Low-Order Modeling of Biomass Particle Mixing and Reaction in a Bubbling-Bed Fast Pyrolysis Reactor

Gavin Wiggins (ORNL)
Stuart Daw (ORNL)
Jack Halow (Separation Design)

AIChE 2014 Annual Meeting
Thursday, Nov. 20, 2014

Computational Pyrolysis Consortium
http://energy.ornl.gov/cpc

Separation Design Group
Technology for a Sustainable Energy Future

Oak Ridge National Laboratory

Background

The work presented here is part of the Computational Pyrolysis Consortium (CPC), a multi-lab activity sponsored by DOE's Bioenergy Technologies Office (BETO).

The main goal of the CPC is to develop computational tools that support the assessment of advanced catalytic technologies for producing infrastructure compatible transportation fuels from biomass-derived pyrolysis oils.

Oak Ridge National Laboratory

NREL National Renewable Energy Laboratory

Pacific Northwest National Laboratory

INL Idaho National Laboratory

Argonne National Laboratory

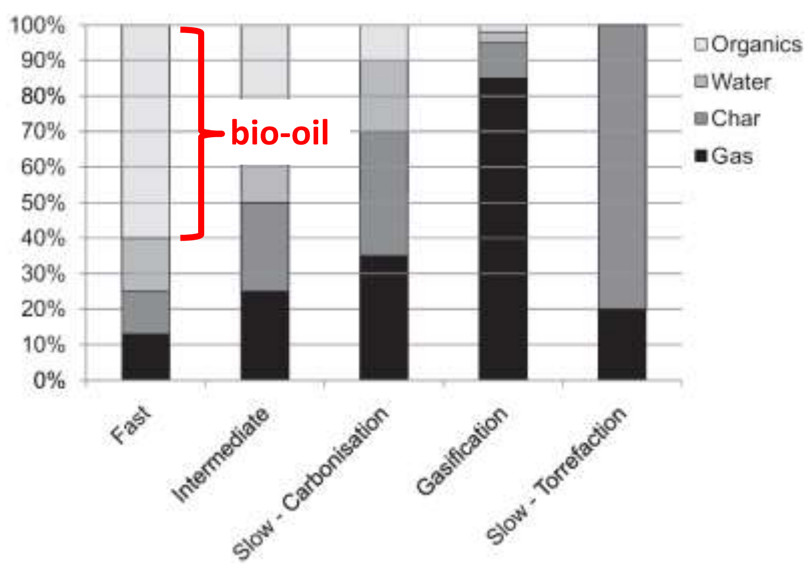
CPC Computational Pyrolysis Consortium

Fast pyrolysis of biomass

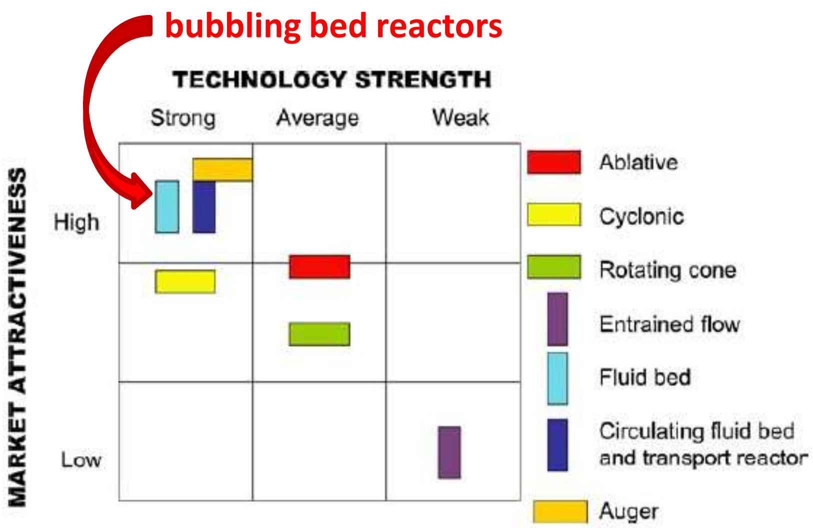
Pyrolysis involves rapid heating of biomass in the absence of air or oxygen to produce noncondensable gases, solid char, and liquid.

Goal of **fast pyrolysis** is to maximize the production of liquid yield (a.k.a. bio-oil or tar).

The liquid can be stored and transported, and used for energy, chemicals or as an energy carrier. [*Bridgwater 2012*]



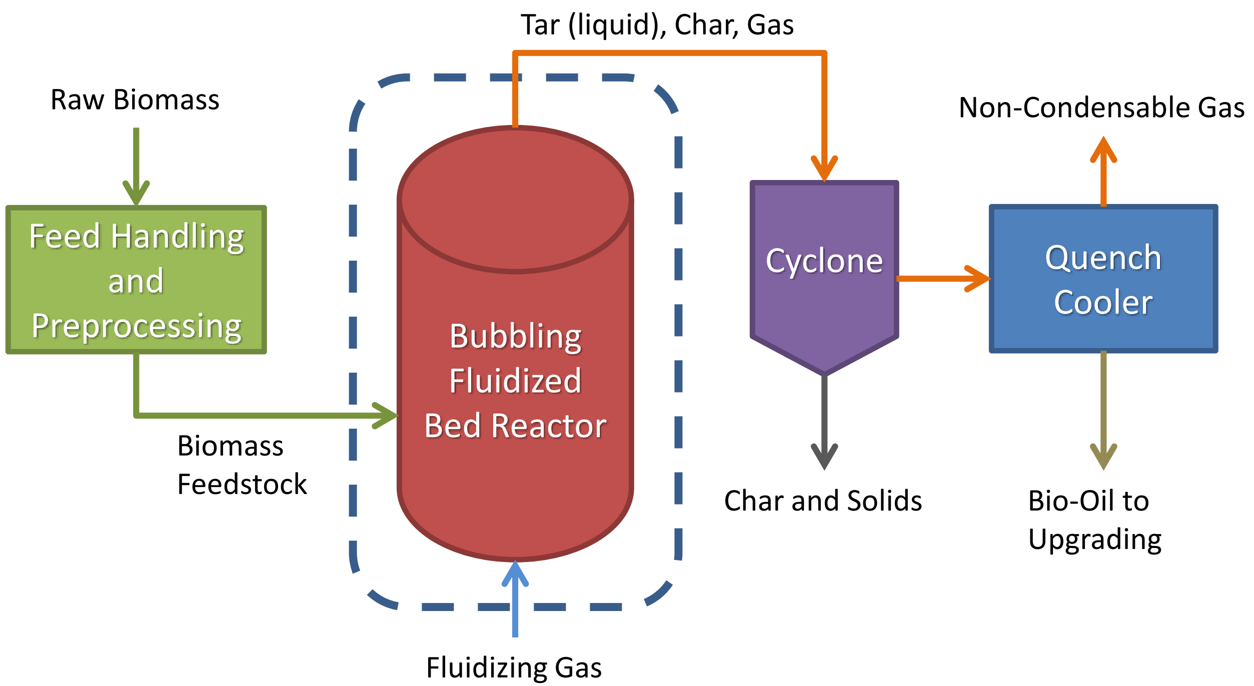
Product distribution from different types of pyrolysis, *Source: Bridgwater 2012*



Commercial potential of fast pyrolysis technologies, *Source: Butler 2011*

Bubbling bed reactors are widely used for fast pyrolysis

- Geldart Group B (sand) bed particles with or without catalysts
- Bed fluidized under no-oxygen conditions
- Raw biomass injected as particles and removed as char
- Biomass typically < 1% of bed mass
- Bed temperature 425-600°C
- Very **rapid heating rate** (up to 1,000°C/s)
- **Mixing and particle RTD** very important to product composition and conversion



Objectives

- Create low-order reactor models (LORM) with the following characteristics
  - fast-executing (can be run on a desktop computer)
  - open-source tool for the broader pyrolysis community
  - account for rate-limiting steps
    - particle-scale mixing
    - heat and mass transfer
    - secondary reactions (including catalytic) of the released pyrolysis gases

- Configure those models to facilitate rapid screening of process and scale-up options for industry and research community

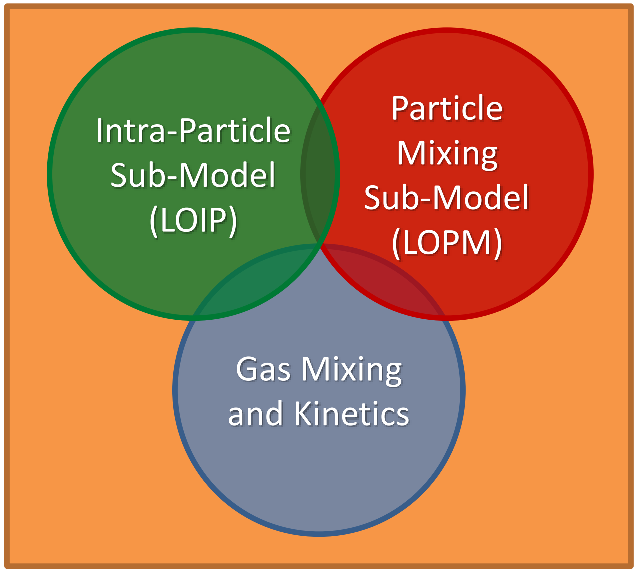
Modeling Approach

focus of today's discussion

Create the following models:

- Sub-model for intra-particle biomass heat-up and reaction
- Statistical biomass particle mixing sub-model
- Gas-phase reaction/convection sub-model for released gases
- Diffusion/boundary layer sub-model for pyrolysis products
- Global reactor model to integrate the sub-models

Integrated Low-Order Reactor Model (LORM)



Biomass Particle-Scale Modeling Challenges

Literature on intra-particle kinetics is inconsistent , typically available for limited experiments.

