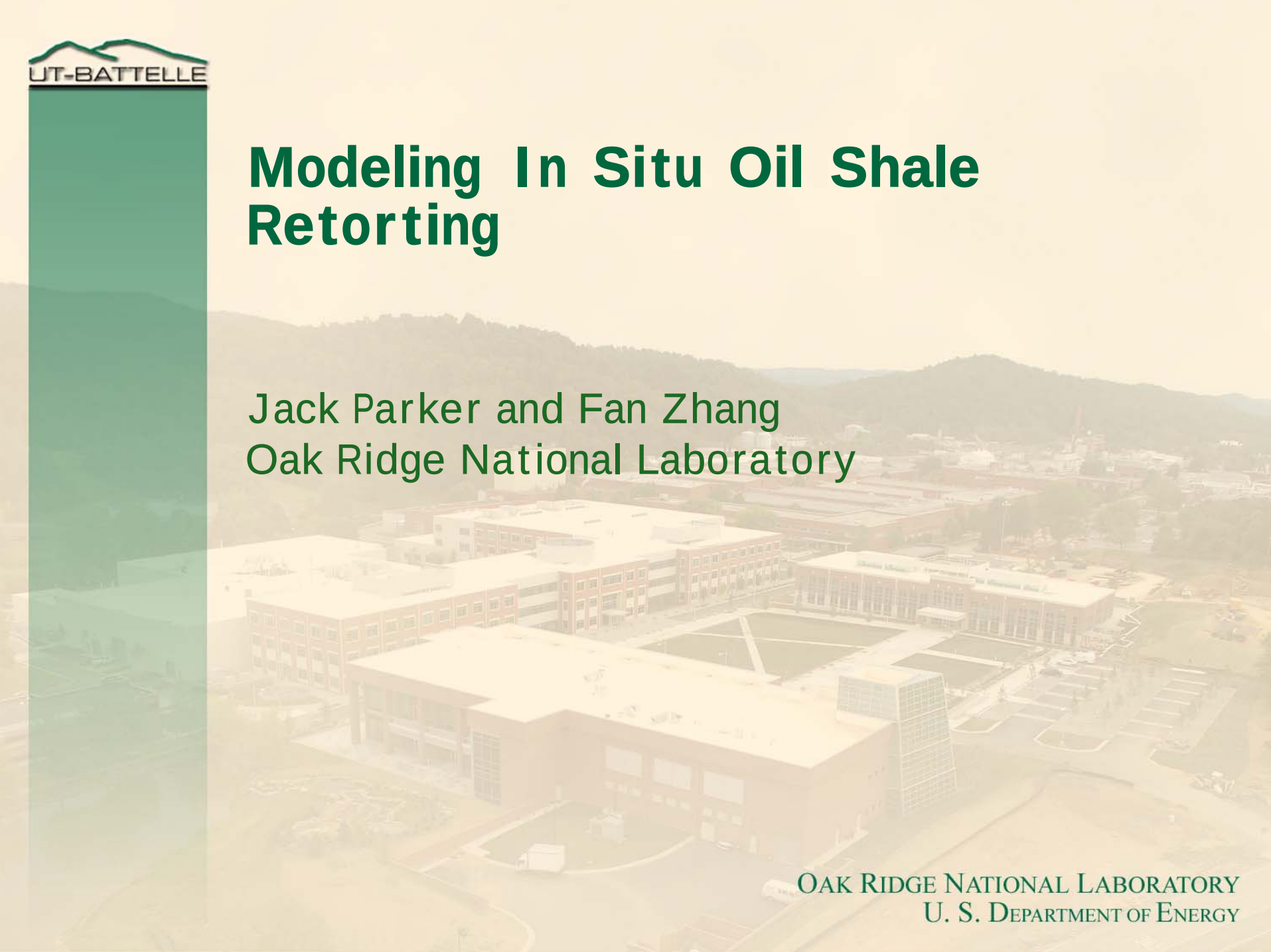
UT-BATTELLE

Modeling In Situ Oil Shale Retorting

Jack Parker and Fan Zhang
Oak Ridge National Laboratory



Overview

- Describe a model for *in situ* oil shale retorting with nonequilibrium fracture-matrix heat and mass transfer
- Compare first-order transfer function approximation and radial matrix diffusion model
- Model validation for laboratory retort experiments
- Practical criteria for use of first-order approach

Model Description

- Transient gas phase flow
- Thermal transport in dual-continuum fracture-matrix medium
- Multispecies transport in dual-continuum medium
- Geochemical model to handle complex kinetic and/or equilibrium-controlled reaction networks
- Implemented in 3-D finite element code

