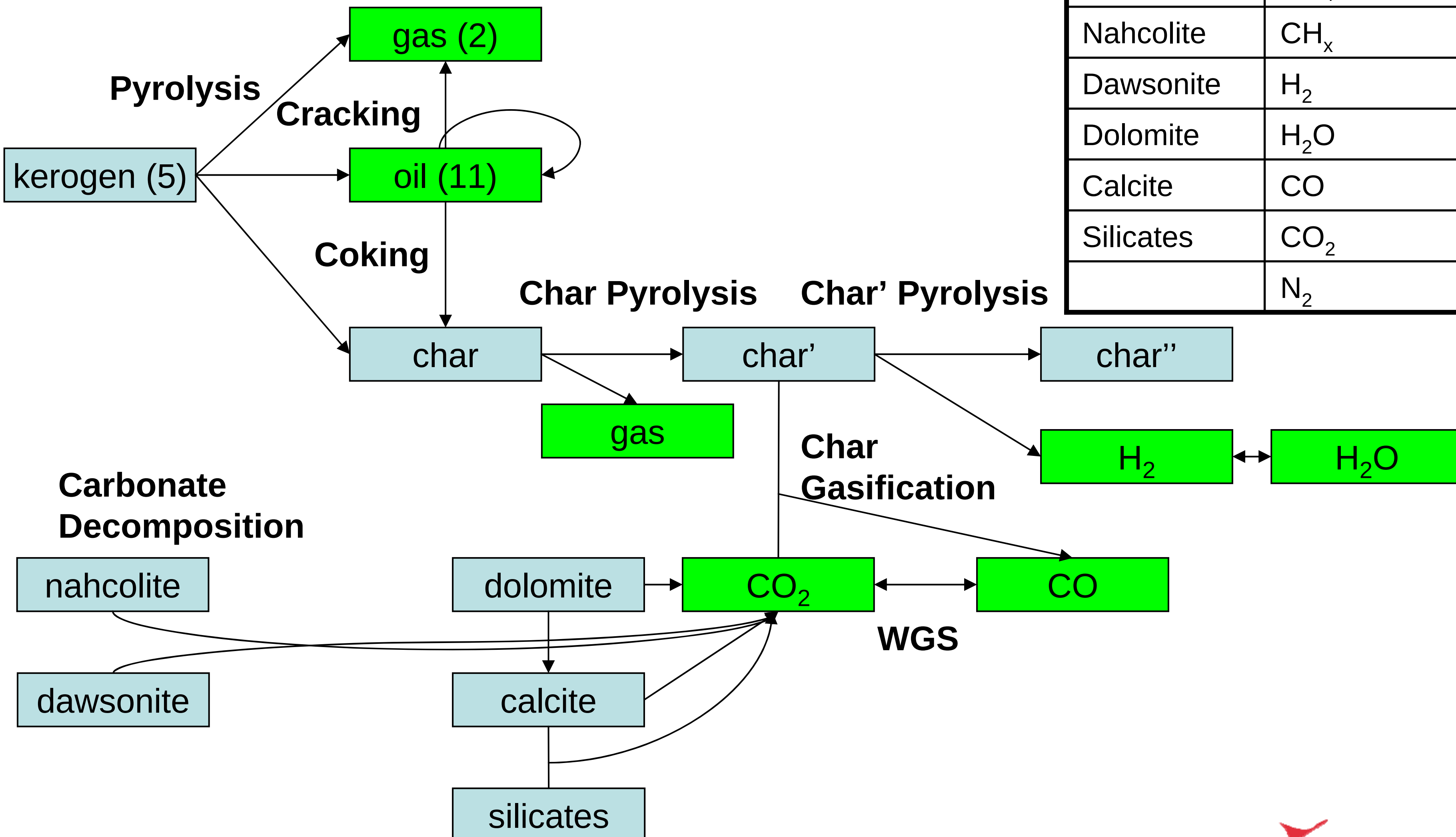
Chemical Reactions

Solid	Gas
Kerogen (5)	Oil vapor (11)
Char (3)	CH_4
Nahcolite	CH_x
Dawsonite	H_2
Dolomite	H_2O
Calcite	CO
Silicates	CO_2
	N_2