[*Chan 1985, Di Blasi 1993, Babu 2003, Gronli 2000, Kersten 2005, Prakash 2008, Shafizadeh 1982*]

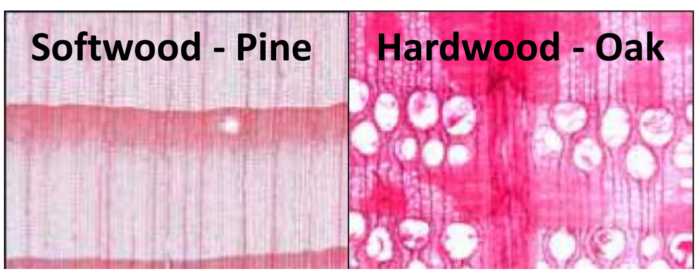
Available pyrolysis models treat biomass particles as “one” size, but grinders and mills often produce broad distributions of sizes.

[*Di Blasi 2002, Bryden 2002, Chaurasia 2003, Cui 2007, Galgano 2003, Galgano 2004, Gronli 2000, Haseli 2011, Janse 2000, Koufopanos 1991, Kung 1972, Larfeldt 2000, Miao 2011, Papadikis 2009*]

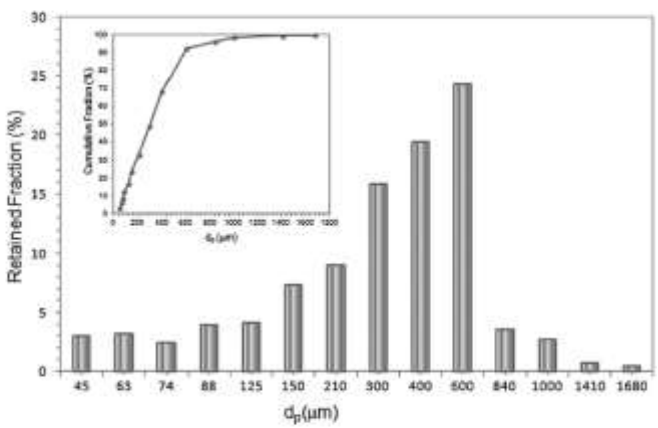
Particle surface boundary conditions are highly complex. [Papadikis2010]

Biomass is typically anisotropic and inhomogeneous with wide variations among different species.

[*Chaurasia 2003, Babu 2004, Gronli 2000, Haseli 2011, Koufopanos 1991, Kung 1972, Larfeldt 2000, Okekunle 2011, Papadikis 2010, Prakash 2009, Pyle 1984, Sadhukhan 2009*]



Source: Wood Handbook 2010



Size distribution for Douglas fir wood chips ground in a hammer mill at 1.6 mm screen size, *Source: Tannous 2013*

Low-Order Intra-Particle (LOIP) Model

Particle Heat-Up

- Most important temperature gradients are along narrowest dimension
- Approximate heat-up as 1-D conduction with average properties and simple B.C.

$$\rho C_p \frac{\partial T}{\partial t} = \frac{1}{r^b}\frac{\partial}{\partial r}\left(k\, r^b \frac{\partial T}{\partial r}\right) + g$$

$$k \left.\frac{\partial T}{\partial r}\right|_{r=R} = h\,(T_\infty - T_R)$$

$$\left.\frac{\partial T}{\partial r}\right|_{r=0} = 0$$

where ρ *= density (kg/m*^{3}*)*

C_p *= heat capacity (J / kg·K)*

k *= thermal conductivity (W / m·K)*

T *= temperature (K)*

T_∞ *= ambient temperature (K)*

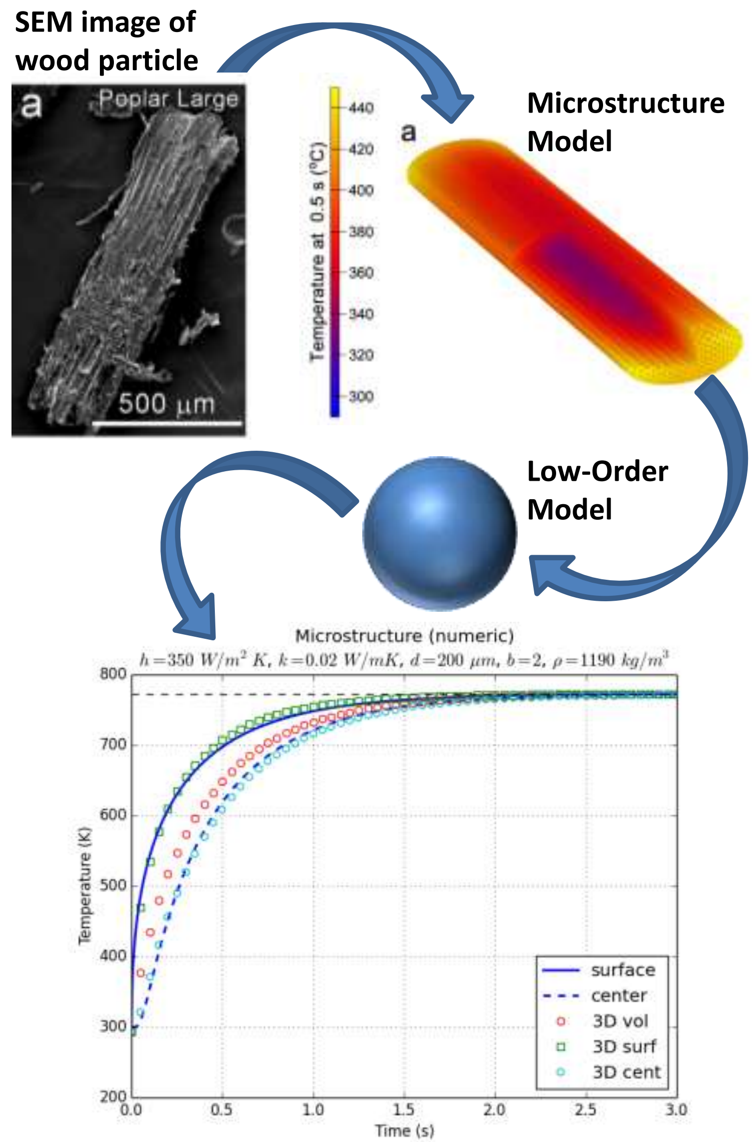
T_R *= surface temperature (K)*

r *= radius (m)*

b *= shape factor of 0=slab, 1=cylinder, 2=sphere*

g *= heat generation (W/m*^{3}*)*

h *= heat transfer coefficient (W / m*^{2}*·K)*

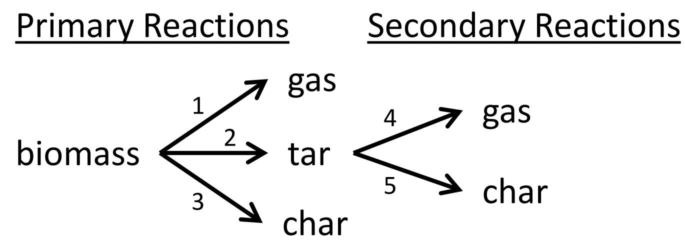


Temperature profile of 3-D microstructure model (NREL) and low-order intra-particle model. Heat transfer via surface convection and conduction only.

LOIP kinetics are based on available data

Available kinetics are typically very simplified

- Primary and secondary reactions produce gas, tar (condensable liquid or bio-oil), and char
- Non-condensable gases
  - light gases such as H_2, CO, CO_2, H_2O, CH_4, etc.
- Condensable volatiles
  - heavy organics and inorganics
  - vapors and aerosols react within and/or outside particle
- Char as solid residue
- Typically 1st order Arrhenius



Chan1985 and Blasi1993 kinetic parameters

Reaction	A (1/s)	E (kJ/mol)
1	1.3e8	140
2	2e8	133
3	1.08e7	121
4	4.28e6	108
5	1e6	108

$$K = A\,e^{-E/(RT)}$$

$$r = K \cdot \rho_i$$

$$\rho_f = \rho_i + r \cdot \Delta t$$

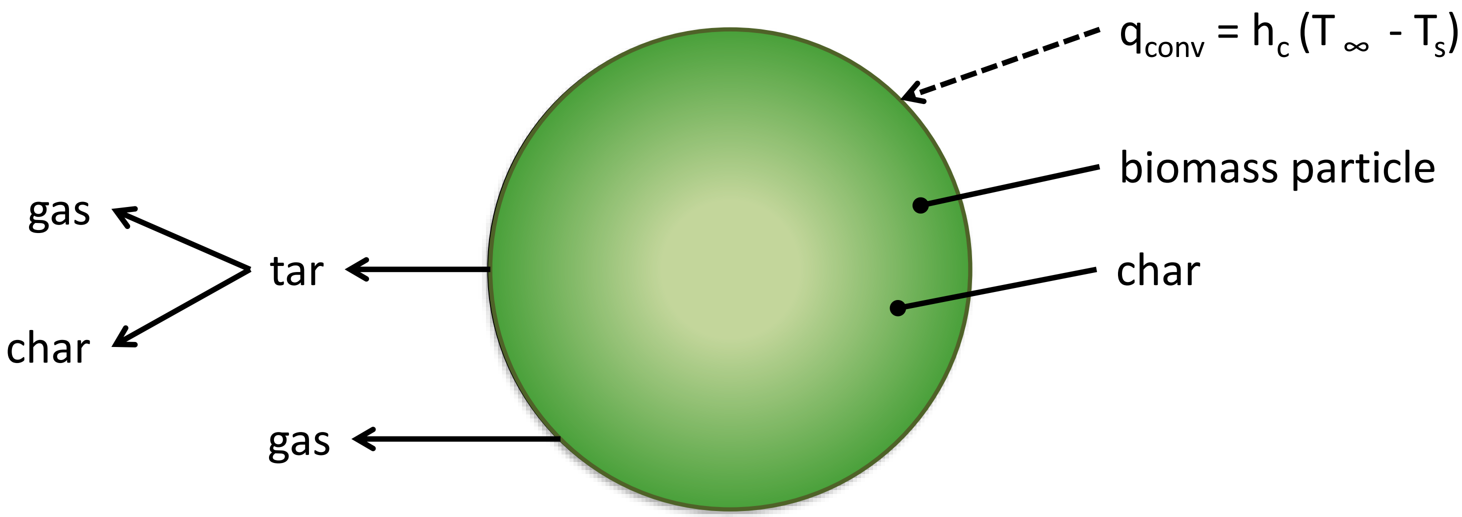
where K = rate constant (1/s)
A = pre-factor (1/s)
E = activation energy (kJ/mol)
R = universal gas constant (kJ / mol·K)
r = reaction rate (ρ/s)
ρ = concentration (kg/m³)
Δt = time step (s)

LOIP model is configured to allow multiple user specified kinetics and internal transport schemes to account for future improvements in kinetic information.

