Modeling the impact of biomass particle residence time on fast pyrolysis yield and composition

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Problem Statement

Complex hydrodynamics and multiphase reactions require expensive computational resources to model fluidized bed reactors.

Reactor simulations often assume a uniform particle temperature thus ignoring effects of temperature gradients within biomass particles.

Biomass particles typically modeled as a single size with a spherical shape.

Kinetic schemes for biomass pyrolysis offer little insight on quality of product yields.

Cold flow bubbling fluidized bed (BFB) experiment at Separation Design, operated by Jack Halow.

Bubbling fluidized bed reactor at NREL for biomass fast pyrolysis experiments.

Background

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

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

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

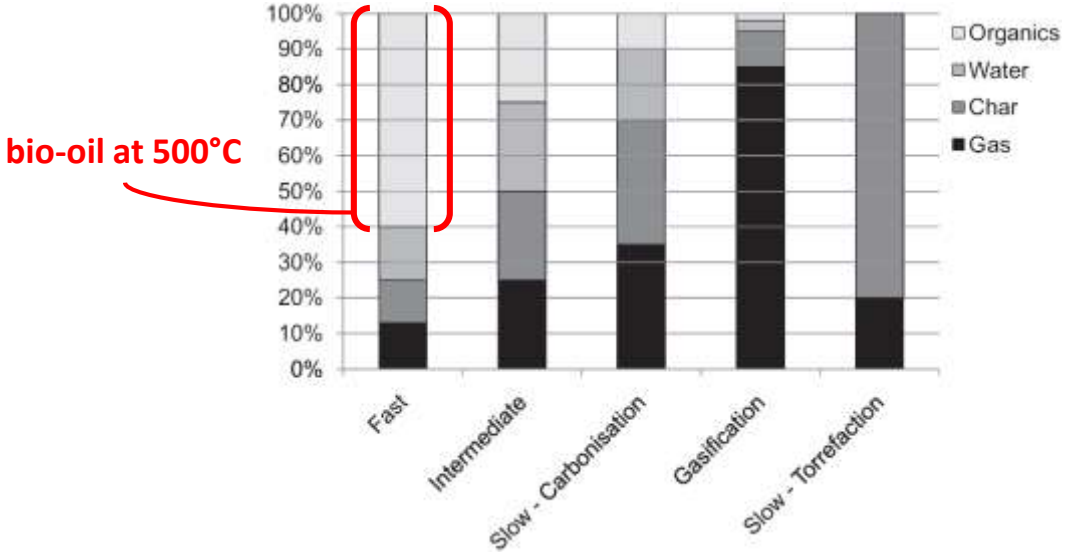
Detailed CFD simulations of mixing require high computational overhead and time, which increase with reactor scale.
[Mellin 2014, Papadikis 2009]

Fast pyrolysis of biomass

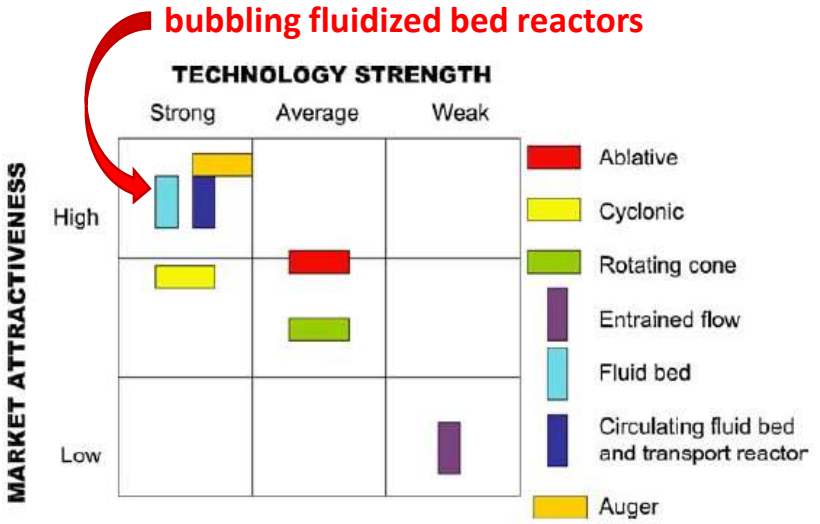
Anaerobic, rapid heating of biomass particles to produce non-condensable gases, solid char, and liquid (condensable vapors).