In Situ Retort Reactions

Description*	Reaction	Kinetics
Primary pyrolysis (m)	$kerogen_{(s)} \rightarrow oil_{(l)} + gas_{(v)} + H_{2\,(v)} + CH_{4\,(v)} + CO_{2\,(v)} + H_2O_{(v)} + char1_{(s)}$	Arrhenius (Campbell et al. 1980)
Secondary pyrolysis (m)	$char1_{(s)} \rightarrow H_{2(v)} + CH_{4(v)} + char2_{(s)}$ $char2_{(s)} \rightarrow H_{2(v)} + ROC_{(s)} + ROH_{(s)}$	Arrhenius with distributed E_{act}
Carbon gasification (m)	$ROC_{(s)} + CO_{2\,(v)} \rightarrow H_{2(v)} + CH_{4(v)} + ROC_{(s)}$	Ergun (Gregg et al 1980; Braun 1981)
Dolomite decomposition (m)	$MgCa(CO_3)_{2(s)} \rightarrow CaCO_{3(s)} + MgO_{(s)} + CO_{2\,(v)}$	Arrhenius (Gregg et al. 1980)
Calcite decomposition (m)	$CaCO_{3(s)} + SiO_{2(s)} \rightarrow Ca_2SiO_{4(s)} + CaO_{(s)} + CO_{2\,(v)}$	Arrhenius (Braun 1981)
Oil coking (f,m)	$oil_{(l)} \rightarrow H_{2(v)} + CH_{4(v)} + ROC_{(s)}$	Empirical function of primary pyrolysis rate and heating rate (Braun 1981)

* m = matrix reaction, f = fracture reaction

In Situ Retort Reactions

Description	Reaction	Kinetics
Water-gas shift (f,m)	$CO_{(v)} + H_2O_{(v)} \leftrightarrow CO_{2\,(v)} + H_{2(v)}$	First-order in all species (Braun 1981)
Bound water loss (m)	$H_2O_{(s)} \rightarrow H_2O_{(v)}$	Constant from 120-360 C (Braun 1981)
Water distillation (f,m)	$H_2O_{(l)} \leftrightarrow H_2O_{(v)}$	Equilibriium
Oil distillation (f,m)	$oil_{(l)} \leftrightarrow oil_{(v)}$	Equilibriium
Combustion (f)	$H_{2(v)} + O_{2(v)} \rightarrow H_2O_{(v)}$ $gas_{(v)} + O_{2(v)} \rightarrow H_2O_{(v)} + CO_{(v)}$ $CH_{4\,(v)} + O_{2(v)} \rightarrow H_2O_{(v)} + CO_{(v)}$ $CO_{(v)} + O_{2(v)} \rightarrow CO_{2\,(v)}$ $oil_{(v)} + O_{2(v)} \rightarrow H_2O_{(v)} + CO_{(v)}$	Instantaneous above 400 C sequentially in order shown if O_2 is present

* m = matrix reaction, f = fracture reaction

Mass Transport Model

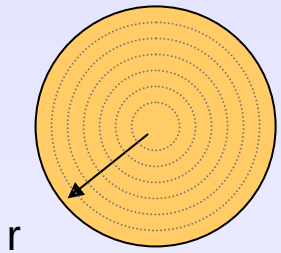
- Mass transport processes in fractures
  - advection
  - dispersion
  - fluxes to/from rock matrix
  - production/loss due to reactions

- Mass transport processes in rock matrix
  - gas phase diffusion
  - fluxes to/from fracture porosity
  - production/loss due to reactions

Rock Matrix Mass Transfer Formulations

- Spherical radial diffusion model

$$\frac{\partial C_m \phi_m}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_m r^2 \frac{\partial C_m \phi_m}{\partial r} \right) + S_m$$



Rock Fragment

- First-order mass transfer model

$$\frac{\partial C_m \phi_m}{\partial t} = \alpha \left(C_f - C_m \right) + S_m$$

An "equivalent" mass transfer coefficient, α, for a given diffusion problem may be derived by equating second moments of the two models yielding

$$\alpha = \frac{60 D_m \phi_m}{d_{eff}^2}$$

where D_m is the effective species diffusion coefficient, ϕ_m is matrix porosity (which varies with time), and d_{eff} = rock fragment diameter

Heat Transport Model

- Thermal processes in fractures
  - gas phase advection
  - thermal gas phase dispersion
  - fluxes to/from rock matrix
  - endothermic/exothermic reactions

- Thermal processes in rock matrix
  - conduction in rock
  - fluxes to/from fracture porosity
  - endothermic/exothermic reactions
  - external thermal source/sink

Rock Matrix Heat Transfer Formulations

- Analogous formulations for radial conduction and first-order heat transfer may be written as discussed for mass transfer
- The "equivalent" first-order model may be written as