Other LOIP Assumptions

- Particle does not shrink or expand during pyrolysis
- Thermal properties (c_p, k) vary with temperature
- Catalytic effects of ash are neglected
- Gases immediately leave the particle
- Effects of mass transport are not accounted for

Will be implemented in future models.

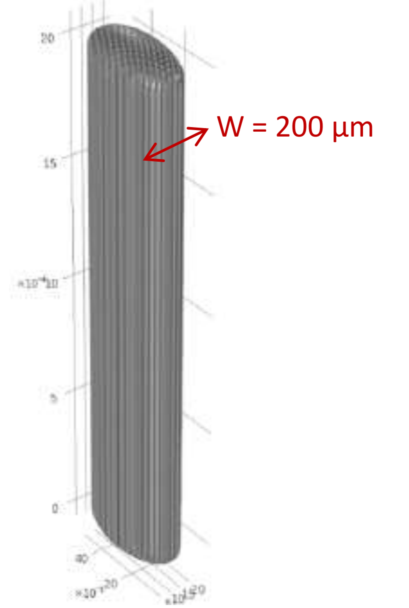


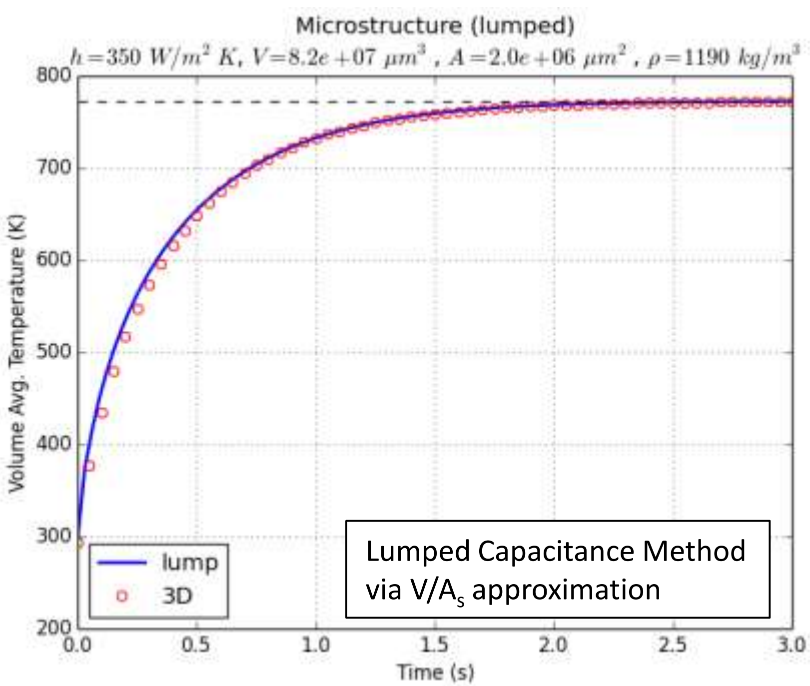
T_∞ = 425-600°C (698-873K)

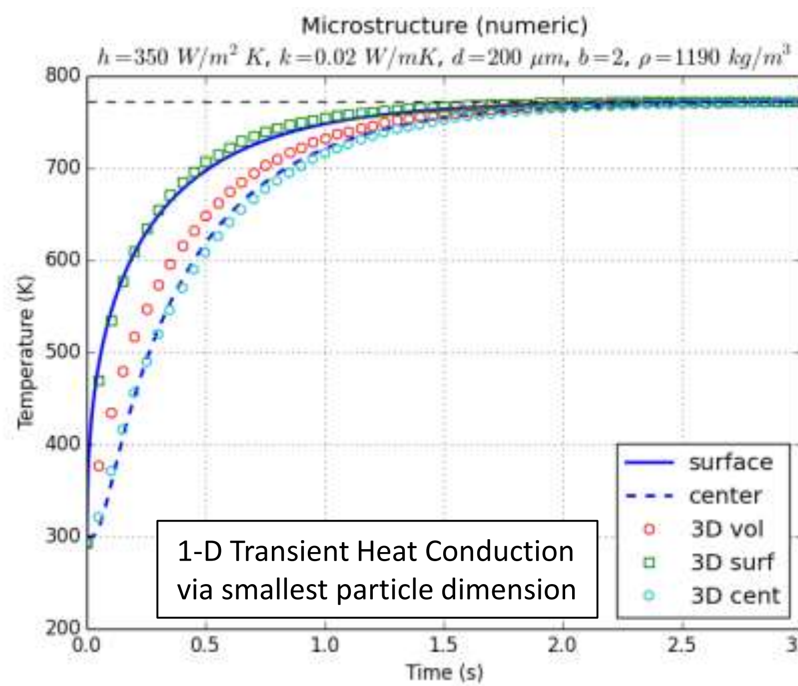
LOIP appears to reasonably approximate 3D heat-up

Low-order vs 3-D Microstructure Model

- Lumped capacitance method agrees with volume avg. 3-D temperature profile for skeletal density of 1190 kg/m^3
- 1-D numerical approach provides good agreement using minimum particle width, spherical shape factor, and k_{eff} value same as N_2 gas
- Lumped method approximated by V/A_s , 1-D transient heat conduction approximated via smallest particle dimension





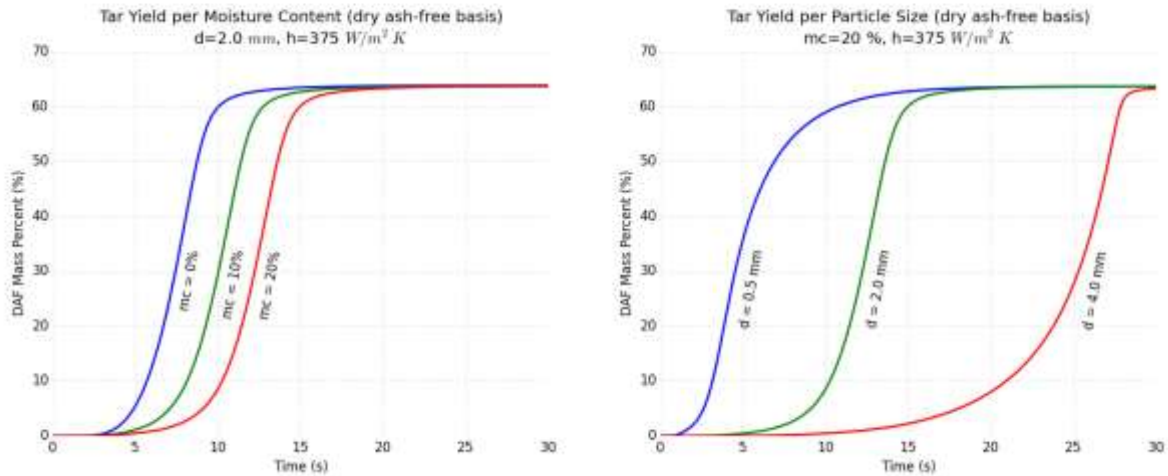


LOIP heat transfer and kinetics reveal important trends

Trends from 1-D transient heat conduction model.

Best Case Scenarios: Offers a liquid yield of ≈64% for a dry 2.0 mm spherical particle. As particle size increases, time to reach peak liquid yield increases.

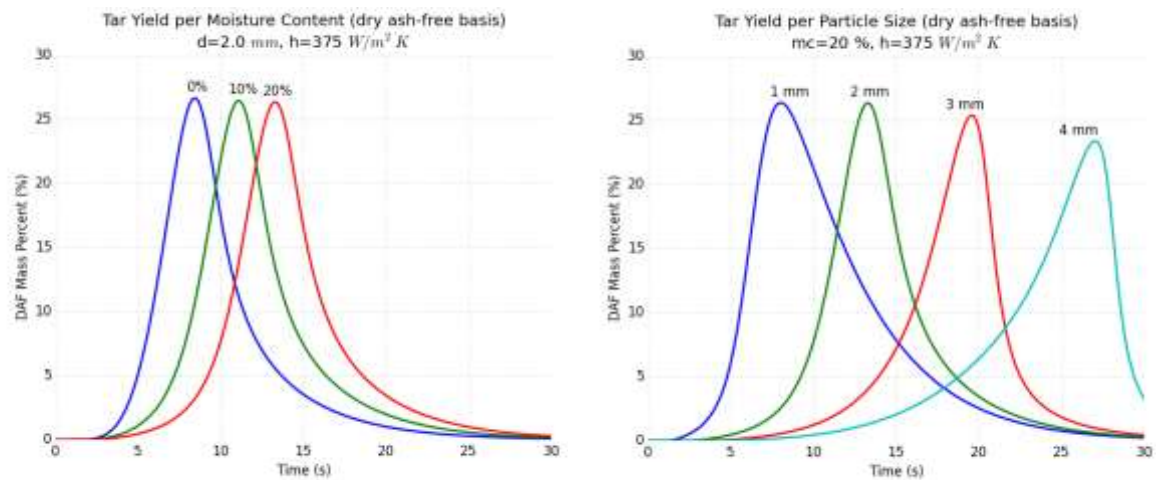
Primary Reactions



Tar yield (aka liquid or bio-oil yield) at different moisture contents (Left) and particle sizes (Right). Represents optimal liquid yield (no secondary reactions) where vapor and gas immediately leave particle.

