Particle-scale computational modeling of woody biomass pyrolysis

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Computational
Pyrolysis
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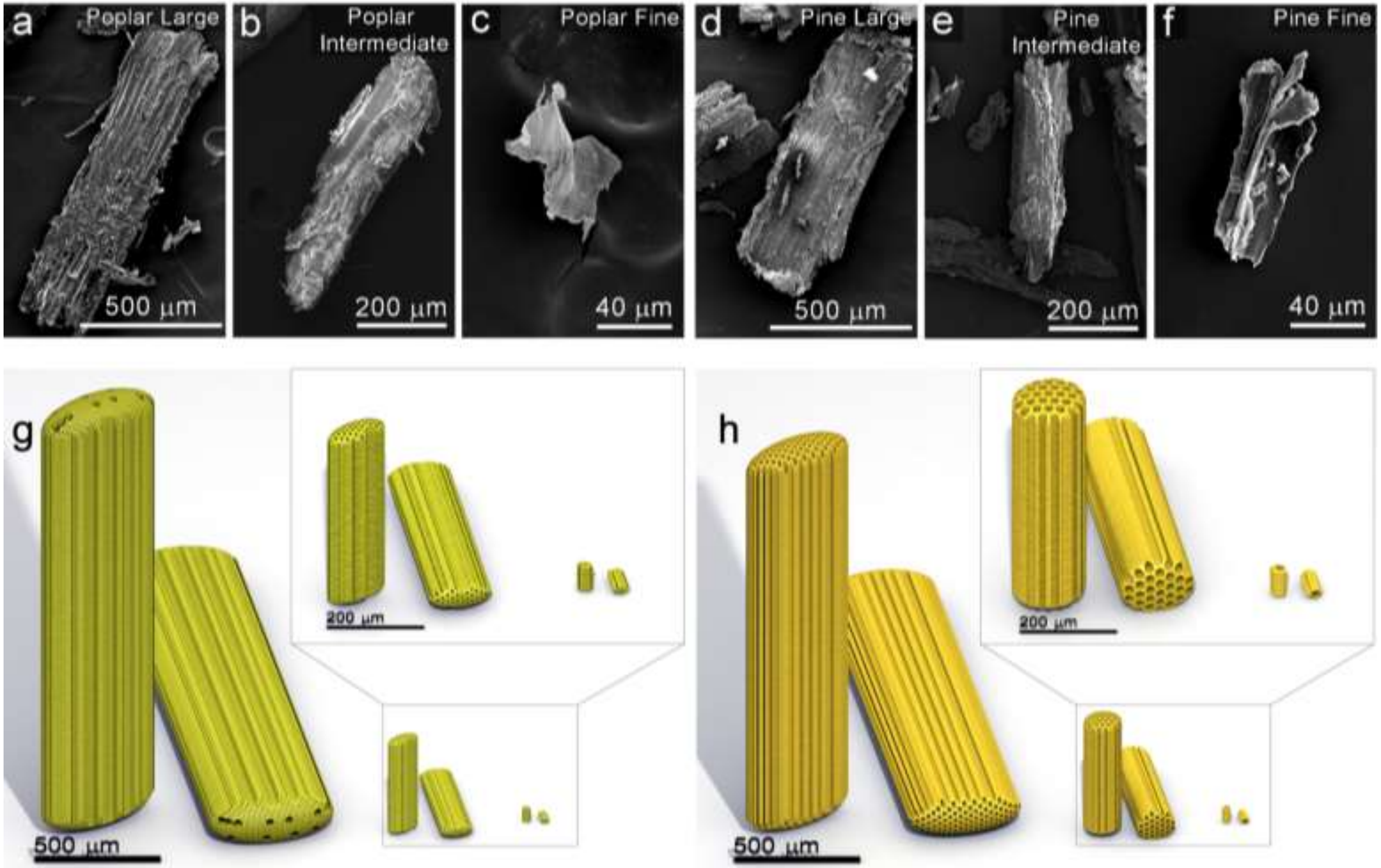
Problem Statement

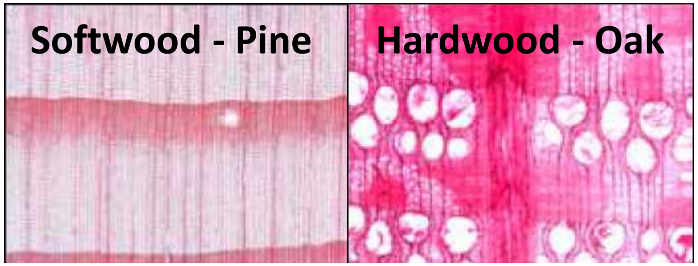
Anisotropic and inhomogeneous properties of wood must be considered to accurately predict intra-particle pyrolysis of wood particles.



Ciesielski, et. al. “Biomass Particle Models with Realistic Morphology and Resolved Microstructure for Simulations of Intra-Particle Transport Phenomena” *Submitted*

Background & Motivation

- Anisotropic and inhomogeneous properties of wood are often not accounted for in low-order models *[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

- Reactor models frequently ignore temperature gradients in large biomass particles *[Cui 2007, Souza-Santos 2010]*

- Kinetic schemes for pyrolysis do not determine the "quality" of liquid yield (a.k.a. tar or bio-oil) *[Bradbury 1979, Chan 1985, Di Blasi 1993, Babu 2003, Di Blasi 2008, Bryden 2002, Gronli 2000, Haseli 2011, Janse 2000, Kersten 2005, Kersten 2013, Koufopanos 1991, Kung 1972, Prakash 2008, Pyle 1984, Thurner 1981]*

- Pyrolysis models treat wood particles as "one" size, ignoring particle size distributions from wood grinders and mills *[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]*

Background & Motivation

- Literature on intra-particle kinetics is inconsistent , various publications offer different kinetic schemes which are typically valid only for a particular experiment
  [*Chan 1985, Di Blasi 1993, Babu 2003, Gronli 2000, Kersten 2005, Prakash 2008, Shafizadeh 1982*]

- 1-D models in literature frequently validate with experimental data for particle sizes > 6 mm, whereas typical size for fast pyrolysis in fluidized bed reactors is < 6 mm
  [*Chan 1985, Di Blasi 2003, Bridgwater 2012, Galgano 2006, Gaston 2011, Gronli 2000, Koufopanos 1991, Meier 2013, Pyle 1984, Rath 2002, Sadhukhan 2009, Trendewicz 2014*]