Goal is to maximize the liquid yield (i.e. bio-oil or tar).

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

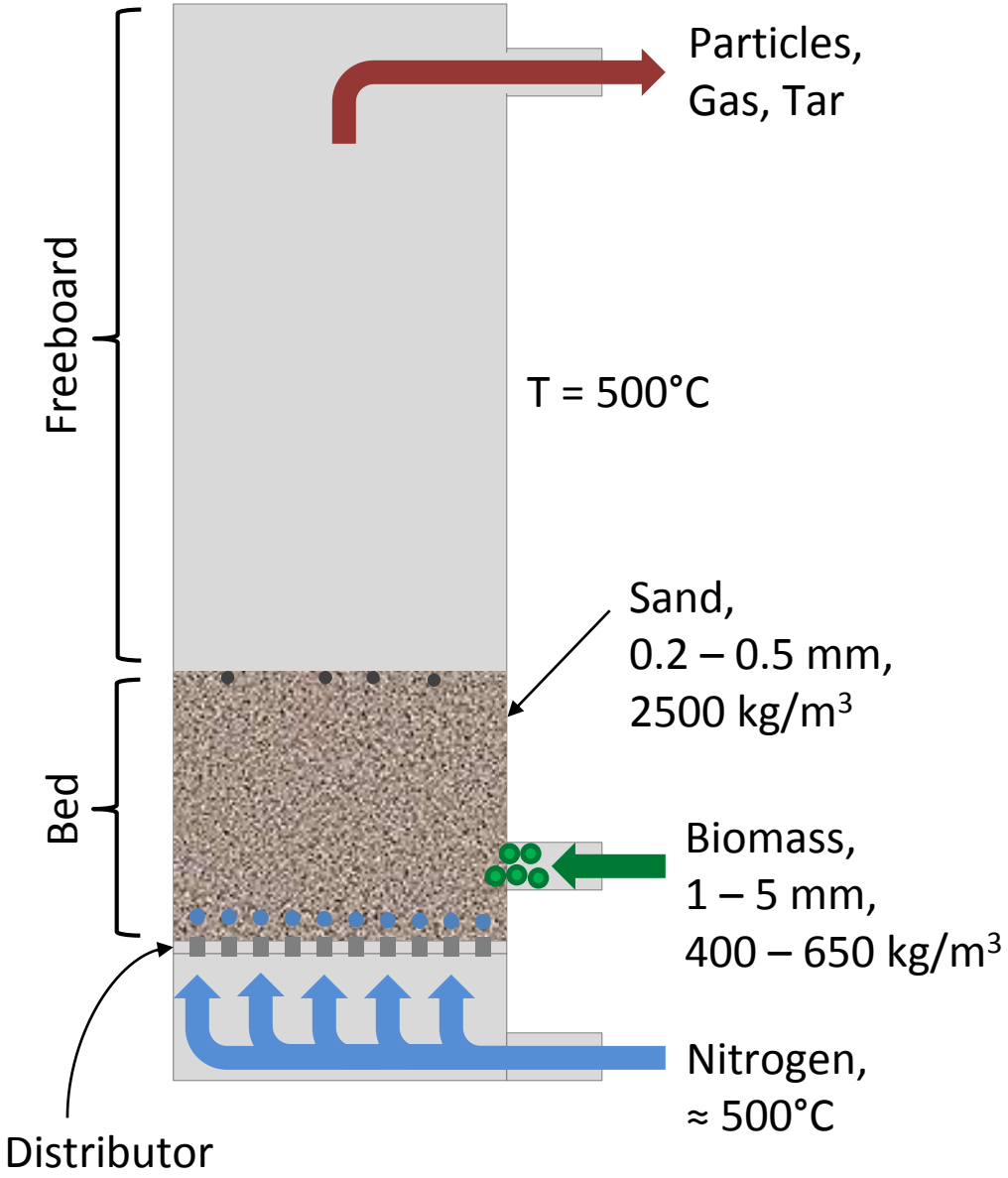


Product distribution from different types of pyrolysis.
Source: Bridgwater 2012.