Kinetics

Reaction	Kinetics	Source
Kerogen Pyrolysis (5)	1^{st} order	Burnham & Braun [1985] Campbell et al. [1978]
Oil Coking (11)	1^{st} order	Burnham & Braun [1985] Campbell et al. [1977]
Oil Cracking (11)	1^{st} order	Burnham & Braun [1985] Bissell et al. [1983]
Char Pyrolysis (2)	1^{st} order Gaussian-distributed E_a	Campbell et al. [1980]
Char Gasification (2)	LHHW	Burnham [1979] (3)*
Water-gas-shift	2^{nd} order, reversible	Braun & Chin [1981]
Carbonate Decomposition (7)	1^{st} order LHHW	Campbell [1978]

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Conservation Equations

Solid Species Mole Balance

$$\begin{Bmatrix}\text{Accumulation}\\ \text{Rate}\end{Bmatrix} = \begin{Bmatrix}\text{Stoichiometry}\\ \text{Matrix}\end{Bmatrix}\begin{Bmatrix}\text{Reaction}\\ \text{Rate}\end{Bmatrix}\begin{Bmatrix}\text{Volume of}\\ \text{solid phase}\end{Bmatrix}$$

$$\frac{dN_{s,i}}{dt} = \sum_j f_{s,i,j} R_j \cdot (1-\varepsilon)V$$

Gas Species Mole Balance

$$\begin{Bmatrix}\text{Accumulation}\\ \text{Rate}\end{Bmatrix} = \begin{Bmatrix}\text{Flow}\\ \text{In}\end{Bmatrix} - \begin{Bmatrix}\text{Flow}\\ \text{Out}\end{Bmatrix} + \begin{Bmatrix}\text{Generation}\\ \text{from reaction}\end{Bmatrix}$$

$$\frac{dN_{g,i}}{dt} = C_{g,i,0} v_0 - C_{g,i} v + \dot{N}_{g,i}$$

$$\dot{N}_{g,i} = \sum_j f_{s,i,j} R_{s,j} \cdot (1-\varepsilon)V + \sum_j f_{g,i,j} R_{g,j} \cdot \varepsilon V$$

$$\begin{Bmatrix}\text{Inlet Molar}\\ \text{Flowrate}\end{Bmatrix} = \begin{Bmatrix}\text{Outlet Molar}\\ \text{Flowrate}\end{Bmatrix} + \begin{Bmatrix}\text{Generation}\\ \text{from Reaction}\end{Bmatrix}$$

$$F_T = F_{T,0} + \sum_i \dot{N}_{g,i}$$

$$\begin{Bmatrix}\text{Inlet Volumetric}\\ \text{Flowrate}\end{Bmatrix} = \begin{Bmatrix}\text{Outlet Volumetric}\\ \text{Flowrate}\end{Bmatrix}\begin{Bmatrix}\text{Ratio of}\\ \text{Molar Flowrates}\end{Bmatrix}$$