- Literature does not report explicit kinetic parameters for different wood types and it is not clear whether the same reaction pathways apply to all wood species
  [Di Blasi 2000, Antal 1995, Calonaci 2010, Kersten 2005, Kersten 2013, Prakash 2008, Shafizadeh 1982, Thurner 1981]

- Validating a specific kinetic scheme could be a major contribution

Objectives

- Accurately predict the pyrolysis of a biomass particle without using expensive HPC resources

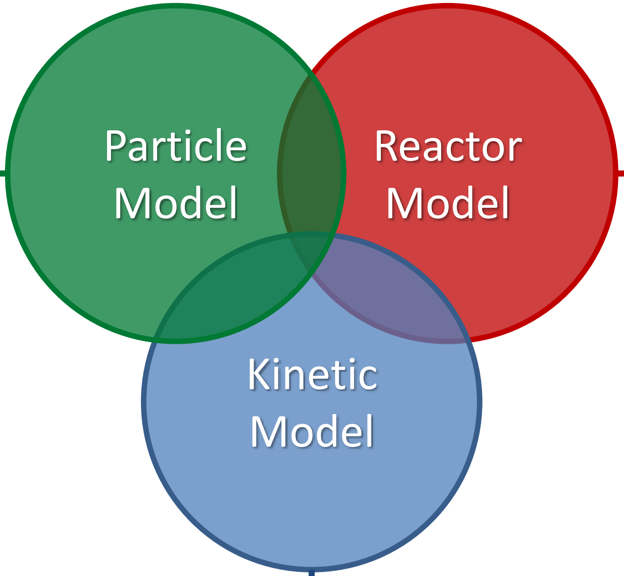
- Couple kinetic reactions to the low-order particle model to enhance reactor models

- Determine effects of wood properties and reactor environment on bio-oil yield and quality

- Use detailed 3-D microstructure models (NREL) to validate and improve low-order particle models for heat transfer in biomass particles at fast pyrolysis conditions

- Quantify the uncertainties associated with assumptions made for low-order particle models

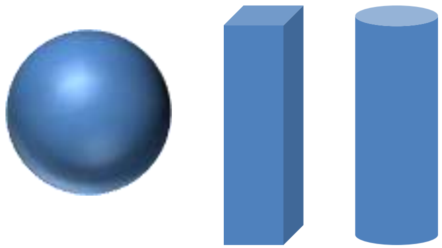
Areas of Pyrolysis Modeling


Particle Model

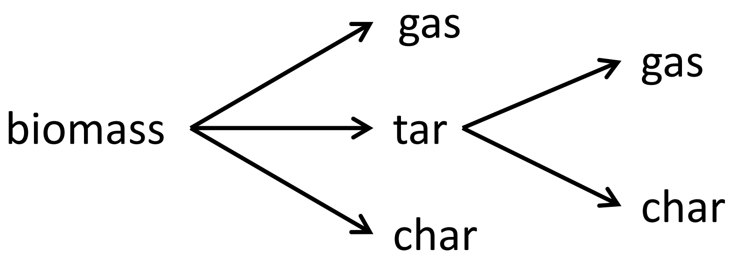
Reactor Model

Kinetic Model

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



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


biomass

gas

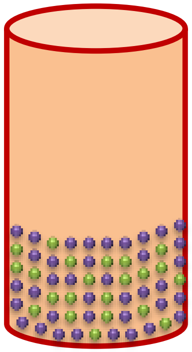
tar

char

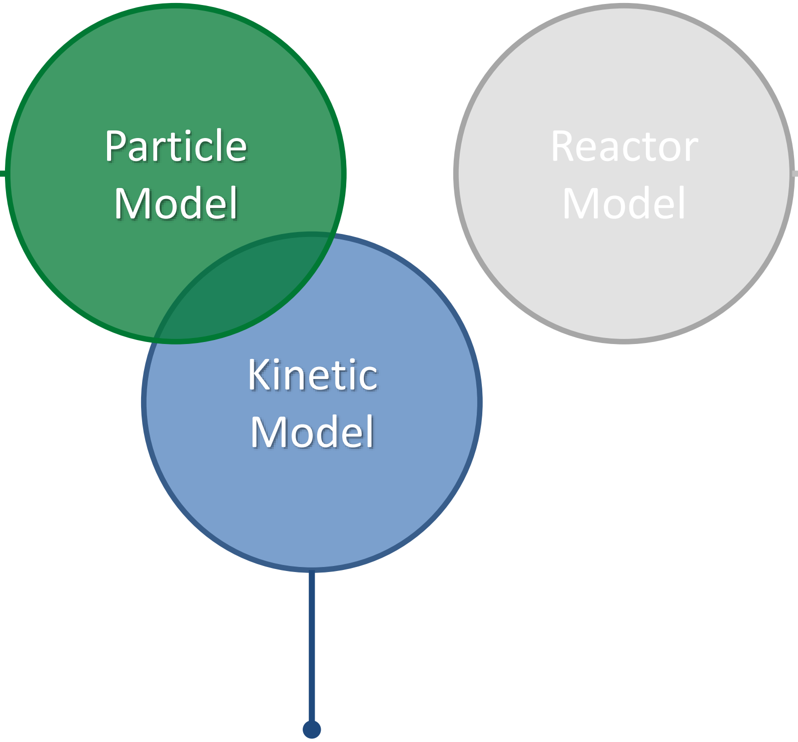
gas

char

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



Current Focus



- heat transfer
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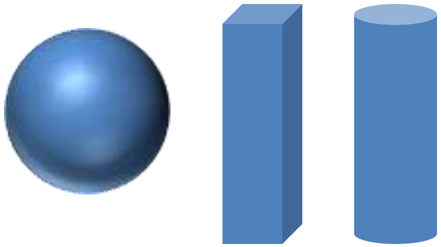