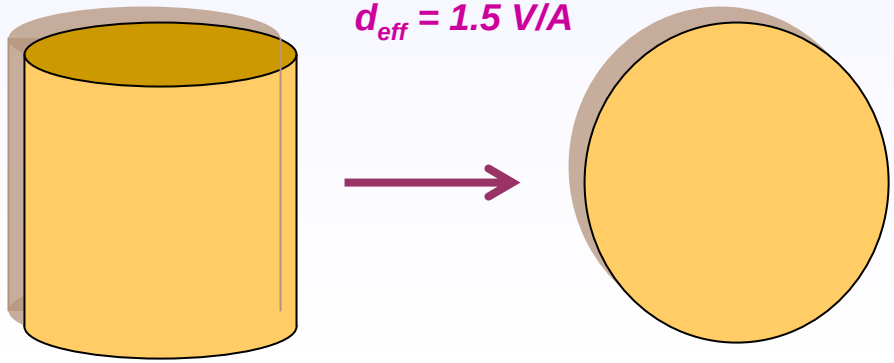
$$\frac{\textit{fracture-matrix heat transfer rate}}{\textit{rock volume}} = \frac{60\lambda}{d_{eff}^2}\left(T_f - T_m\right)$$

where λ is thermal conductivity, T_f is fracture temperature, T_m is average rock matrix temperature, and d_{eff} is effective rock diameter

Laboratory Block Retort Study (Gregg et al, 1990)

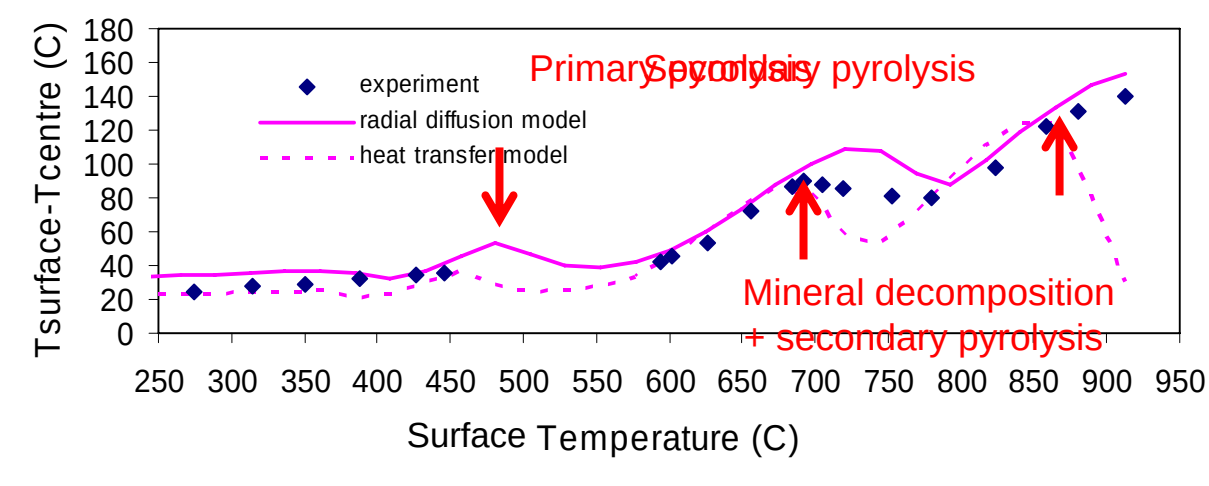
- Large 17 cm block with 18 deg C/h heating rate
- Small 2.5 cm block with 120 deg/h heating rate
- Argon sweep gas at fixed flow rate
- Off-gas analyzed for various components
- Shale composition:
  - Fischer assay 23 gal/T
  - Dolomite 38 wt%
  - Calcite 8.2 wt%