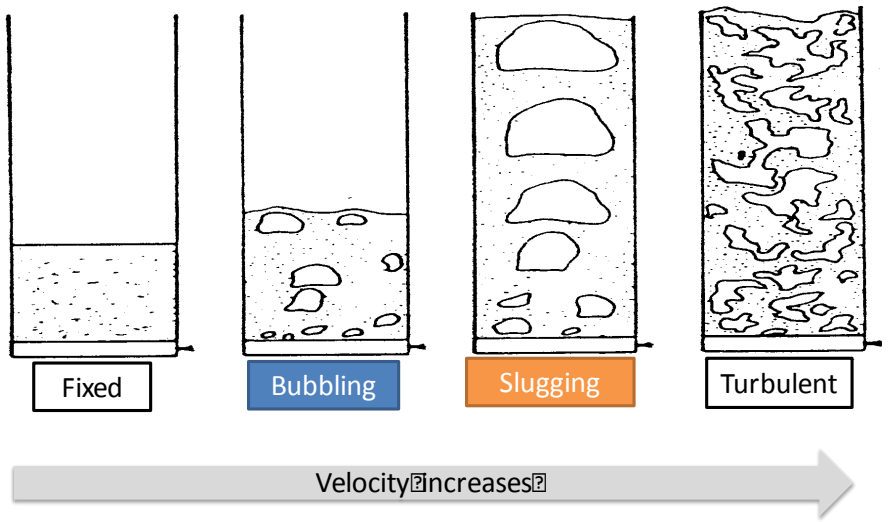


Commercial potential of fast pyrolysis technologies.
Source: Butler 2011.

Bubbling fluidized bed (BFB) pyrolysis reactors



2-inch diameter fluidized bed reactors at NREL. Source: Rick French, Mark Jarvis.



Objectives

Summarize literature on particle residence time distributions (RTDs) and kinetic schemes for bubbling and circulating fluidized bed reactors at fast pyrolysis conditions.

Demonstrate how RTDs can be combined with reaction kinetics and mass balances to create low-order reactor model.

Compare predicted pyrolysis yields to experiments and more detailed computational simulations.

Residence time distribution of pyrolyzing particles

Develop reactor "agnostic" approach for modeling net yields from BFB reactors with different residence time distributions (RTDs).

Series CSTR – variable axial dispersion

$$E(t) = \left(\frac{t}{\tau_i}\right)^{N-1} \left(\frac{1}{\tau_i (N-1)!}\right) e^{-t/\tau_i}$$

where E = exit age distribution, RTD (1/s)
τ_i = avg. residence time in stage (s)
N = number of mixing stages
t = time (s)

Van de Vusse – small + large scale mixing

$$E(t) = \left(\frac{q}{r}\right)^{\frac{N-1}{N}} \left(\frac{N}{\tau}\right) e^{-Nt/\tau} g(at)$$

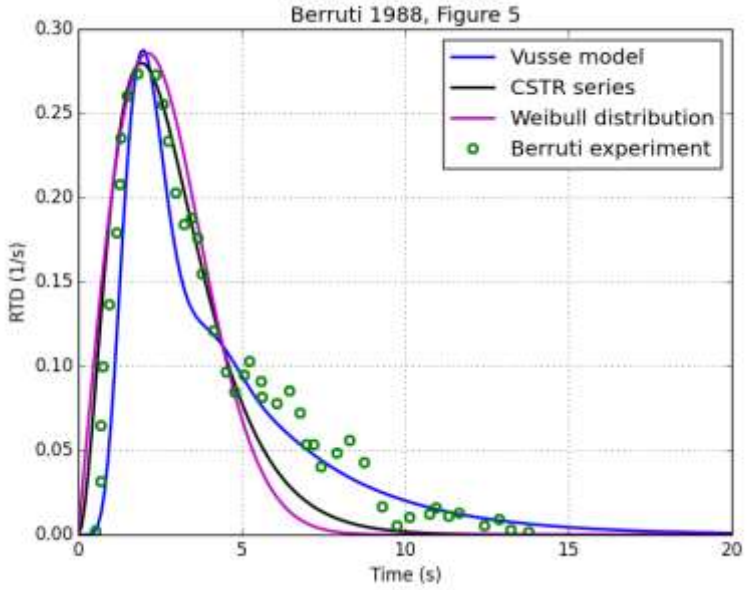
where q = volumetric feed rate (m^3/s)
r = volumetric recirculation rate (m^3/s)
τ = overall residence time (s)
g(at) = circulation function