Worst Case Scenarios: Drastically decreases max liquid yield to ≈27% for a dry 2.0 mm spherical particle. As particle size increases, time to reach peak liquid increases while the max yield decreases.

Primary+Secondary Reactions



Tar yield at different moisture contents (Left) and particle sizes (Right). Represents the effect of secondary reactions cracking tar to gas and char.

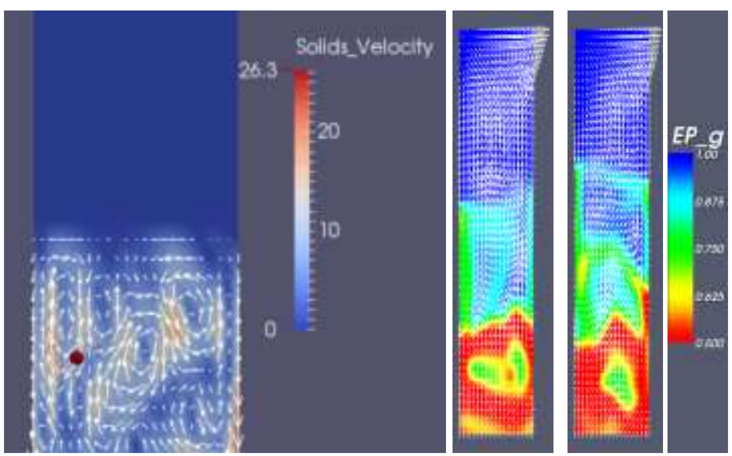
Particle and Gas Mixing Challenges

Turbulent mixing of biomass particles in bubbling beds is highly complex.
[*Xiong 2013, Papadikis 2010, Radmanesh 2005*]

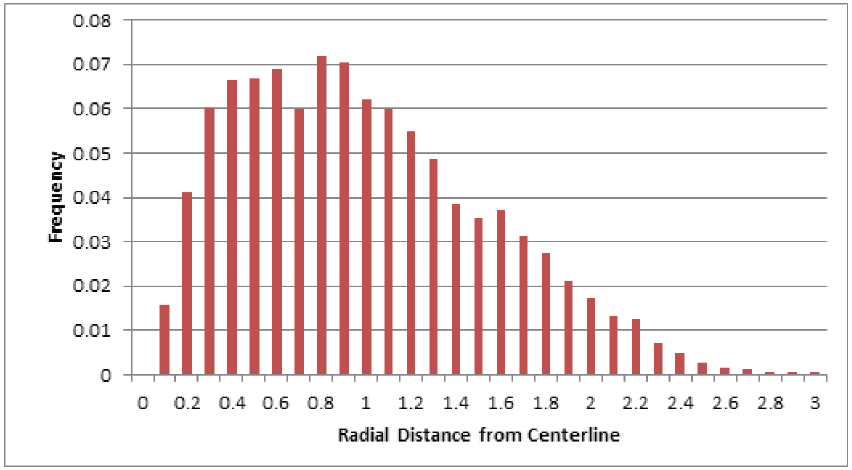
Mixing depends on particle properties (size, density) and local flow conditions and involves recirculation and segregation.
[*Di Blasi 2008, Cui 2007, Wang 2005, Kunii 1991*]

Internal temperature and concentration gradients can be significant as reactor scale increases.

Detailed CFD simulations of mixing require high computational overhead and time, which increase with reactor scale.
[*Mellin 2014, Papadikis 2009*]



MFIX simulation of pyrolysis bubbling bed - (Left) solids velocity cm/s and (Right) particle void fraction.



Radial distribution for entire bed of particles in an experimental fluidized bed, *Source: Separation Design Group*.

Low-Order Particle Mixing (LOPM) Model

Langevin Model

$$m\frac{d^2x}{dt^2} = -\lambda\frac{dx}{dt} + \eta(t)$$

where x = distance, t = time, m = particle mass,
λ = friction coefficient,
$\eta(t)$ = stochastic perturbations

Paul Langevin
(1872-1946)

- Originally proposed by Paul Langevin to describe Brownian motion
  Langevin, Paul. "Sur la théorie du mouvement brownien." CR Acad. Sci. Paris 146.530-533 (1908)

- We propose a modified version of this model for biomass particles in bubbling beds for the **vertical direction**

$$m\,\frac{d^2z}{dt^2} = -\lambda\,\frac{dz}{dt} + f_s + f_{t_z}$$

where f_s = mean segregation force in axial direction, f_{tz} = turbulence force in axial direction

- A similar force balance can be written for **horizontal particle position** except that we assume no time-average drag or gravitational forces

$$m\,\frac{d^2h}{dt^2} = -\lambda\,\frac{dh}{dt} + f_c + f_{t_h}$$

where f_c = horizontal force via convection toward wall, f_{th} = turbulence force in horizontal direction

The LOPM is formulated as a random walk

- Approximating derivatives over discrete time intervals and combining and rearranging terms for **vertical motion**

$$z(t+1) = a \cdot z(t) + b \cdot z(t-1) + c + s_z(t)$$

where $z(t)$ = axial position at time t, $s_z(t)$ = turbulence term, Gaussian distributed
a, b, c = empirical parameters that reflect time average forces

- a, b, and c can be estimated with experimental particle position time series

- Stochastic inputs (s_z , s_r , s_h) can be estimated from stepwise prediction errors

- For **horizontal motion**

$$h(t+1) = a \cdot h(t) + b \cdot h(t-1) + s_r(t)\, g(z) + s_h(t)$$

where $h(t)$ = lateral position at time t, $s_r(t)$ = probability particles entrained in sideways convective flow
$g(z)$ = amplitude of local convective flows with height, $s_h(t)$ = small scale turbulence, Gaussian distribution
a, b = empirical parameters that reflect time average forces

- In vectorized form, the random walk can be applied to thousands of particles simultaneously and adjusted at each time step for changing particle properties

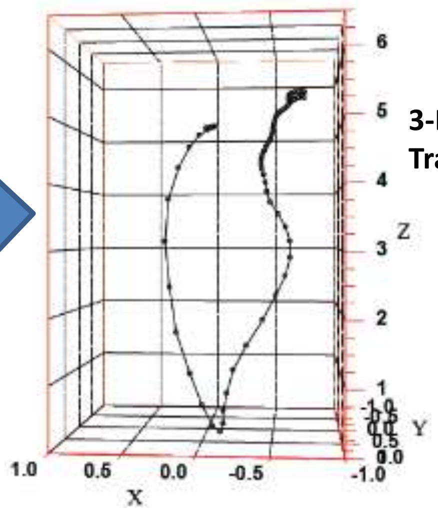
See Ind. Eng. Chem. Res., 2014, 53 (41), pp 15836–15844 for more details.

Experimental validation of LOPM predictions

- Simulated biomass (tracer) particles are constructed by inserting tiny neodymium magnets into balsa wood cylinders (typically > 1 mm diameter, 0.4-1 g/cc)
- Bed particles (207 µm glass, 2.5 g/cc) are fluidized with ambient air ($1.0 \leq U/U_{mf} \leq 5.0$)
- Single tracer particles are injected in bed at specific fluidization conditions and tracked
- Special algorithms de-convolute signals to give 3-D particle trajectory
- Experimental facility at Separation Design Group Lab, designed and operated by Jack Halow

Tracer Particle (simulated biomass particle)

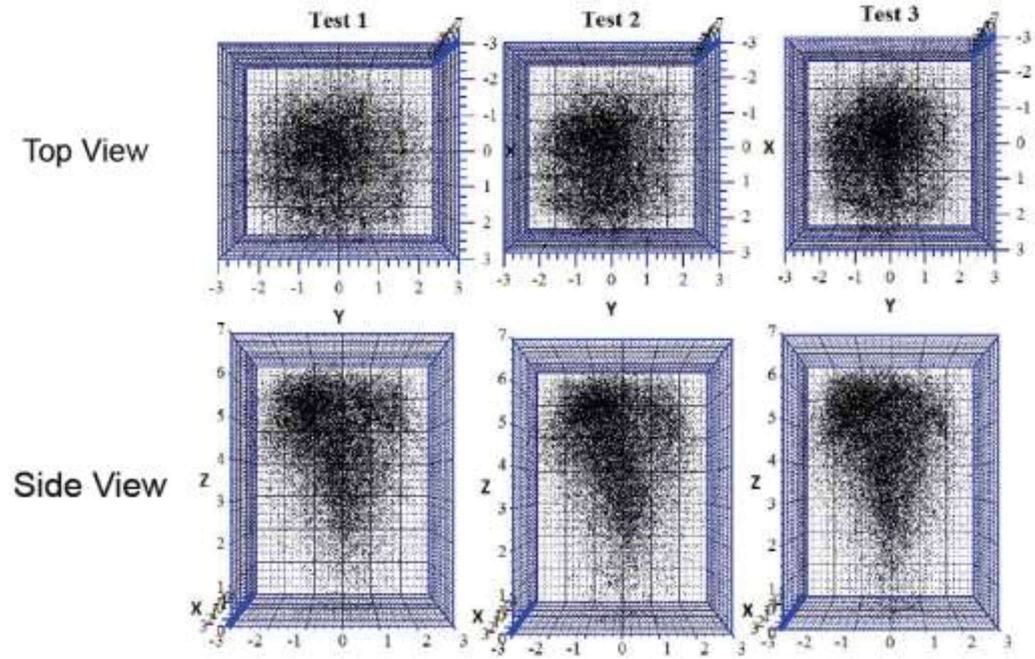
Experimental Setup



3-D particle Trajectory

Both LOPM & experiments yield particle RTDs

Trajectories map of 3-D time-average mixing.