Compute "equivalent" spherical diameter
$d_{eff} = 1.5\ V/A$



Temperature in Large Block During Retorting

17 cm block with 18 deg/h heating rate

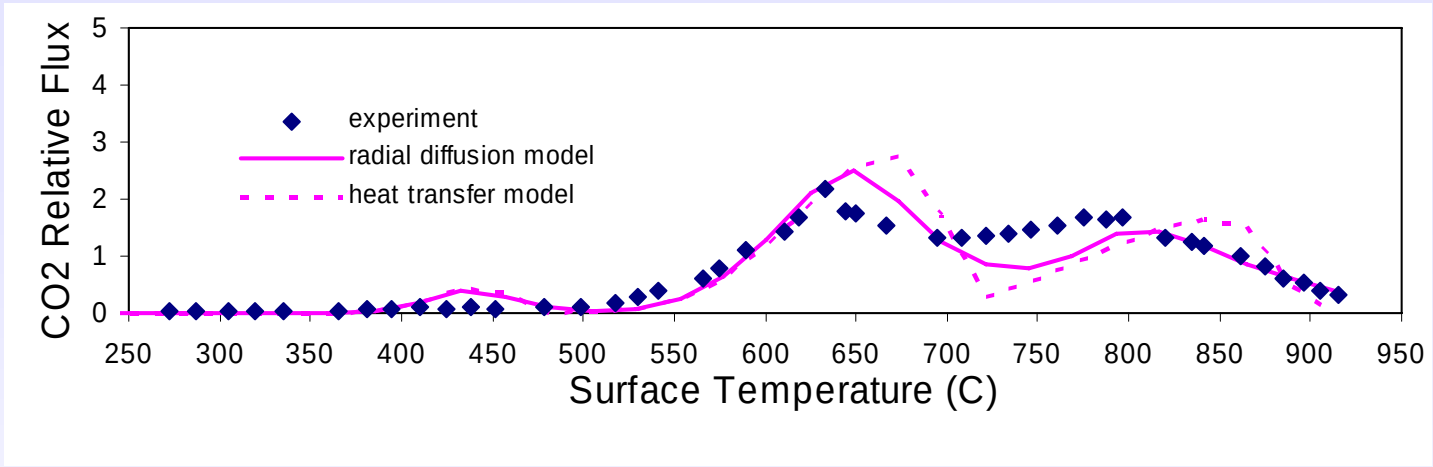


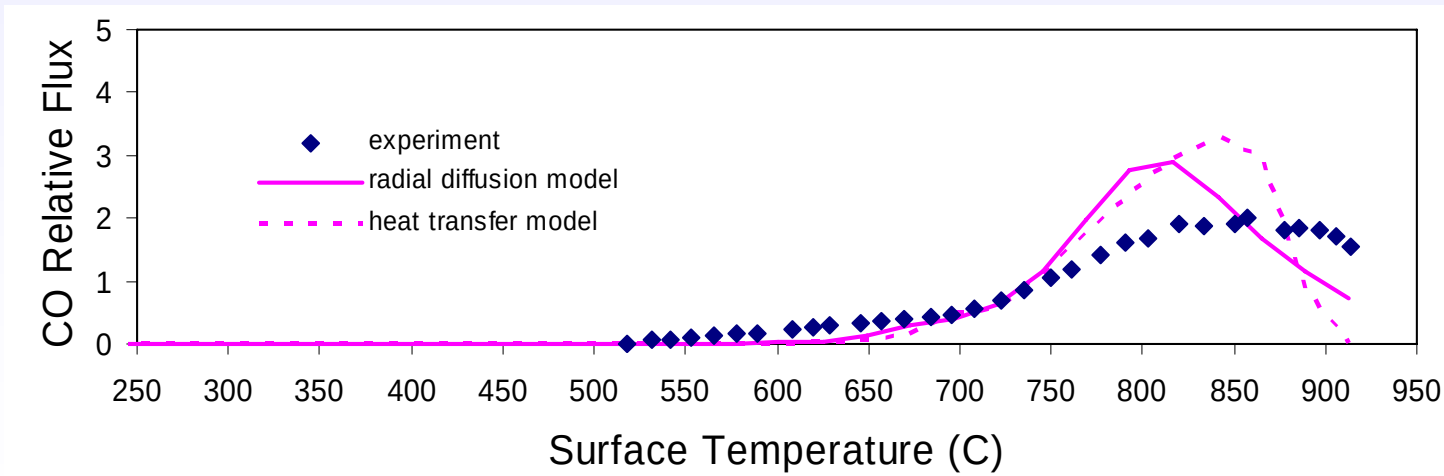
- $T_{surface} - T_{center}$ for FO model computed as 2 x ($T_{surface} - T_{average}$)
- Increasing deviations between FO and radial models at high temps
- Reactions reaching completion sooner with FO model for this experiment; effective diameter behaves smaller than 1.5 V/A
- Reaction kinetics controlled by avg temp for first-order model but by temperature distribution for radial model