Weibull distribution – power law scaling

$$E(t) = \frac{K}{\theta}\left(\frac{t}{\theta}\right)^{K-1} e^{-\left(\frac{t}{\theta}\right)^{K}}$$

where K = shape parameter
represents mixing in CSTR
θ = scaling parameter
time of particle movement

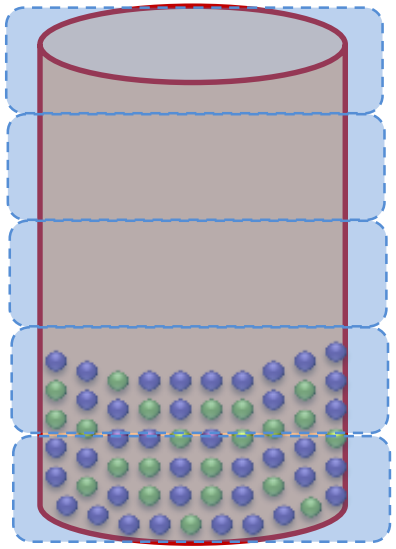
Experimental data can be approximated with simple functions and physically relevant parameters.



Comparison of RTD models with Berruti 1998 bubbling bed experiment with particle d = 450 µm and ρ = 82 kg/m^3.

Represent reactor as a series of plug flow (PFR) and/or stirred tank reactors (CSTR).

Each section is a stage (N) where number of stages determined by RTD of that particular reactor.



Available kinetics are typically very simplified

Primary and secondary reactions produce gas, tar (condensable liquid or bio-oil), and char.

Non-condensable gases

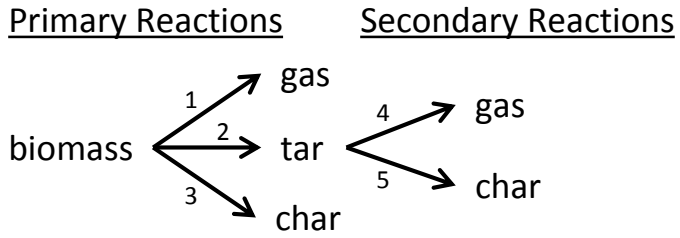
- light gases such as H_2, CO, CO_2, H_2O, CH_4, etc.

Condensable volatiles (tar)

- heavy organics and inorganics
- vapors and aerosols react within/outside particle

Char as solid residue.

Typically 1st order Arrhenius rate equation with product yields reported on a **mass basis**.



Chan1985 and Blasi1993 kinetic parameters

Reaction	A (1/s)	E (kJ/mol)
1	1.3×10^8	140
2	2.0×10^8	133
3	1.1×10^7	121
4	4.3×10^6	108
5	1.0×10^6	108