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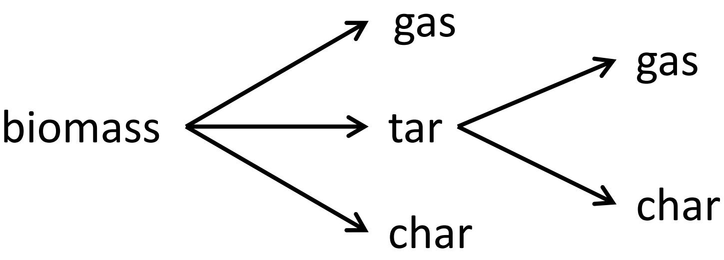

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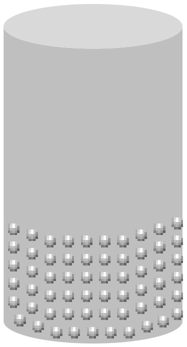
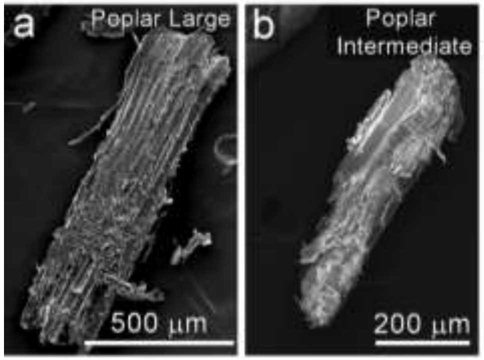
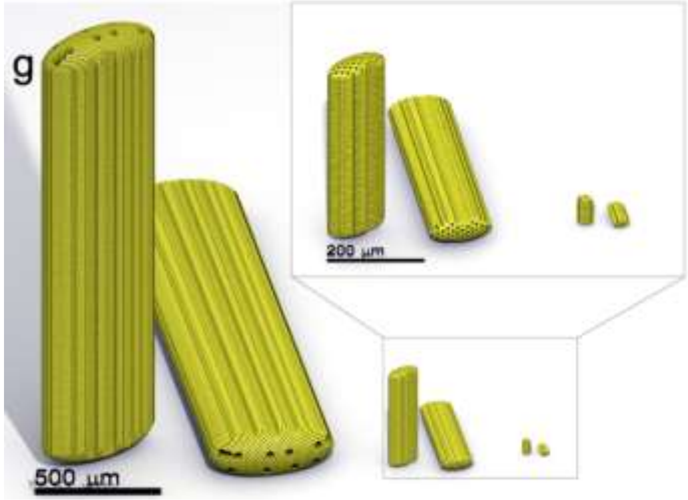


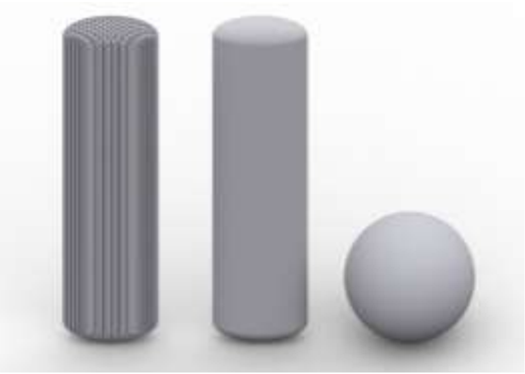
Validate Low-order Models with 3-D Models

Micrographs of wood particles

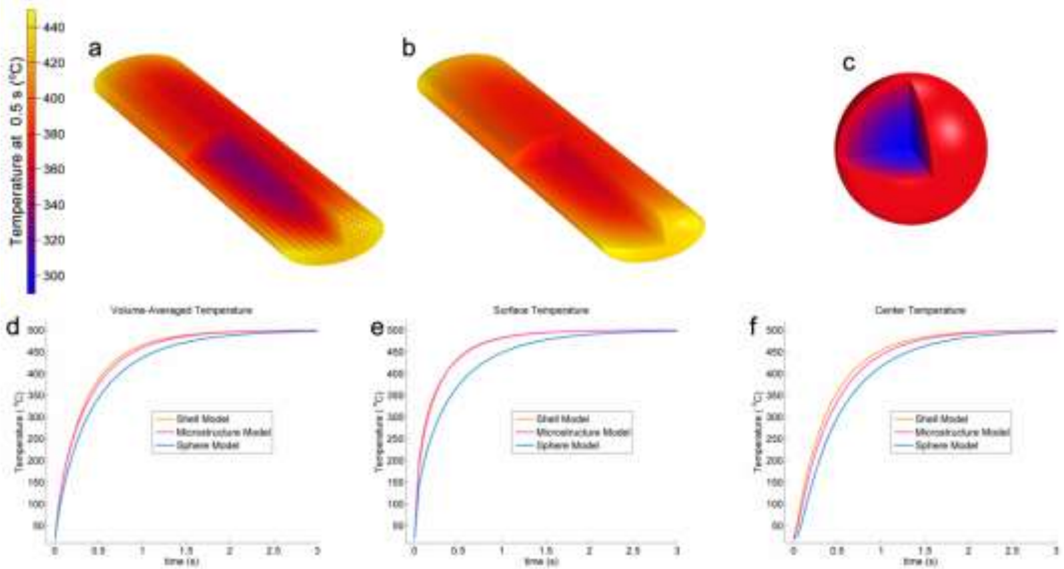


Construct 3-D particle geometries from imaging and analysis

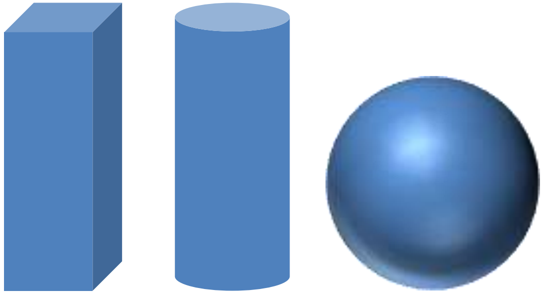




Analyze 3-D particle models at fast pyrolysis conditions



Validate and compare 3-D model results with low-order models



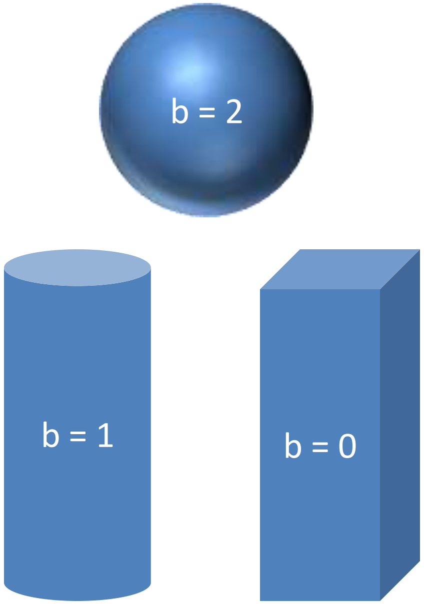
Ciesielski, et. al. "Biomass Particle Models with Realistic Morphology and Resolved Microstructure for Simulations of Intra-Particle Transport Phenomena" *Submitted*