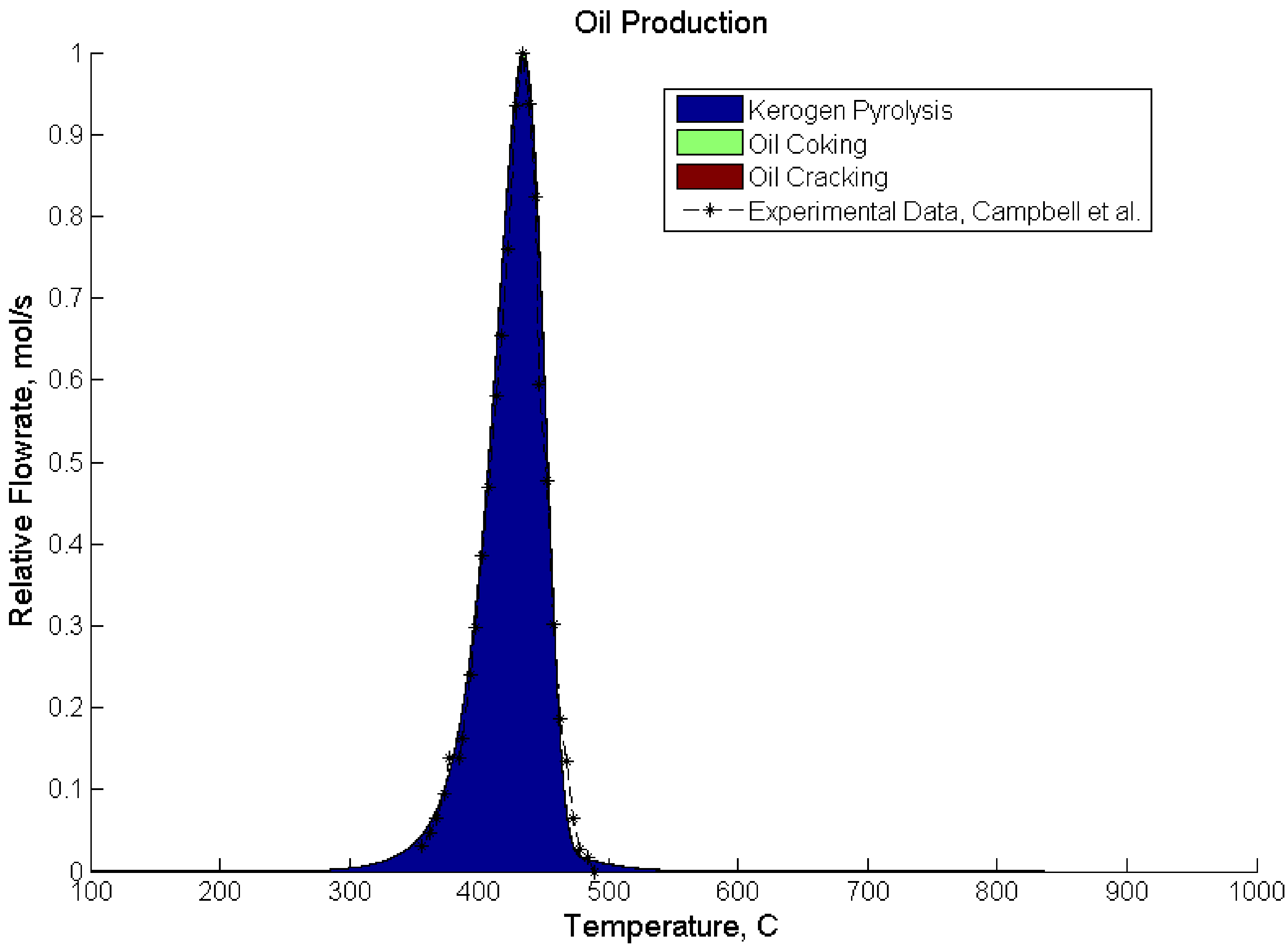
$$v = v_0 \left(\frac{F_T}{F_{T,0}}\right)\left(\frac{T}{T_0}\right)$$