$$K = Ae^{-E/RT}$$

$$\frac{\partial \rho}{\partial t} = K\rho$$

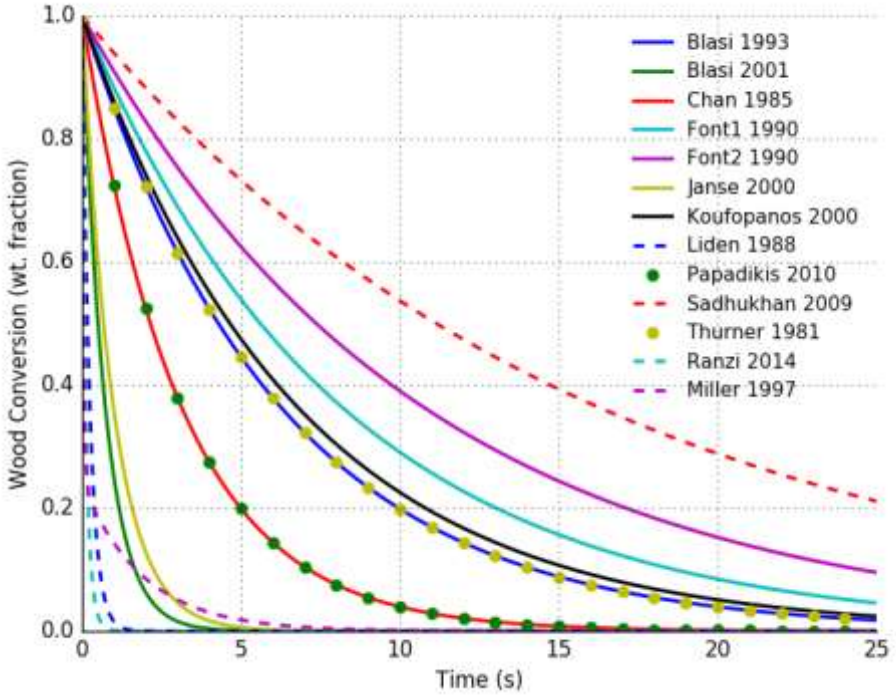
where *K = rate constant (1/s)*
A = pre-factor (1/s)
E = activation energy (kJ/mol)
R = universal gas constant (kJ / mol·K)
T = temperature (K)
ρ = concentration (kg/m³)
t = time (s)

Primary pyrolysis yields vary with kinetic scheme

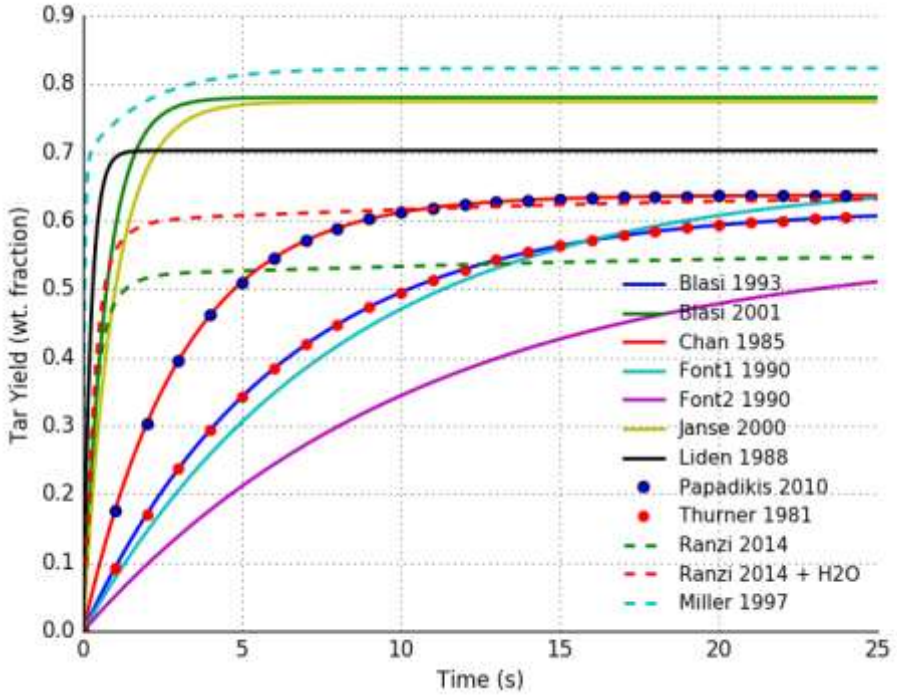
Tar yields vary from ≈ 50 – 80 wt% of original feedstock.

Some schemes utilize similar kinetic parameters.

Rate of devolatilization depends on kinetic scheme used in model.



Wood conversion from primary reactions at 500°C (773K). All schemes are first-order Arrhenius rate equations.