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)

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

- Improved lumped capacitance method (Bi <= 20)

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

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

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

Source: Keshavarz 2006

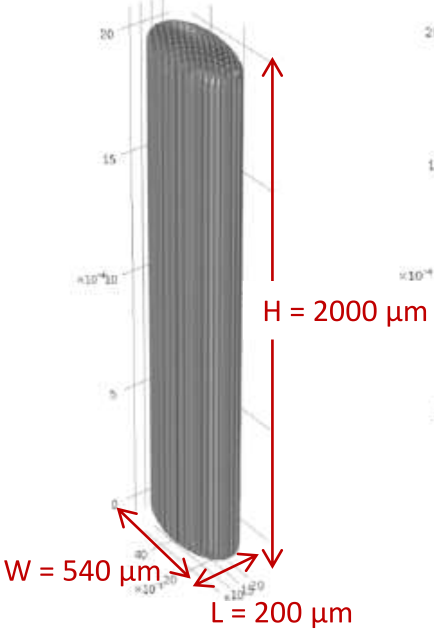
Parameters and Assumptions

3-D Models	**Low-order Models**
volume and density of sphere and shell are equal, ρ = 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·K	shell diameter as average of L+W
C_p = (103.1+3.86*T) J/kg·K	k = 0.12 (wood) - 0.02 (N_2 gas) W/m·K
identical thermal capacity	C_p = (103.1+3.86*T) J/kg·K
spatial distribution of mass	

V_A (solid) < V_B

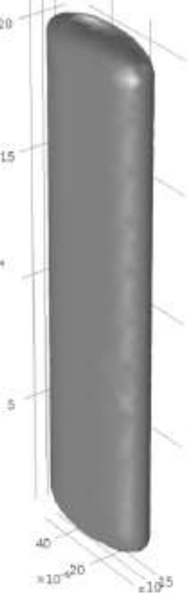
mass = $V_A\ \rho_A = V_B\ \rho_B$

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



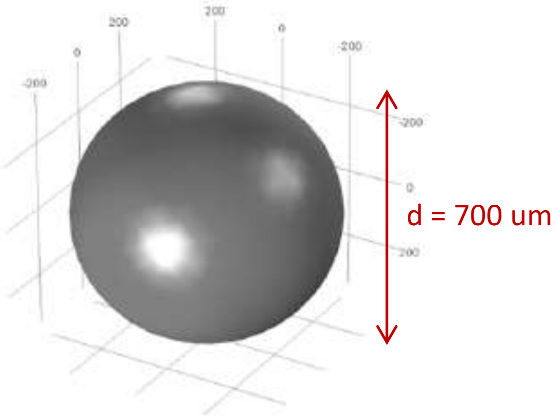
V_A, ρ_A

Microstructure (porous)



V_B, ρ_B

Shell (solid)



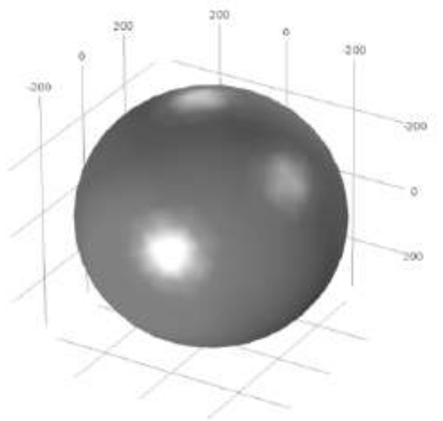
V_B, ρ_B

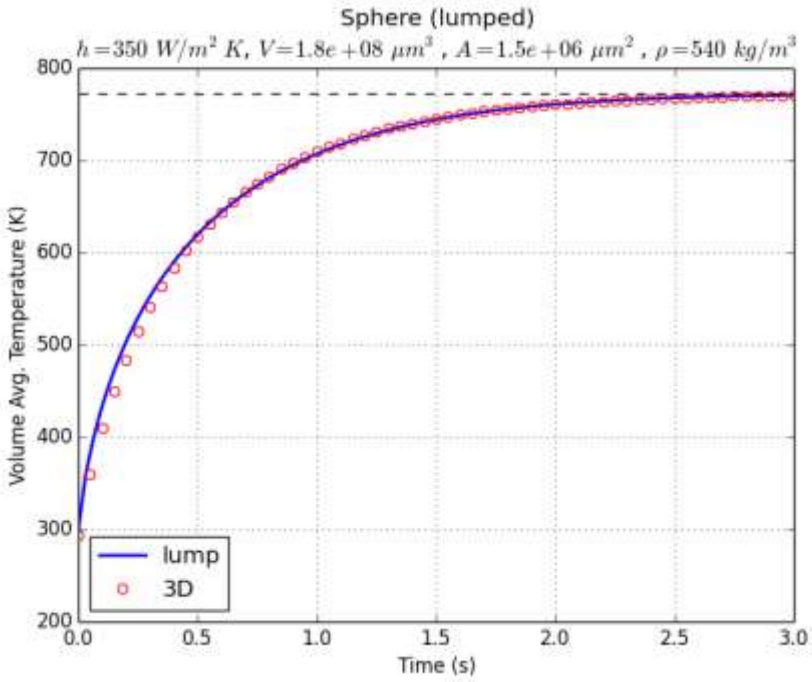
Sphere (solid)