OAK RIDGE National Laboratory

Relative CO_2 and CO Flux for Large Block Retort

17 cm block with 18 deg/h heating rate





Reactions peak later and reach completion earlier with first-order models

OAK RIDGE National Laboratory

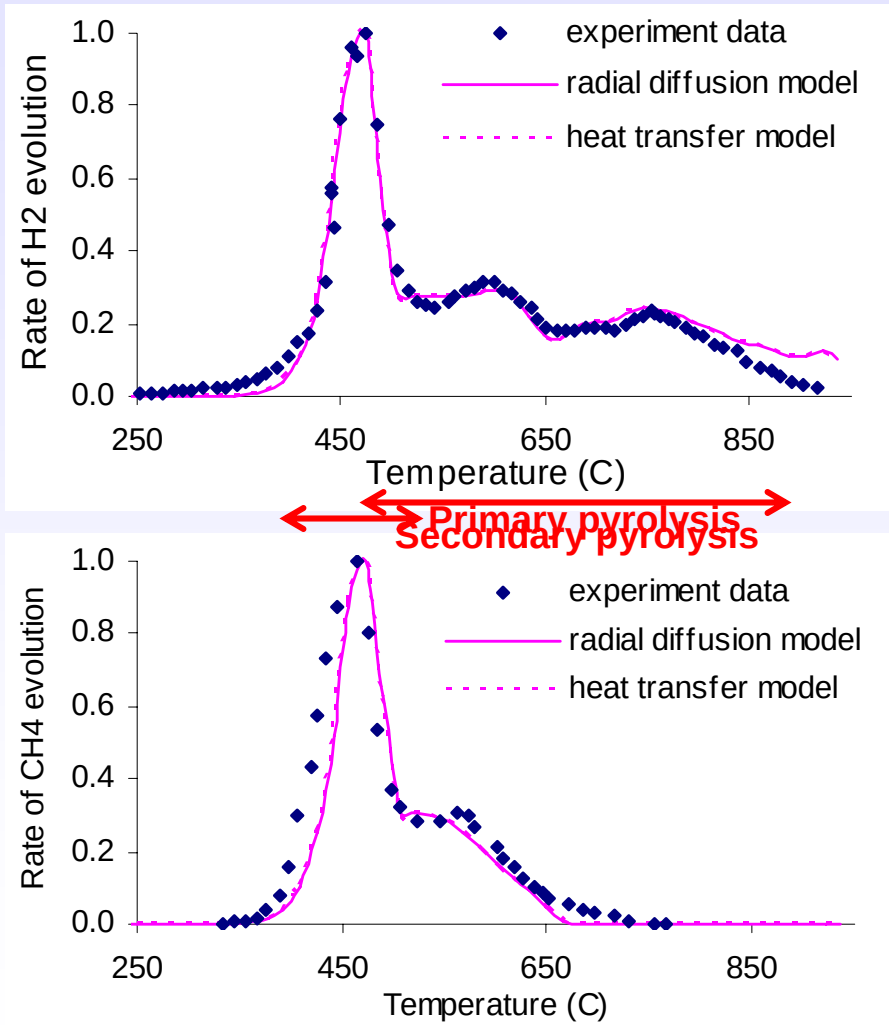
Final Large Block Retort Results (t = 50 hrs)

17 cm block with 18 deg/h heating rate

Property	Measured	Radial Model	First-Order Model
Oil yield (% Fischer assay)	91.2	92.0	92.0
Total mass loss (%)	35.5	34.6	35.3
Total CO_2 gas evolved (L)	1059	1040	1075
Total CO gas evolved (L)	546	600	634
Total CH_4 gas evolved (L)	46.2	39.8	39.8
Total H_2 gas evolved (L)	112.7	113.1	115.0
Residual organic carbon (wt %)	7.83	3.91	6.41
Residual carbonates (wt%)	4.82	5.52	2.17