Solution Method

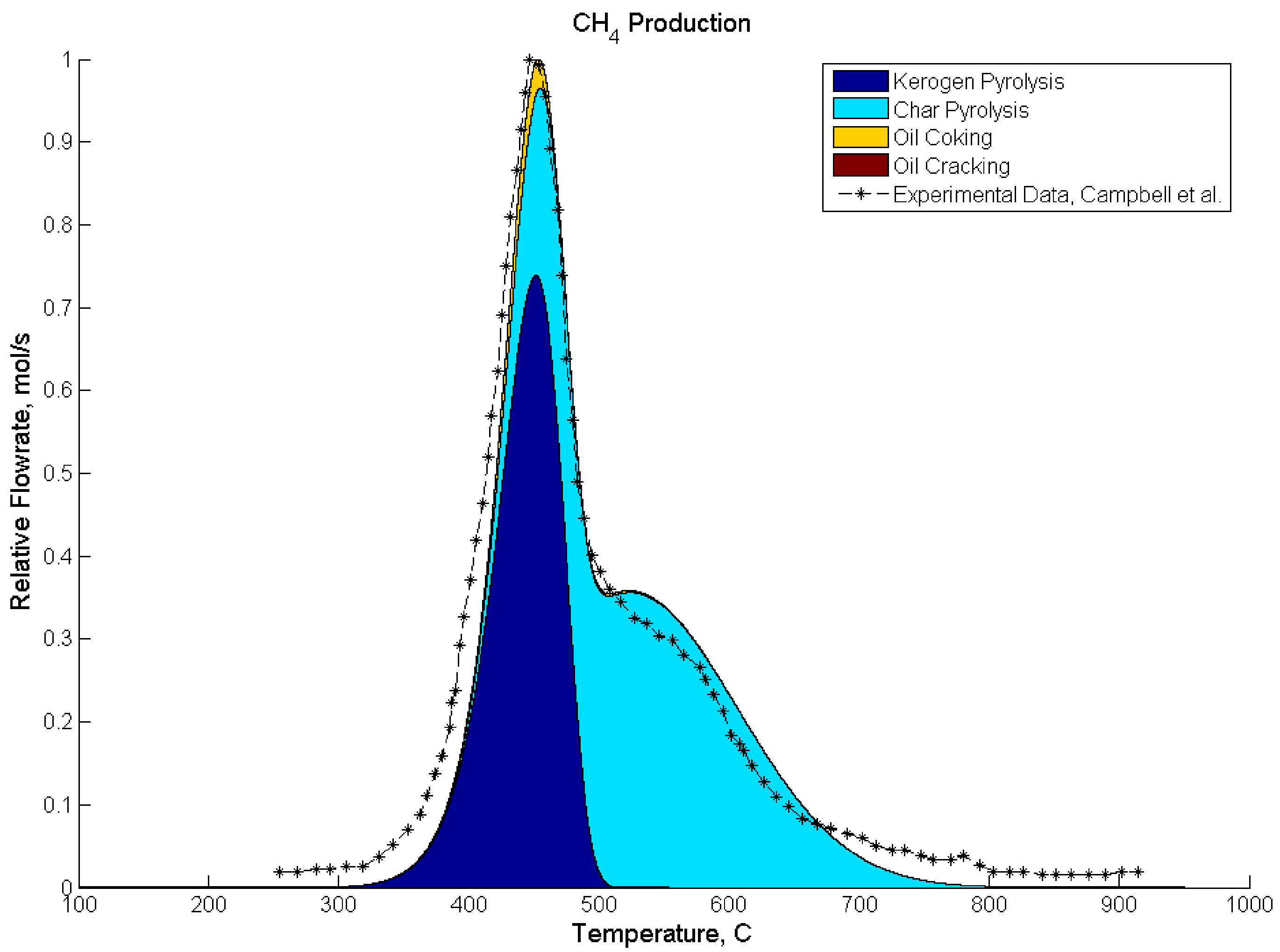
- 0D Model
  - Each mole balance equation is an ODE
  - Furnace temperature increases linearly with time
  - Retort sweep gas flow rate determines product residence time
  - Integrate ODE system with MATLAB ODE15s