Sphere Results

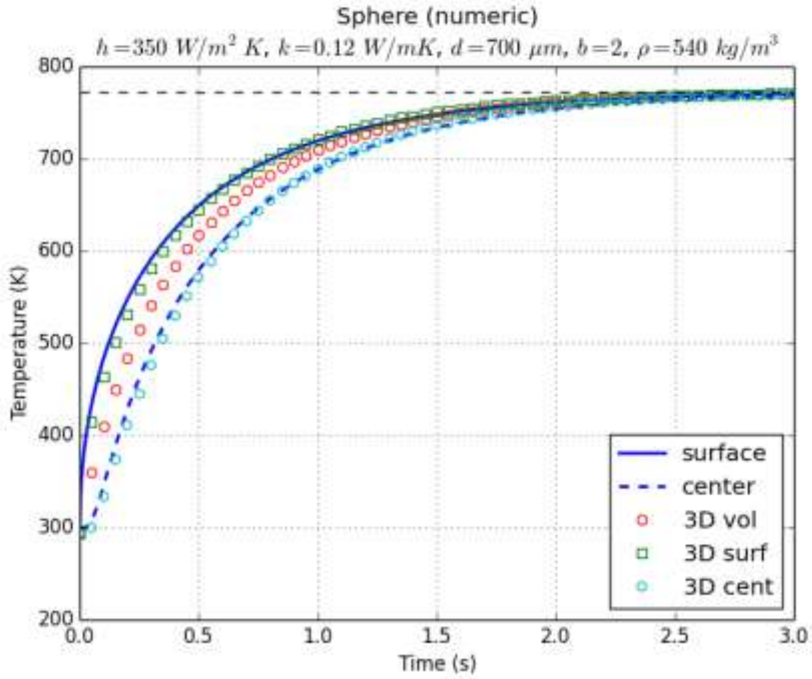
Low-order vs 3-D Sphere

- lumped method agrees with volume avg. temperature profile of 3-D sphere
- 1-D numerical model agrees with surface and center temperature profiles of 3-D sphere




Sphere (lumped)

$h=350\ W/m^2\ K,\ V=1.8e+08\ \mu m^3\ ,\ A=1.5e+06\ \mu m^2\ ,\ \rho=540\ kg/m^3$

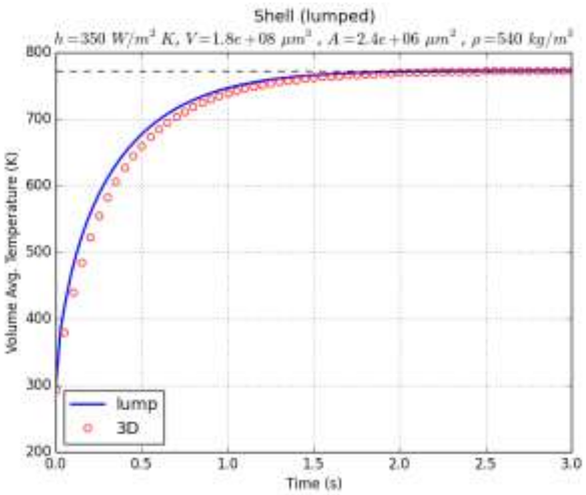

Sphere (numeric)

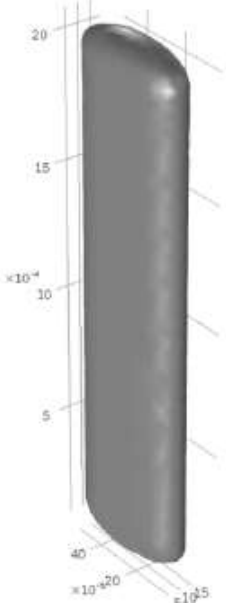
$h=350\ W/m^2\ K,\ k=0.12\ W/mK,\ d=700\ \mu m,\ b=2,\ \rho=540\ kg/m^3$