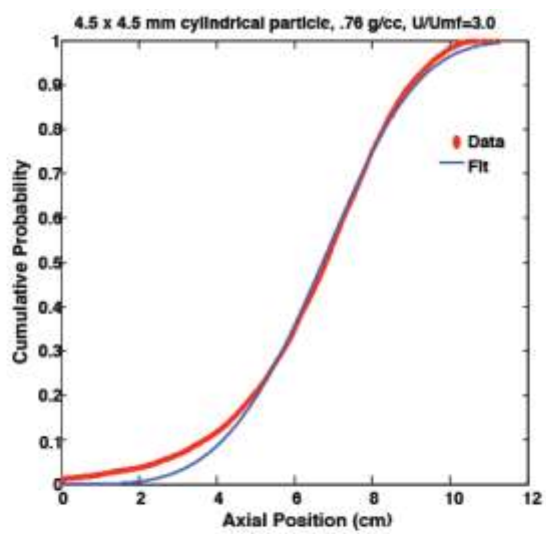


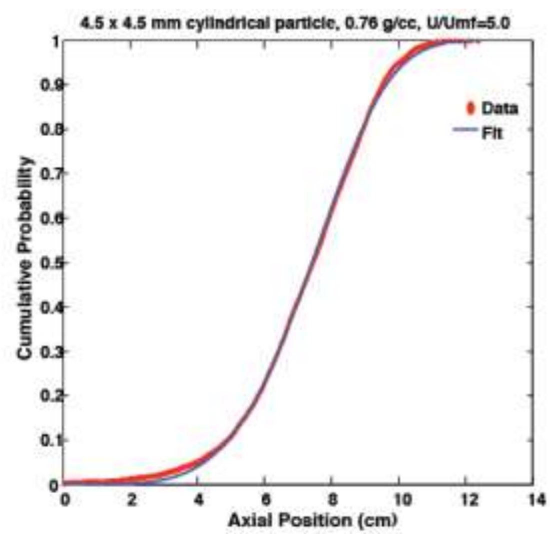
Vertical mixing profiles follow Weibull statistics.

$$f(z) = \frac{k}{\lambda}\left(\frac{z}{\lambda}\right)^{k-1} e^{-(z/\lambda)^k}$$

$$C(z) = 1 - e^{-(z/\lambda)^k}$$

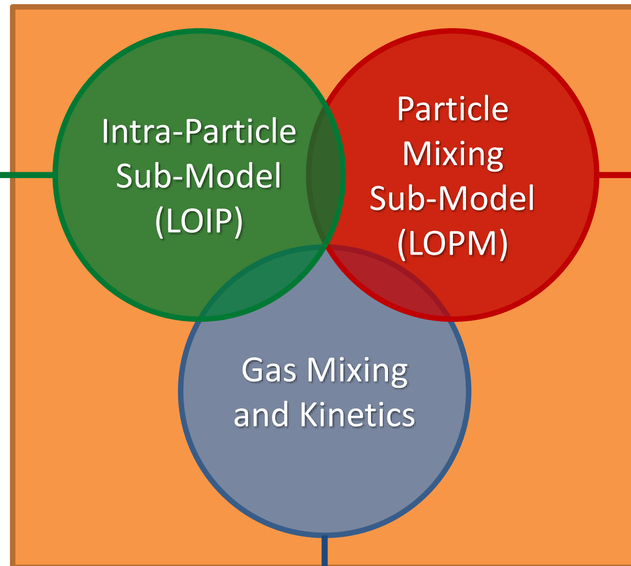
where $f(z)$ = probability density function
$C(z)$ = cumulative distribution function
k = shape parameter
λ = scale parameter
z = axial position

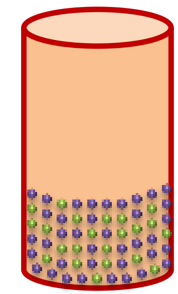




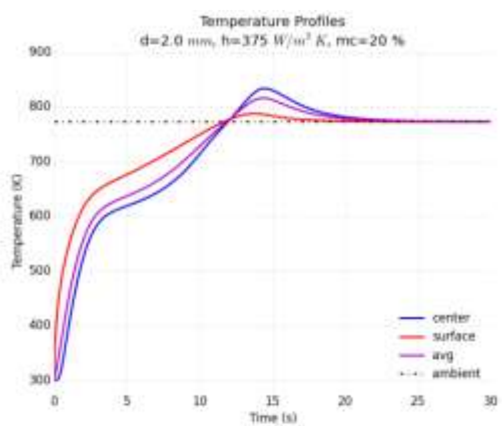
Integrated Pyrolysis Reactor Model

Integrated Low-Order Reactor Model (LORM)

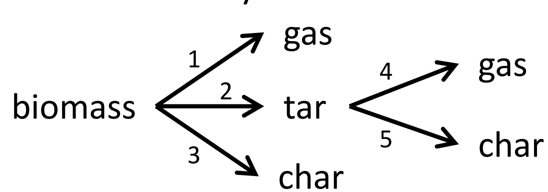




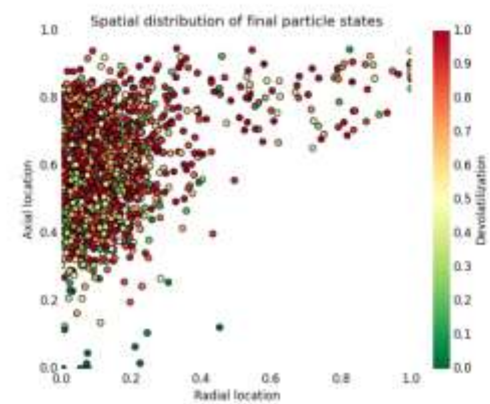
- heat transfer
- mass transport
- thermal properties
- physical characteristics
- moisture content



- chemical species
- devolatilization rate
- liquid yield
- secondary reactions



- fluidization scheme
- residence times
- reactor height / diameter
- bed height
- feedstock injection



- LOIP sub-model tracks gas release and evolution of multiple particle sizes
- LOPM sub-model mixes particles via random walk with changing parameters
- Released gases undergo further reaction and mixing before exiting reactor

Results of LOIP and LOPM studies to date

- Complex 3D intra-particle heat transfer appears to be reasonably well approximated by simplified 1D model with appropriate thermal property assumptions

- Available simple pyrolysis kinetics appear to yield realistic trends in liquid yield with particle size and moisture, but more detailed kinetics are needed to account for liquid product composition

- Biomass particle RTDs generated by simple random walks appear to be consistent with magnetic tracer measurements and exhibit Weibull statistics

- More experimental/CFD data are needed to correlate the random walk parameters with particle properties and fluidization conditions

Next Steps…

- Add more detailed intra-particle mass transfer and kinetics (Ranzi2008, 2013) to the LOIP

- Add improved estimates for the impact of particle properties on the LOPM random walk parameters (based on CFD and/or experiments)

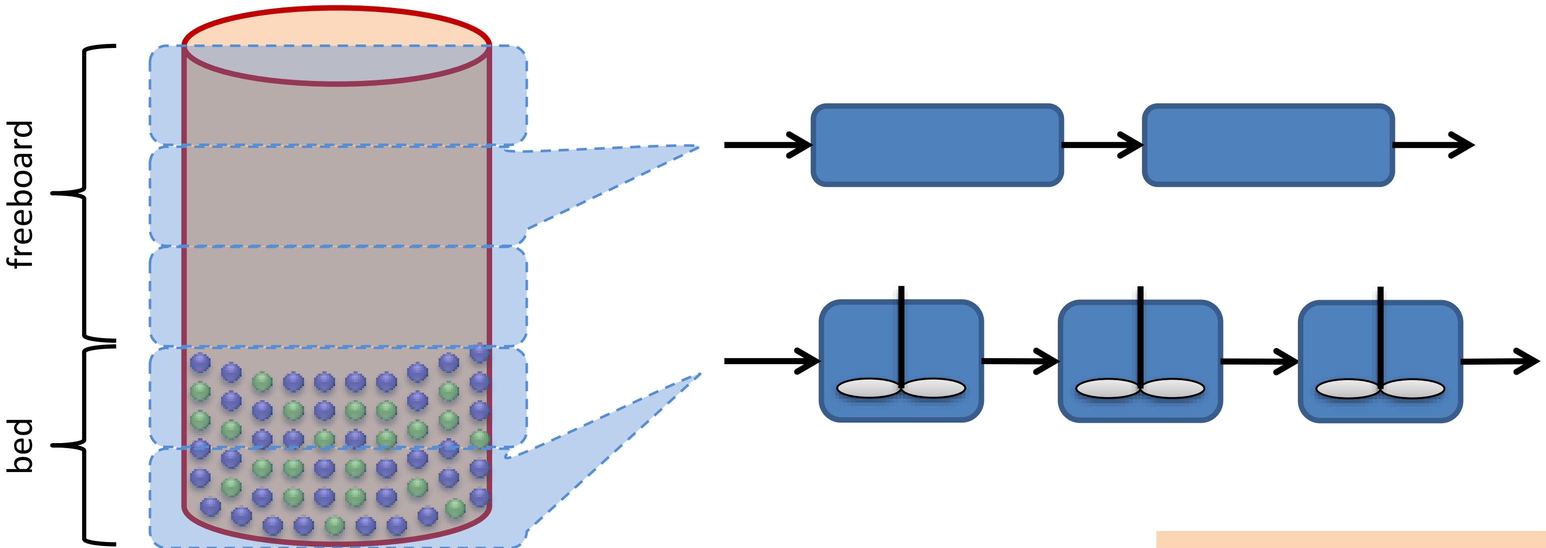
- Develop sensitivity trends (for operating, feedstock, and scale parameters) in raw bio-oil yield and quality from combined LOIP+LOPM simulations