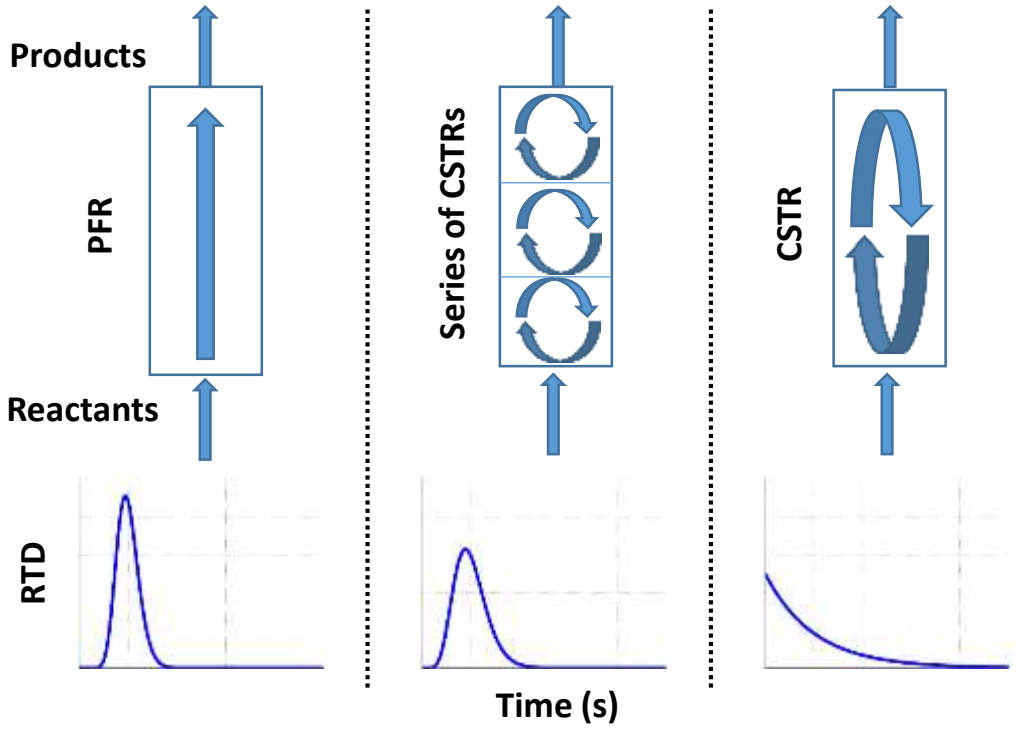


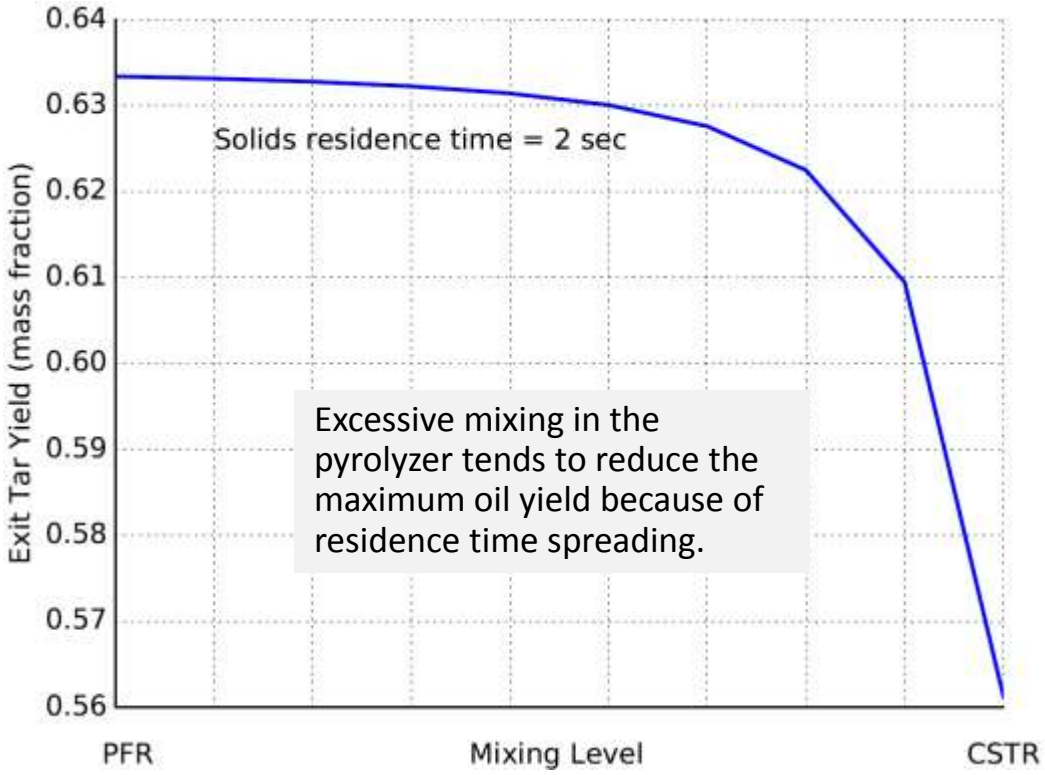
Tar yield from primary reactions at 500°C (773K). All schemes are first-order Arrhenius rate equations.