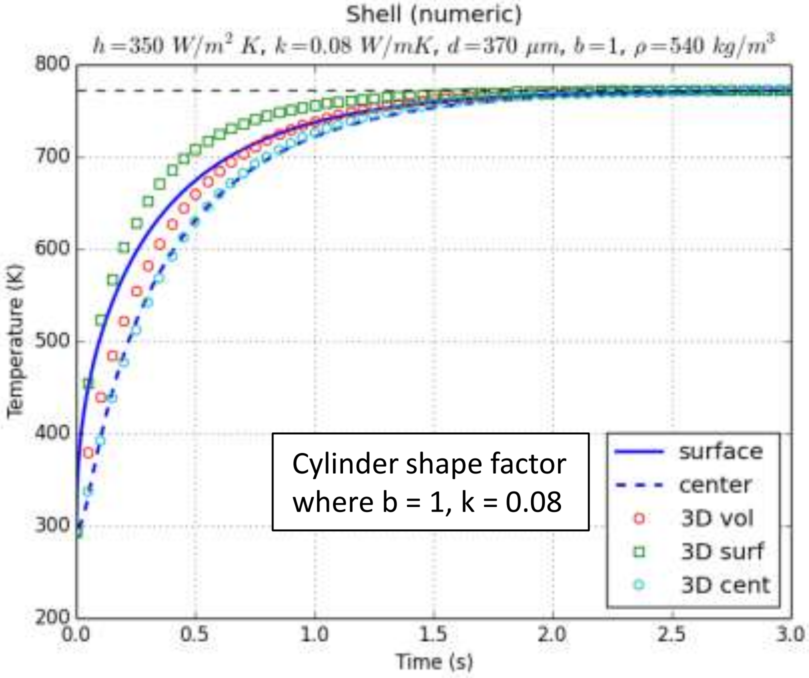
Shell Results

Low-order vs 3-D Shell

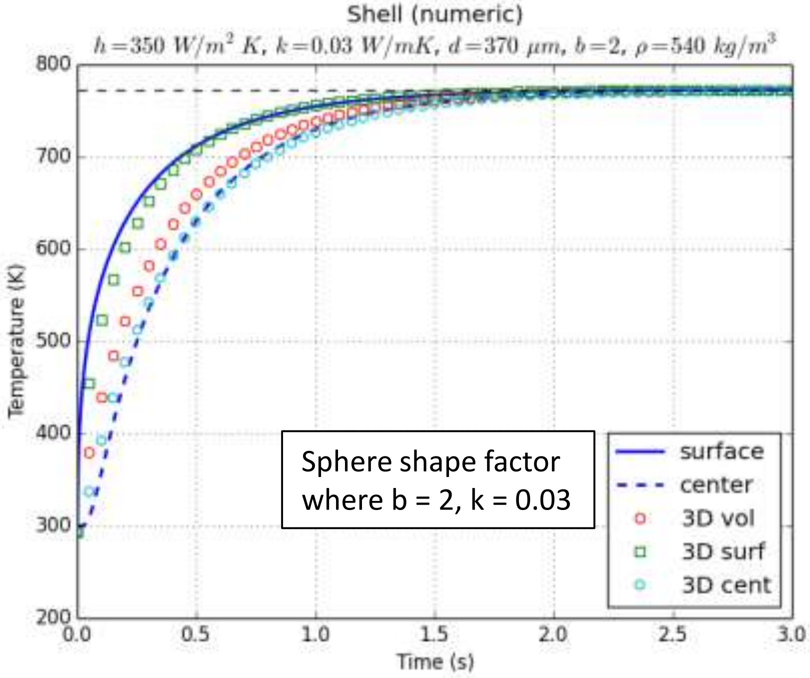
- lumped method agrees with 3-D volume avg. temperature
- k_{eff} between k_{wood} and k_{gas}
- spherical shape factor for 1-D model more effective than cylinder







Cylinder shape factor where b = 1, k = 0.08

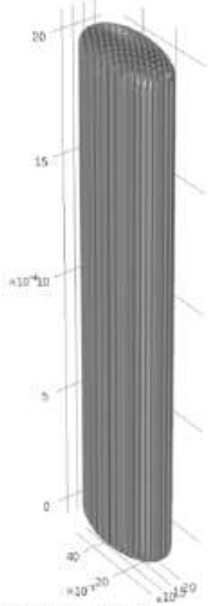


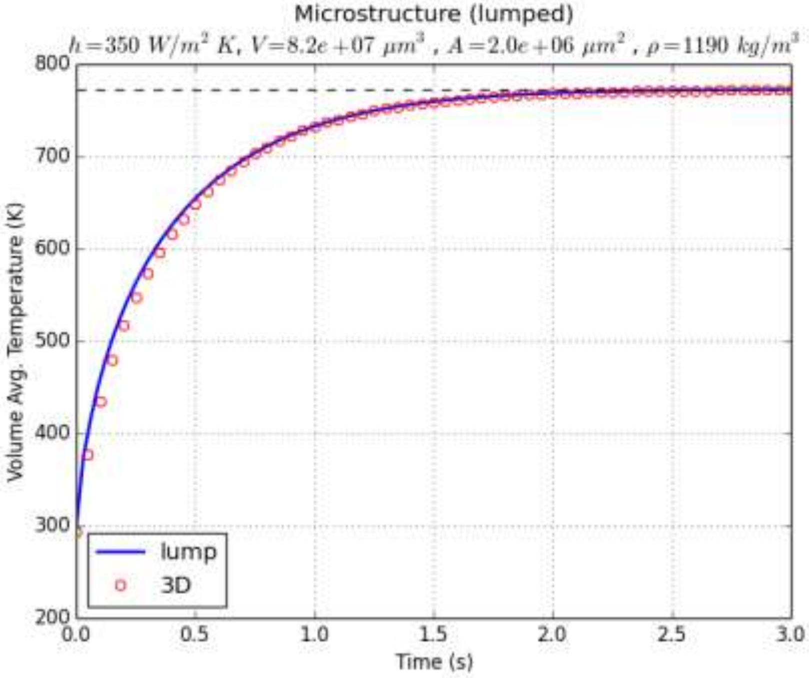
Sphere shape factor where b = 2, k = 0.03

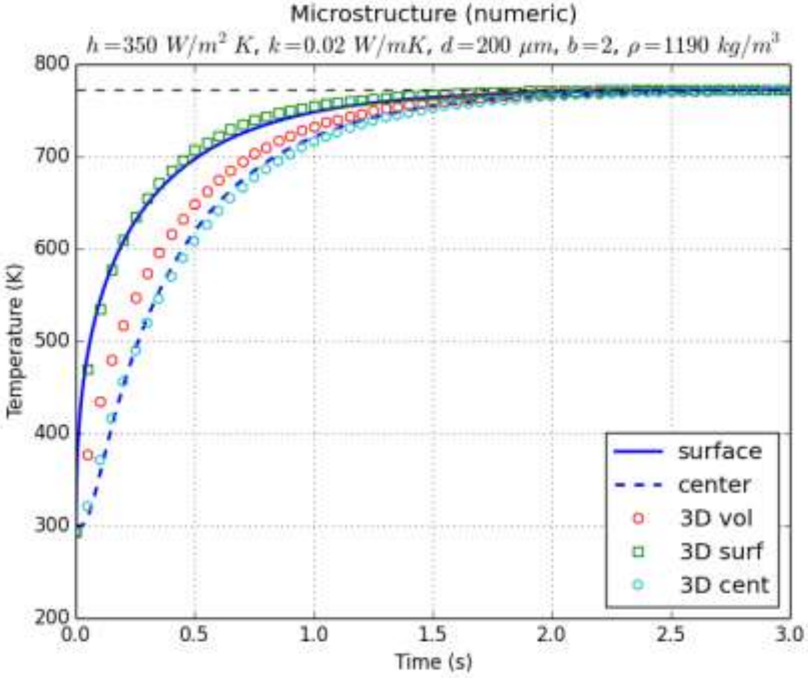
Microstructure Results

Low-order vs 3-D Microstructure

- lumped method agrees with 3-D results for skeletal density of 1190 kg/m^3
- 1-D approach provides good agreement using minimum particle width and spherical shape factor
- k_{eff} value same as N_2 gas