- Compare above sensitivity predictions with available experimental lab and pilot data

- Conduct/select specific experiments needed to confirm prediction accuracy of models and better inform scale-up

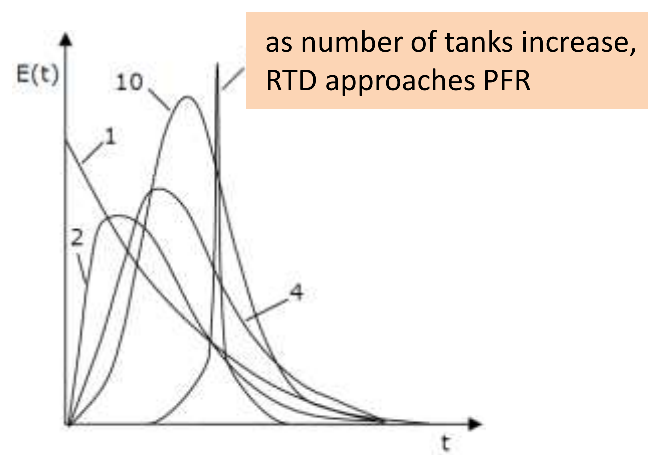
Next Steps…

- Model gas RTD as combination of PFRs and CSTRs based on CFD and experimental measurements



$$E(t) = \frac{t^{\,n-1}}{(n-1)!\,\tau_i^n}\, e^{-t/\tau_i}$$

where $E(t)$ *= residence time distribution function*
t *= time*
n *= reactors*
τ_i *= residence time in one of the reactors*



RTD for 1, 2, 4, 10 tanks and a PFR, *Source: Wittrup 2007*

Acknowledgements

Prasad Gupte: DOE Project Manager

U.S. Department of Energy, Bioenergy Technologies Office

Emilio Ramirez, Sreekanth Pannala, Charles Finney, Stuart Daw

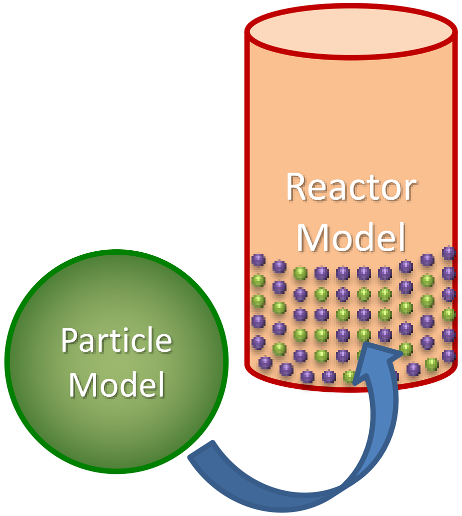
ORNL CPC Team Members

Collaborators

Peter Ciesielski, *National Renewable Energy Lab*

Victor Walker, Tyler Westover, *Idaho National Lab*

Jack Halow, *Separation Design Group*



Publications on the LOIP and LOPM sub-models are in process and supplemental information will be available on the CPC website.

Gavin Wiggins: wigginsg@ornl.gov

Computational
Pyrolysis
Consortium

CPC website: http://energy.ornl.gov/cpc

GitHub

Python code: https://github.com/pyrolysis

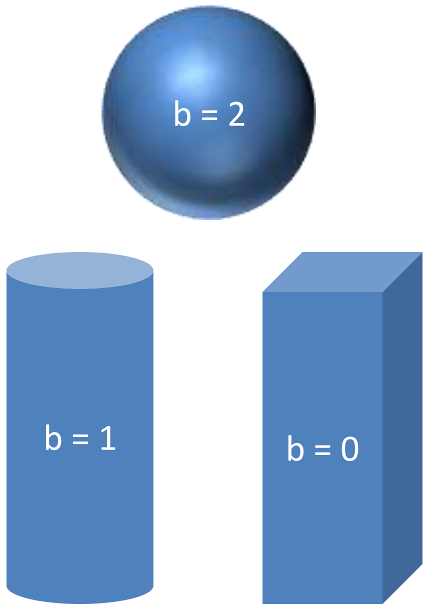
Backup Slides

Transient Heat Transfer Equations

Low-order Particle Models

- 1-D transient heat conduction

$$\rho\, c \frac{\partial T}{\partial t} = \frac{1}{r^b}\frac{\partial}{\partial r}\left(k\, r^b \frac{\partial T}{\partial r}\right) + g$$



- Lumped capacitance method (Bi < 0.1)

$$\frac{\theta}{\theta_i} = \frac{T - T_\infty}{T_i - T_\infty} = \exp(-Bi \cdot Fo)$$

$$Bi = \frac{h\, L_c}{k}$$

- Improved lumped capacitance method (Bi <= 20)

$$\theta_p = \exp\left(-\frac{1}{\frac{m+1}{m+3} Bi + 1} Bi\, Fo\right)$$

$$Fo = \frac{\alpha\, t}{{L_c}^2}$$

Source: Keshavarz 2006

Parameters and Assumptions

3-D Models	Low-order Models
volume and density of sphere and shell are equal, $\rho = 540\ kg/m^3$	
microstructure density represented as cell wall density	
heat transfer via conduction and convection at surface (no kinetic reactions)	
$k = 0.12\ W/m\cdot K$	shell diameter as average of L+W
$C_p = (103.1+3.86*T)\ J/kg\cdot K$	$k = 0.12$ (wood) - 0.02 (N_2 gas) $W/m\cdot K$
identical thermal capacity	$C_p = (103.1+3.86*T)\ J/kg\cdot K$
spatial distribution of mass	

V_A (solid) < V_B

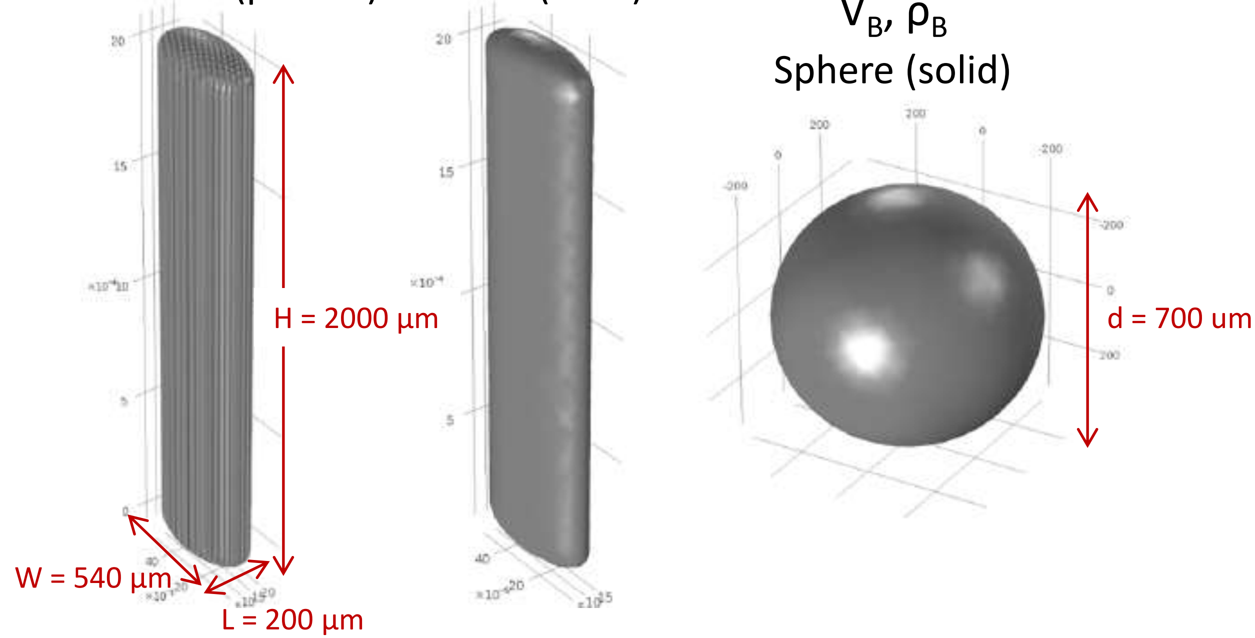
mass = $V_A\,\rho_A = V_B\,\rho_B$

$\rho_A = V_B\,\rho_B / V_A$

V_A, ρ_A Microstructure (porous)

V_B, ρ_B Shell (solid)

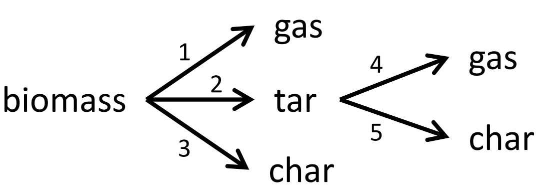
V_B, ρ_B Sphere (solid)



Particle parameters affect pyrolysis yields thru the reaction steps

Even the simplest proposed kinetic schemes involve both parallel and sequential competing reactions.