Low-order reactor model approach

We use low-order reactor mixing models to estimate residence times of biomass particles and the resulting oil yield.

These models account for particle and gas circulation in the pyrolyzer to link particle models with overall performance.



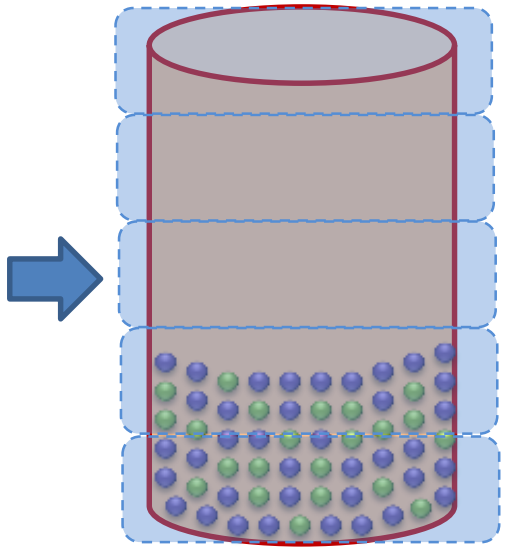


Pyrolysis reactor as a series of CSTRs

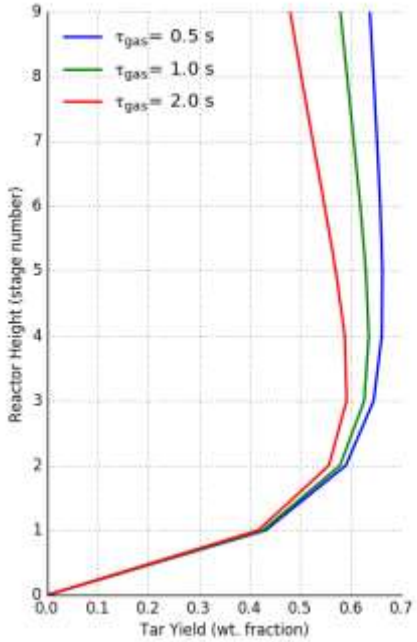
Bubbling fluidized bed reactor can be represented as a series of CSTRs at steady-state conditions.

Kinetic parameters from Liden 1988.

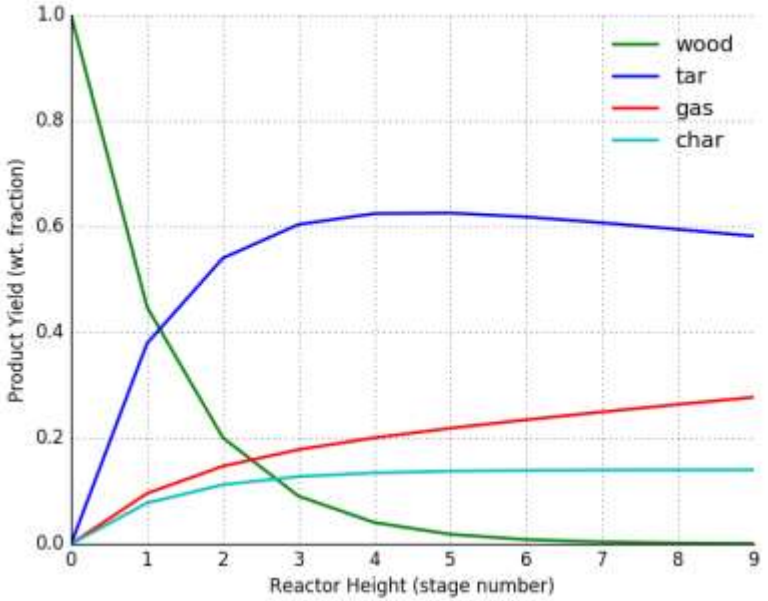
Overall gas and solid residence time divided into each stage.