Relative H_2 and CH_4 Flux for Small Block Retort

2.5 cm block with 120 deg/h heating rate



OAK RIDGE National Laboratory

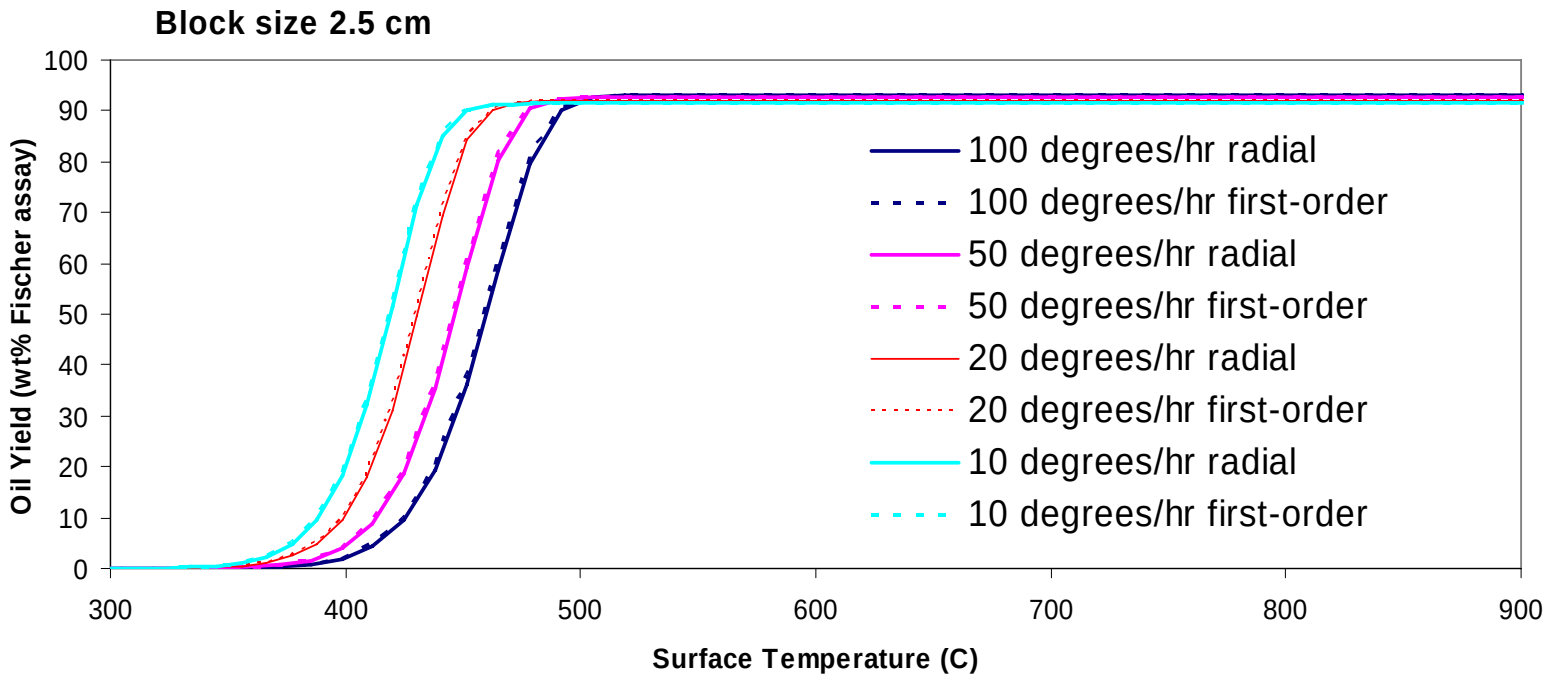
Computational Effort

- When solving a problem involving many nodes discretizing a fracture continuum, each fracture node will have
  - N_r additional matrix nodes for a radial model with N_r unknown temperature and species concentrations governed by nonlinear PDEs, or
  - a single set of unknown temperature and species concentrations governed by single additional ODEs for first-order model.
- The computational effort for a radial matrix model relative to a first-order model will be on the order of $N_r/2$ times greater, depending on the effort to solve flow and reaction equations
- To model a distribution of block sizes with the radial approach, computational effort would increase roughly proportional to the number of size fractions, while very little additional effort would be required using the first-order approach

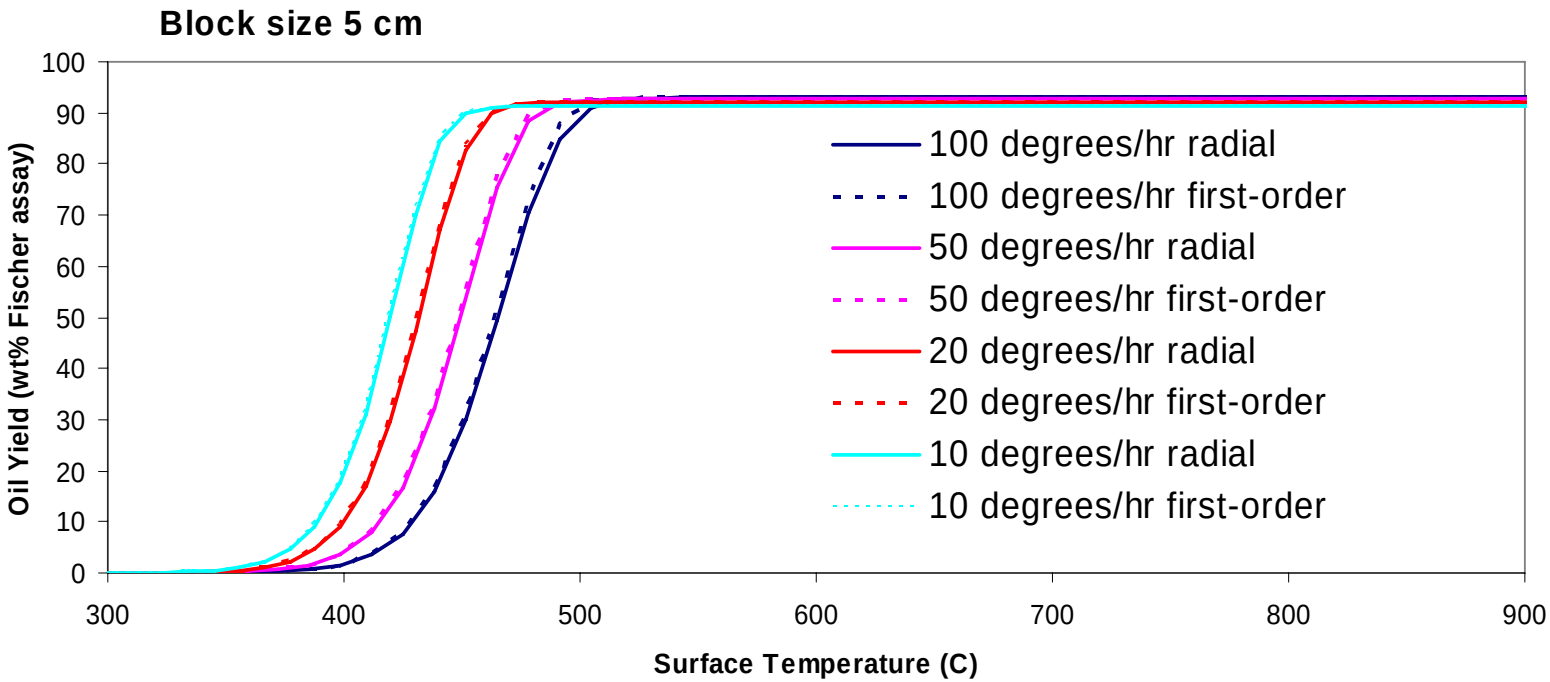
Model Comparison for a Range of Conditions