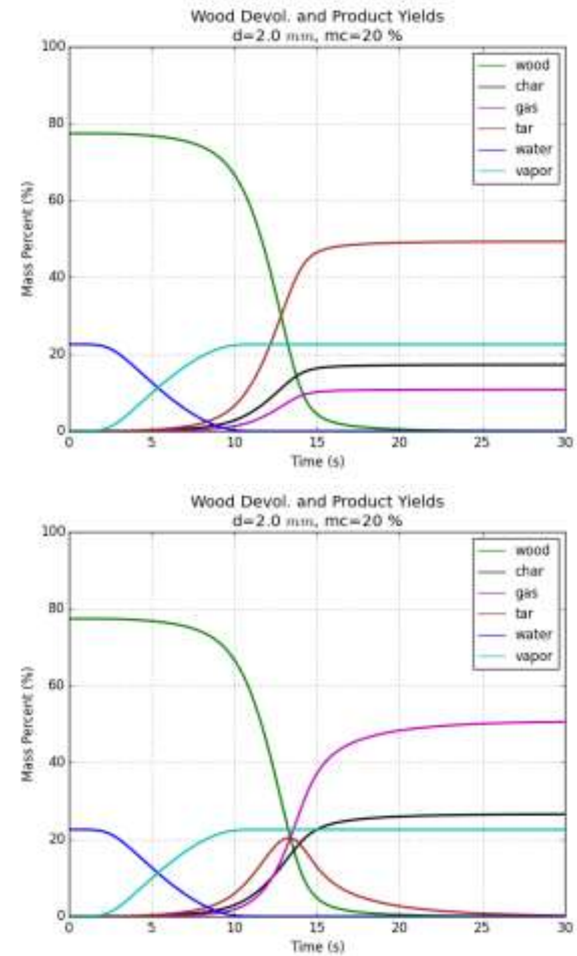
Primary Reactions   Secondary Reactions



Reaction	A (1/s)	E (kJ/mol)
1	1.3e8	140
2	2e8	133
3	1.08e7	121
4	4.28e6	108
5	1e6	108

Best Case Scenarios: Liquid yield is high if the optimal tar formation temperature is reached quickly and the tar products escape quickly from the particle and encounter no further char or catalysts in the reactor to drive the secondary reactions.

Worst Case Scenarios: Liquid yield is low if tar formation is slow (vs. the primary gas and char reactions) and/or the initial tar has opportunities to crack within or outside the particle. Particle mass transport and reactor mixing determine the importance of the secondary reactions.

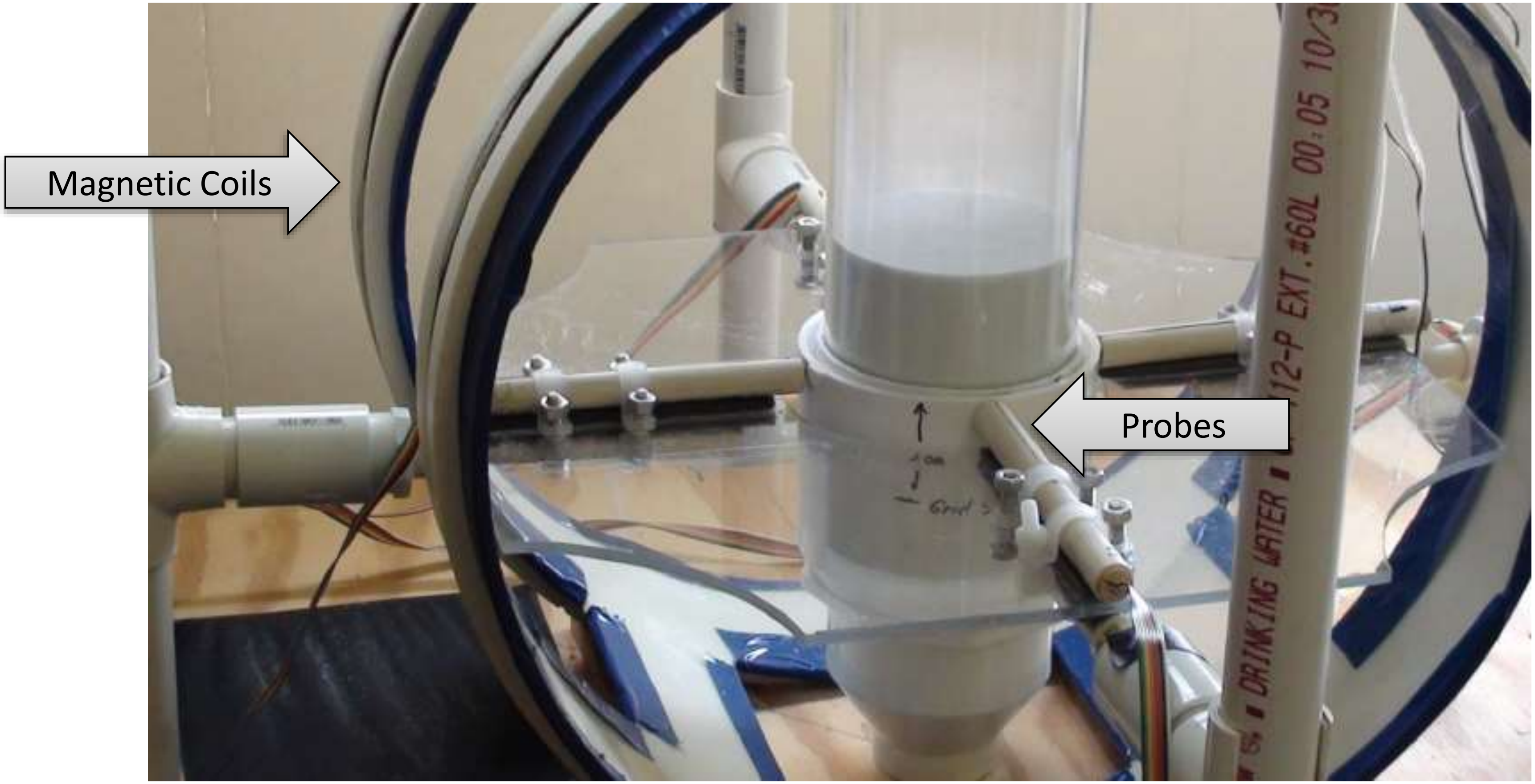


Wood devolatilization and product yields for 2 mm particle at 20% moisture content.

(Top) Optimal conditions within particle
(Bottom) Worst-case scenario

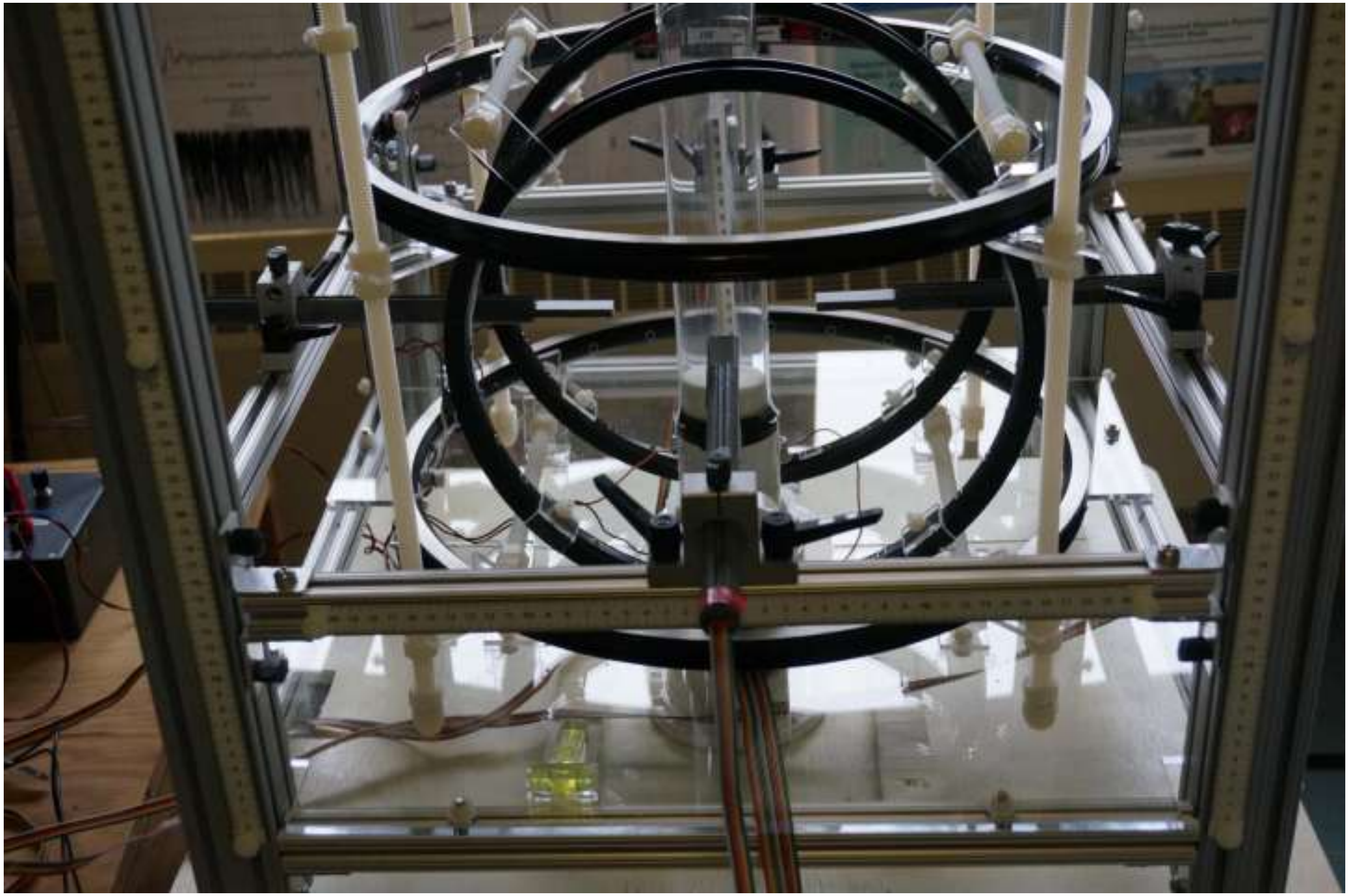
Experimental Setup

- Probes aligned North, South, East, West
- Helmholtz coils modify earth's magnetic field in bed
- Non-metallic bed and supports
- 100 Hz sampling rate, 5 minute runs (30,000 data points)
- Porous plate distributor