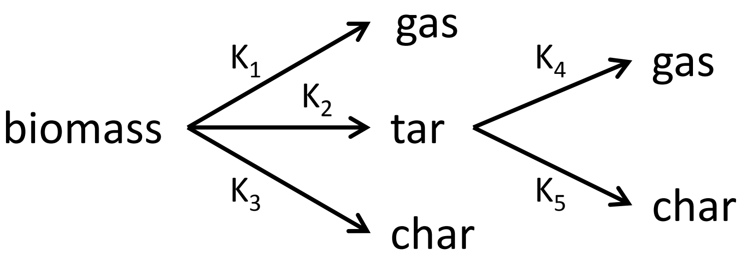




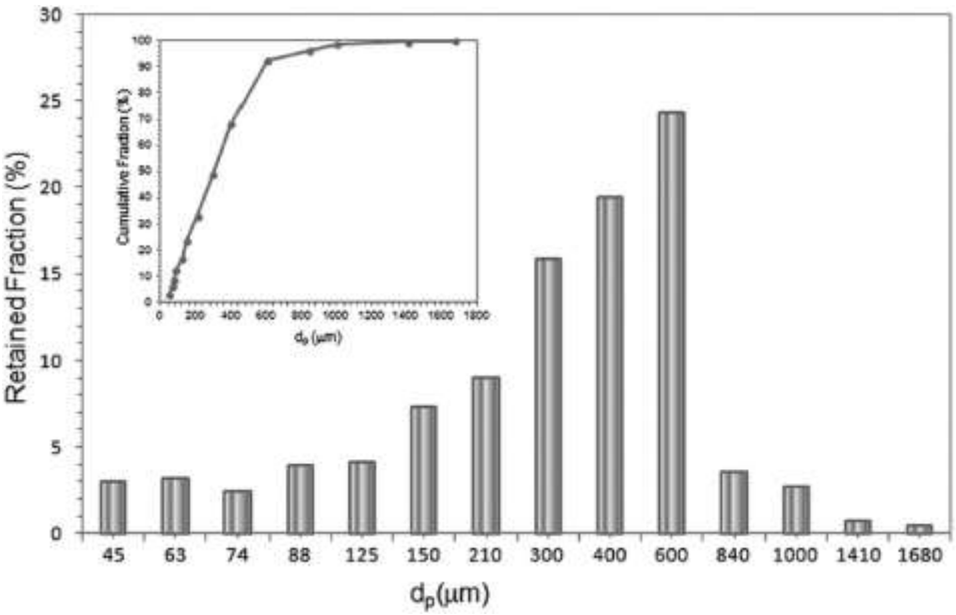
Tar Production Rate vs Particle Size

Particle Size Distribution and Tar Yield

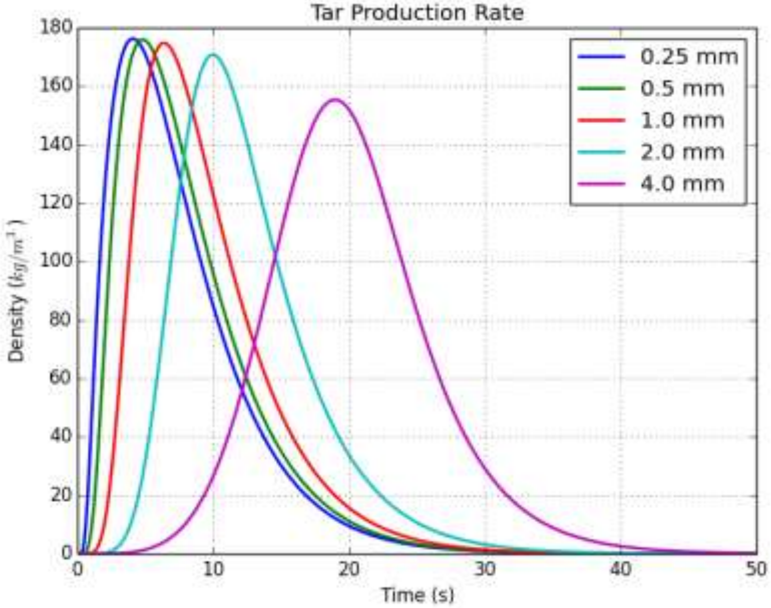
- feedstock is not a uniform size
- particle size will affect tar production and resident time distributions in the reactor



Source: Thurner 1981, Chan 1985



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



Summary

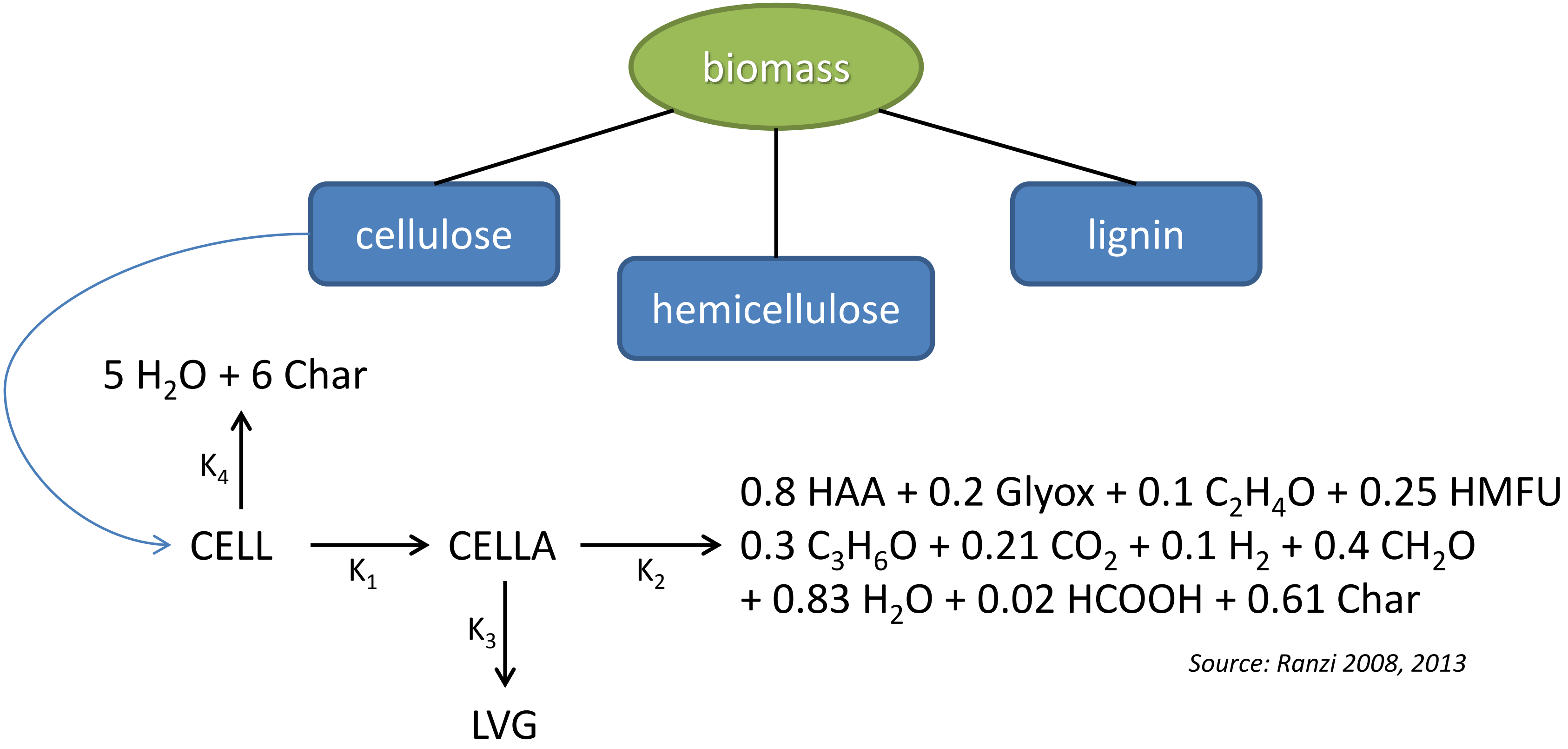
- Low-order numerical models provide accurate results with an appropriate k_{eff} and diameter value
- Particle size distribution suggests modeling as a single particle size is not realistic
- Ranzi kinetic scheme is only known approach for predicting chemical species from biomass pyrolysis
- Lumped analysis methods provide a good estimate of volume averaged temperature profiles for complicated shapes as long as surface area and volume are known