Results

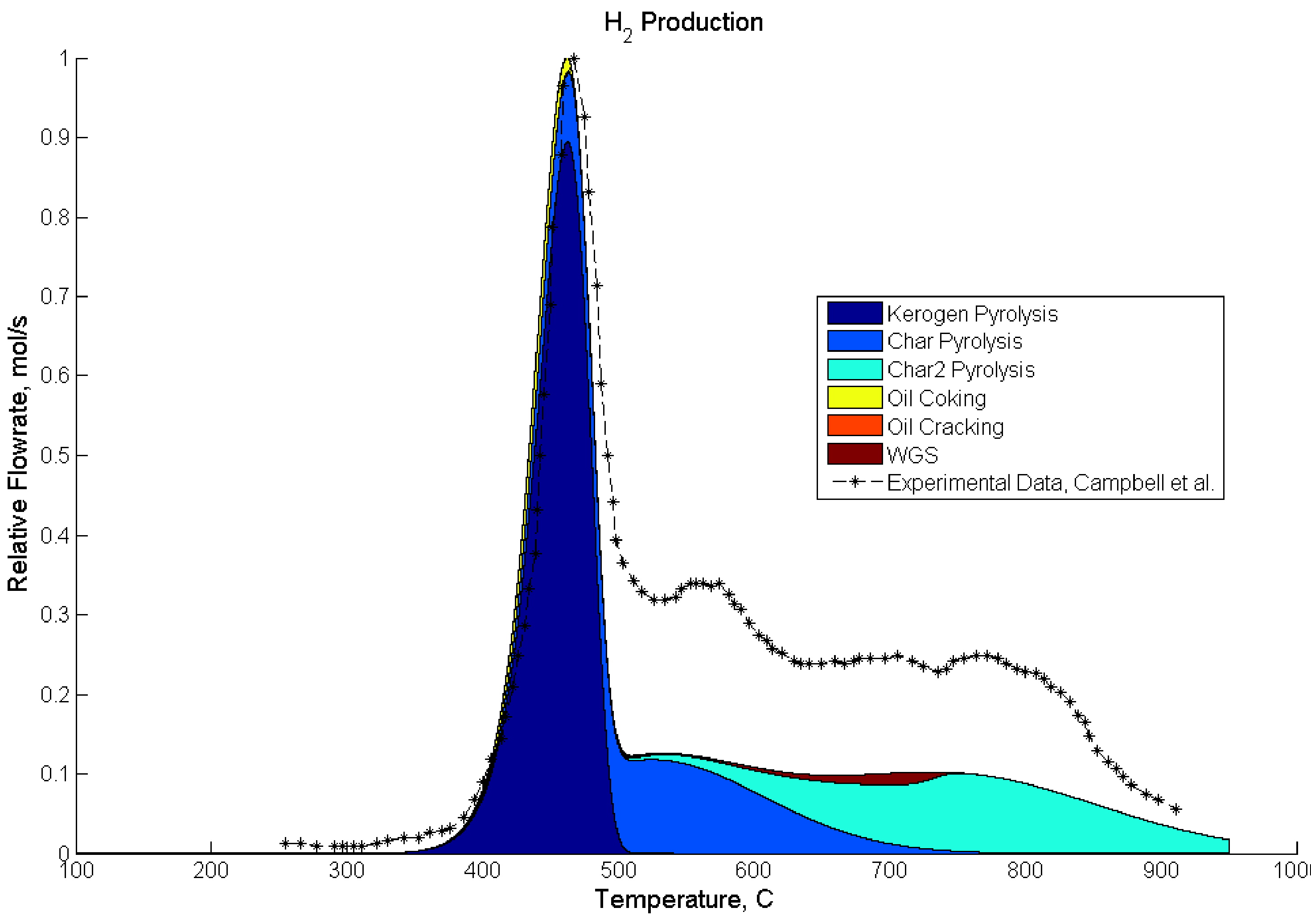
Oil Production



Methane Production



H_2 Production



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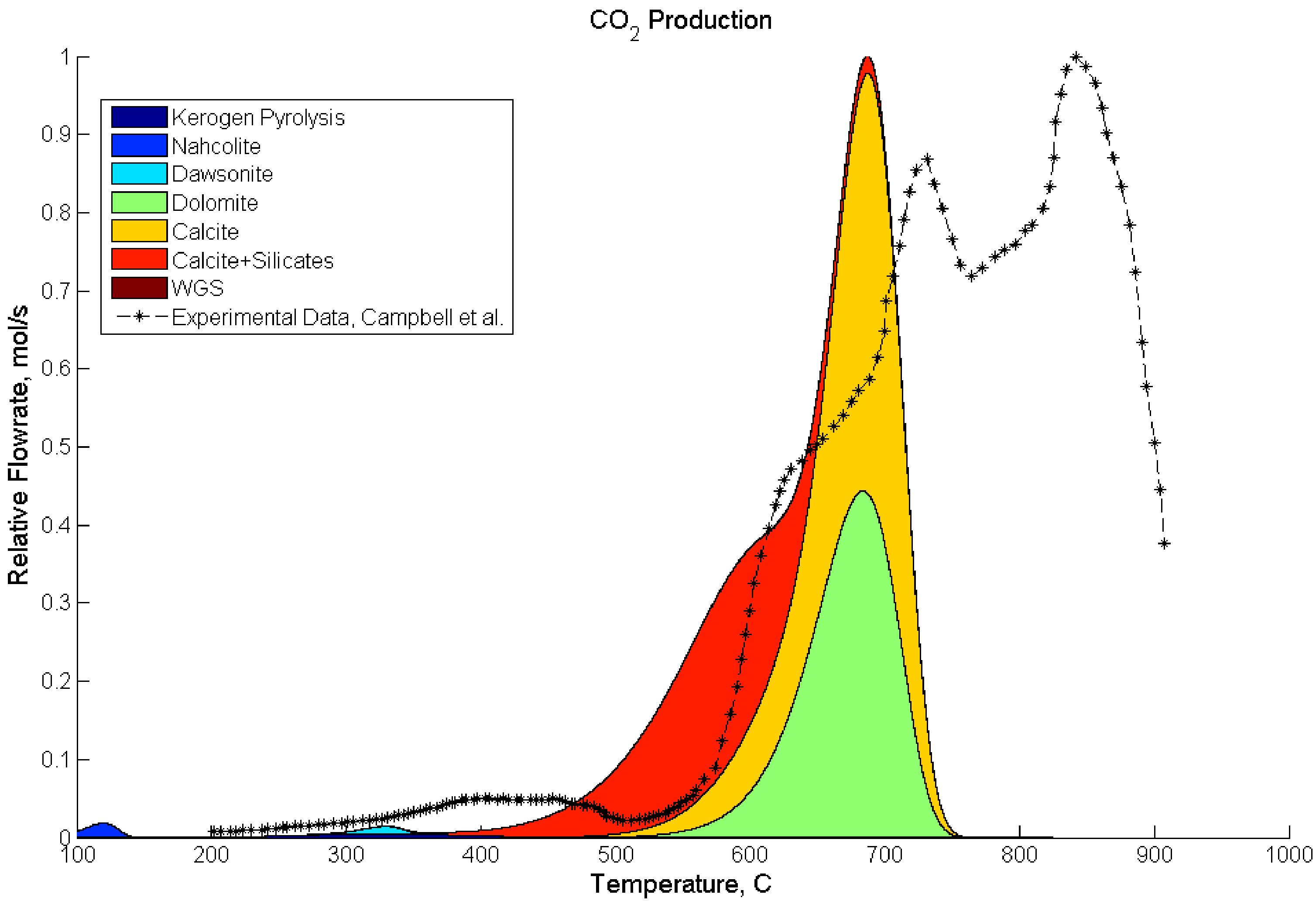
CO_2 Production



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Conclusions

- Kinetic model can reproduce trends in laboratory data
- Next Steps
  - Improve lumped species model for oil composition
  - Perform sensitivity analyses
  - Develop particle model w/ mass and heat transport

Questions?

Conservation Equations: 1D

Solid-phase Mass Balance

$$\{\text{Solid Accumulation}\} = \{\text{Reaction}\}$$

$$\frac{\partial\left((1-\phi)C_{s,i}\right)}{\partial t} = \dot{R}_{s,i}$$

Gas-phase Mass Balance

$$\{\text{Gas Accumulation}\} = \{\text{Diffusion}\} + \{\text{Convection}\} + \{\text{Reaction}\}$$

$$\frac{\partial\left(\phi C_{g,i}\right)}{\partial t} = \underline{\nabla}\cdot\left(D_{i,m}\underline{\nabla}\frac{C_{g,i}}{C_{g,t}} + \frac{-\kappa}{\mu}\underline{\nabla}p\, C_{g,i} \right) + \dot{R}_{g,i}$$

Particle Energy Balance

$$\{\text{Heat Acummulation}\} = \{\text{Conduction}\} + \{\text{Generation by Reaction}\}$$

$$\left(\rho_s c_{p,s}\right)\frac{\partial T}{\partial t} = \underline{\nabla}\cdot\lambda_s\underline{\nabla}T - \sum_{j}^{n\_rxn} h_{rxn,j}R_j$$

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