- Compare oil yield vs. time for
  - radial and first-order heat/mass transfer models
- For block sizes of
  - 2.5, 5, 10, 20 cm diameter
- For surface heating rates of
  - 10, 20, 50, 100 deg C/hr

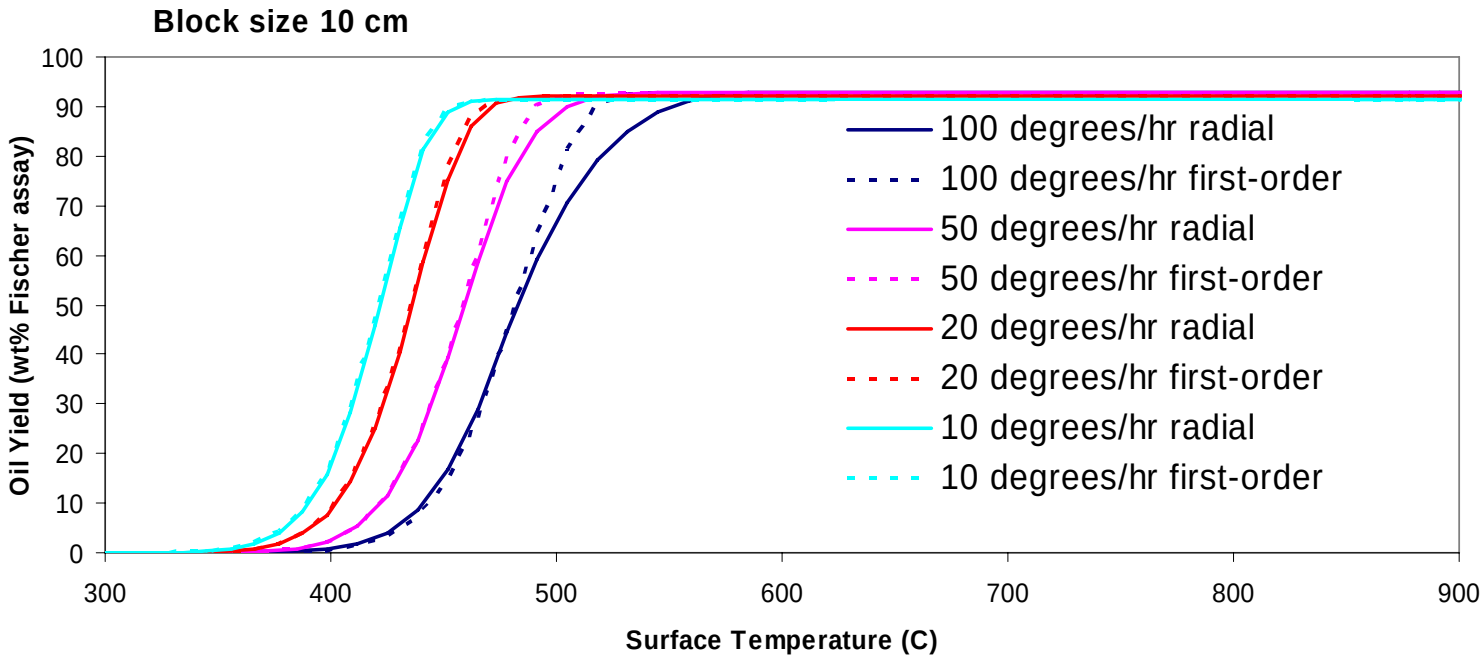
Oil Yield vs Time for 2.5 cm Blocks



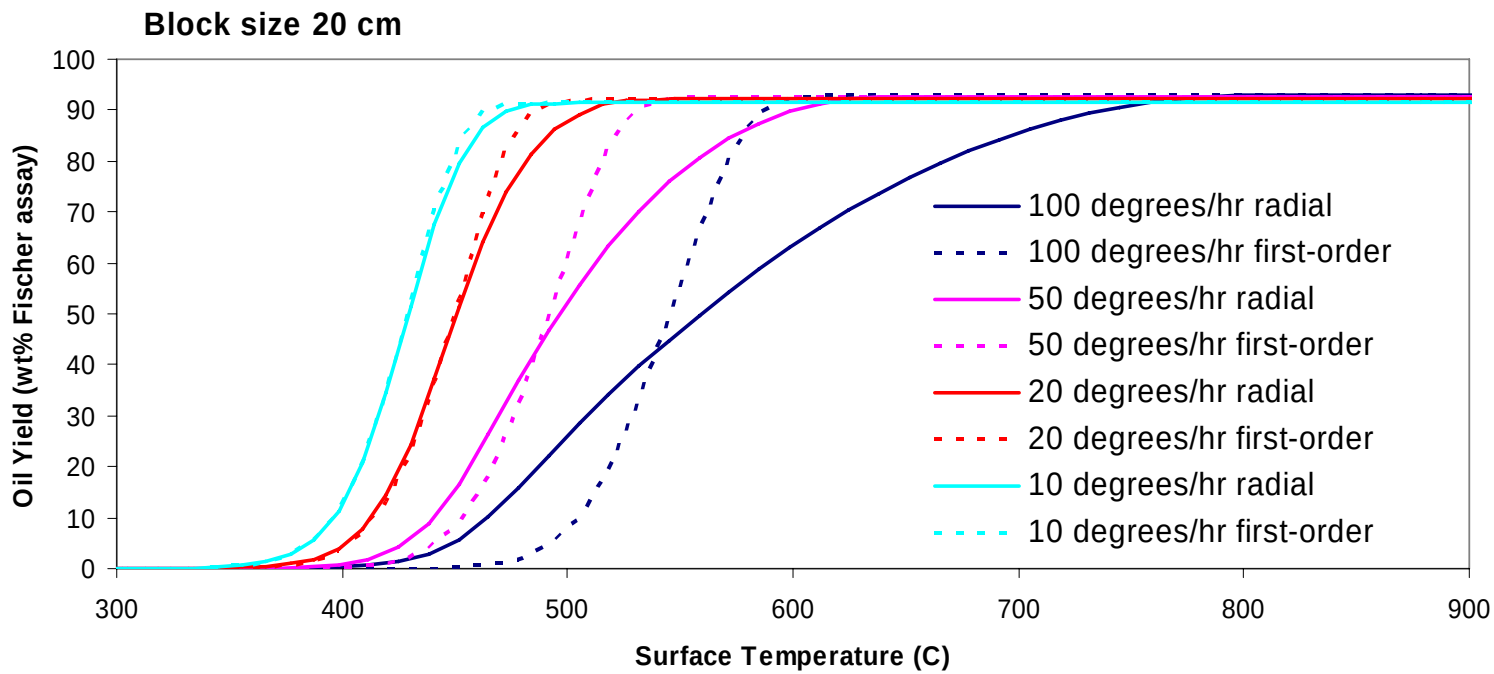
Oil Yield vs Time for 5 cm Blocks



Oil Yield vs Time for 10 cm Blocks



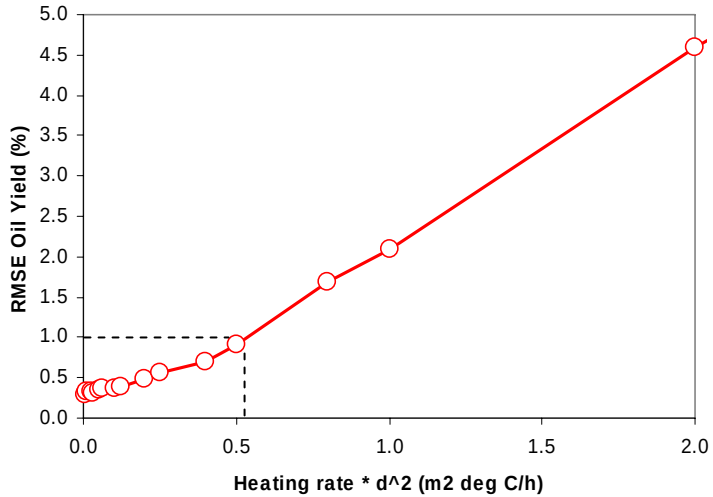
Oil Yield vs Time for 20 cm Blocks



Conclusions

- RMSE deviation between oil yield for first-order and radial models increases with heating rate and d_{eff}^2
- Deviation is <1% if

  d_{eff}^2 x heating rate < 0.5 m^2 deg / h



- For block sizes and heating rates within this limit, the first-order heat/mass transfer approach provides comparable accuracy with much less computation effort and the ability to efficiently model a distribution of block sizes