Next Steps…

- Effects of moisture content on product yield and devolatilization rate
- Organize particle size distribution into families
- Develop pyrolysis maps to estimate tar yield and quality for different biomass feedstocks and reactor conditions
- Continue comparison of 3-D microstructure models vs 1-D approach for various particle sizes
- Compare different kinetic schemes and wood properties (Cp, k as functions of temperature)
- Develop a correlation for the effective thermal conductivity

Next Steps…

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



biomass

cellulose

hemicellulose

lignin

$$\mathrm{CELL} \xrightarrow{K_4} 5\,H_2O + 6\,\mathrm{Char}$$

$$\mathrm{CELL} \xrightarrow{K_1} \mathrm{CELLA}$$

$$\mathrm{CELLA} \xrightarrow{K_3} \mathrm{LVG}$$

$$\mathrm{CELLA} \xrightarrow{K_2} 0.8\,\mathrm{HAA} + 0.2\,\mathrm{Glyox} + 0.1\,C_2H_4O + 0.25\,\mathrm{HMFU} + 0.3\,C_3H_6O + 0.21\,CO_2 + 0.1\,H_2 + 0.4\,CH_2O + 0.83\,H_2O + 0.02\,HCOOH + 0.61\,\mathrm{Char}$$

Source: Ranzi 2008, 2013

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

Acknowledgements

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Oak Ridge National Lab

Peter Ciesielski

National Renewable Energy Lab

Victor Walker, Tyler Westover

Idaho National Lab

Computational Pyrolysis Consortium

CPC

Members of the Computational Pyrolysis Consortium (CPC)

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

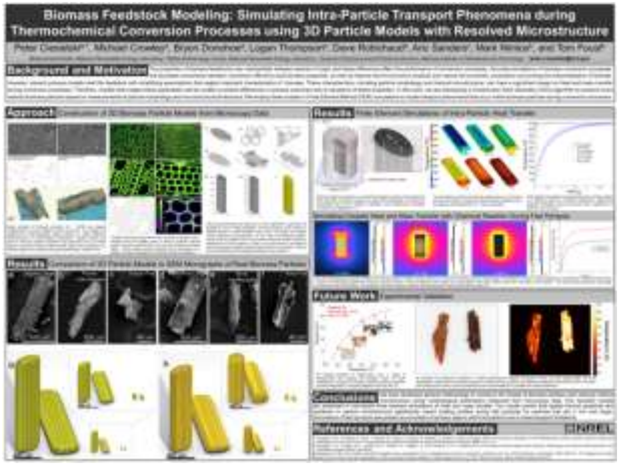
- Biomass feedstock characterization tools and data
- Model component and data sharing/archiving mechanism

Argonne National Laboratory

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

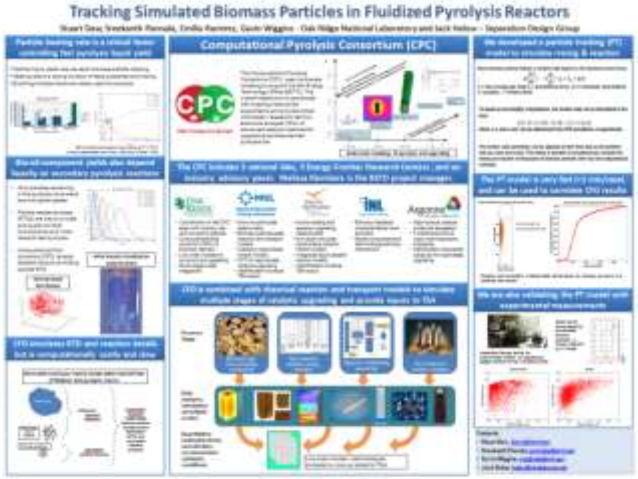
Assess the commercial feasibility of advanced catalytic technologies for producing infrastructure compatible transportation fuels from biomass-derived pyrolysis oils.

Posters at TCS 2014


Biomass Feedstock Modeling: Simulating Intra-Particle Transport Phenomena during Thermochemical Conversion Processes using 3D Particle Models with Resolved Microstructure

3-D microsturcture models

"Simulations of microscale, intra-particle heat and mass transport during fast pyrolysis using biomass particle models with resolved internal microstructure" by Peter Ciesielski, et al. (NREL)


Tracking Simulated Biomass Particles in Fluidized Pyrolysis Reactors

Reactor models

"Tracking of simulated biomass particles in bubbling fluidized beds" by Stuart Daw, et al. (ORNL)

Questions ?

OAK RIDGE National Laboratory

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CPC Computational Pyrolysis Consortium

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

GitHub

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