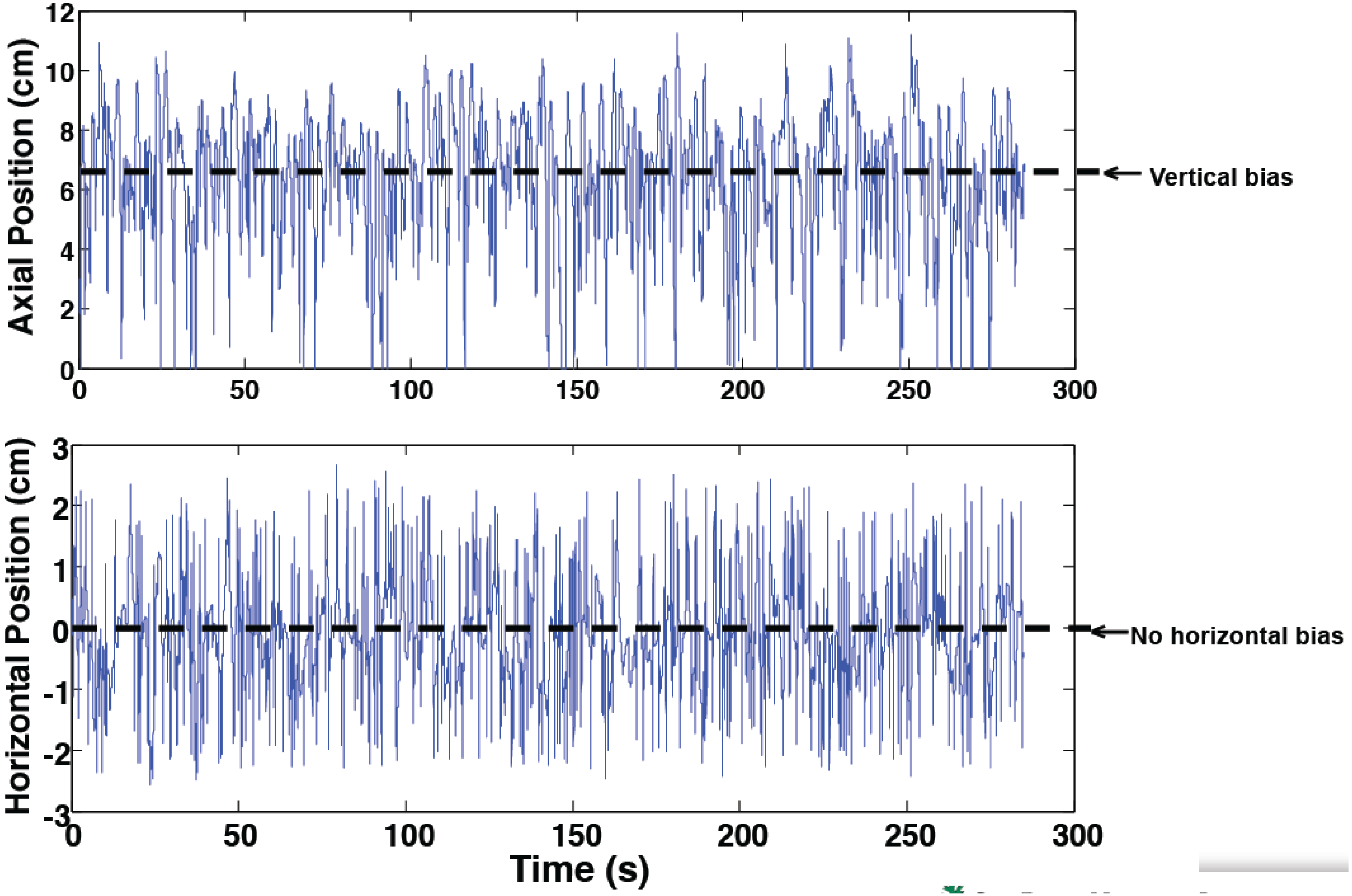


Experimental Setup

Experimental Setup

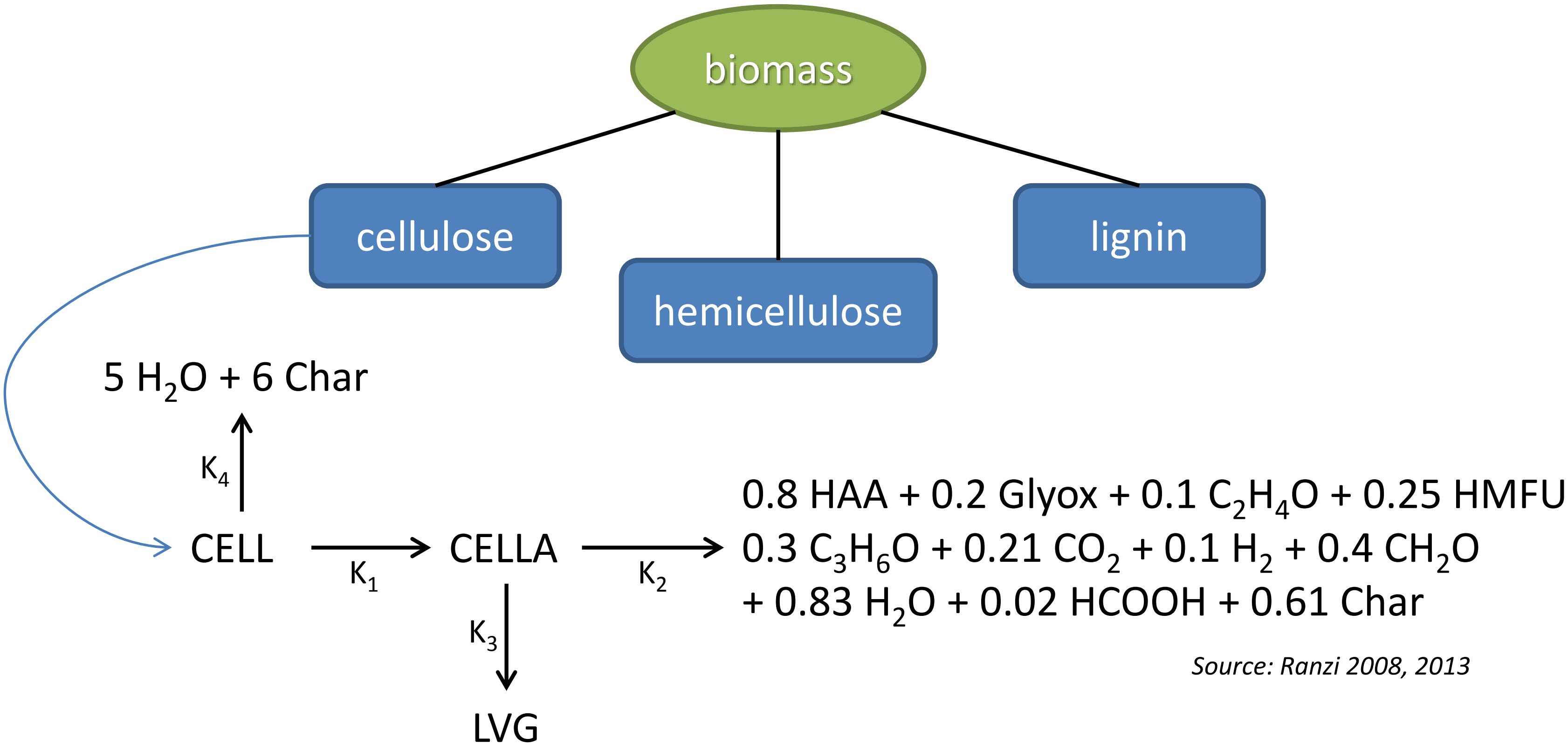


Time series data reveal particle motion dynamics



Next Steps…

- Couple the Ranzi kinetic scheme to the heat transfer model to estimate chemical species from biomass pyrolysis



Source: Ranzi 2008, 2013

- Develop an appropriate definition for the “diameter” or “size” of a wood particle that is used for pyrolysis modeling

Computational Pyrolysis Consortium (CPC)

CPC

Members of the Consortium

Oak Ridge National Laboratory

- Coordination of the CPC team with industry advisors and university partners
- CFD of biomass pyrolysis reactors
- Low-order models for pyrolysis and upgrading reactors
- Multi-stage model integration

NREL National Renewable Energy Laboratory

- Micro-to-pilot-scale reactor data
- Biomass particle-scale reaction and transport models
- Catalytic vapor-phase kinetic models
- CFD of vapor-phase catalytic upgrading
- Identification of critical TEA inputs

Pacific Northwest National Laboratory

- Hydro-treating and aqueous upgrading catalyst data
- Non-polar and polar liquid phase catalytic kinetic models
- Integrated liquid catalytic reactor models
- Identification of critical TEA inputs

INL Idaho National Laboratory

- Biomass feedstock characterization tools and data
- Model component and data sharing/archiving mechanism

Argonne National Laboratory

- Vapor-phase catalytic molecular energetics
- Fundamental bio-oil vapor thermodynamic properties
- Identification of potential catalysts for vapor-phase upgrading

Assess the commercial feasibility of advanced catalytic technologies for producing infrastructure compatible transportation fuels from biomass-derived pyrolysis oils.