BFB pyrolysis reactor as a series of CSTR reactors. For this example, N = 5 and $\tau_i = \tau_{total} / N$.



Tar yield along height of reactor at different gas residence times with τ_{solid} = 4s, N = 9 at 500°C.



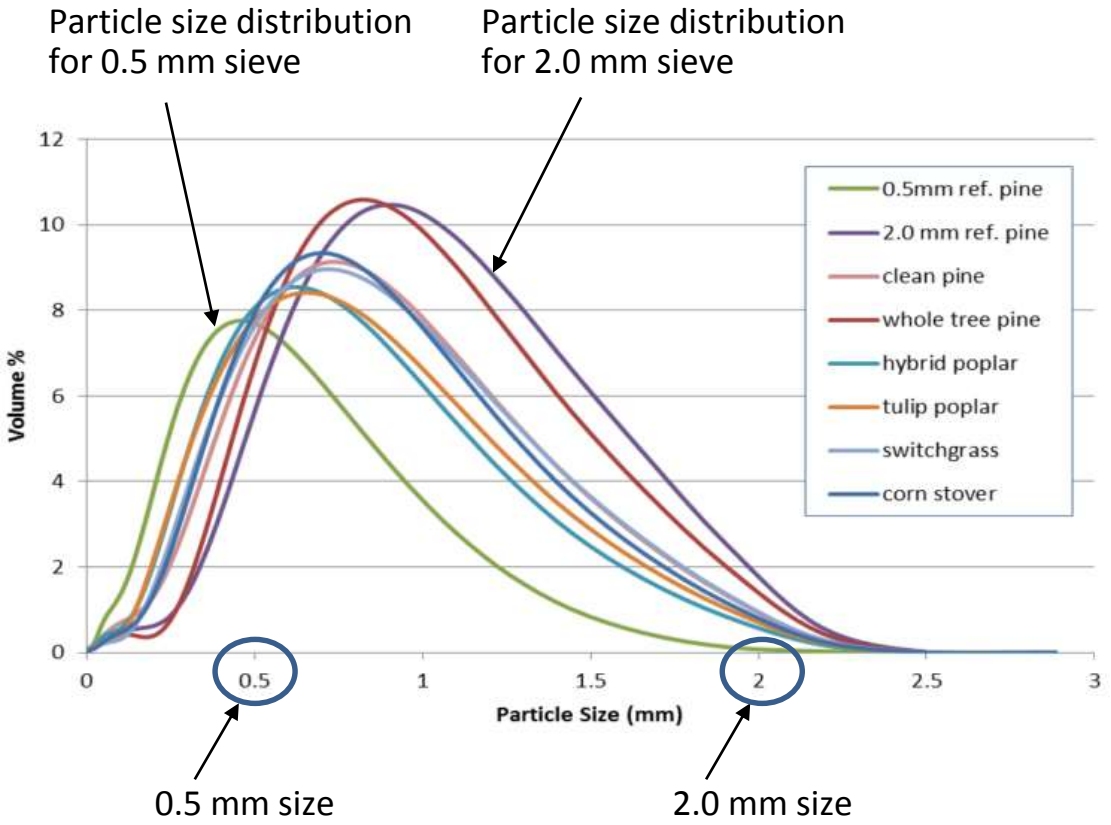
Product yields based on Liden 1988 kinetics at 500°C with τ_{gas} = 1s, τ_{solid} = 3s and N = 9.

Comminution produces broad range of particle sizes

Reactor models often assume a uniform particle size based on sieve (mesh) size.

Size reduction equipment produces a broad range of particle sizes which must be accounted for in reactor models.

Neglecting particle size distributions in reactor models can significantly affect predicted pyrolysis yields.



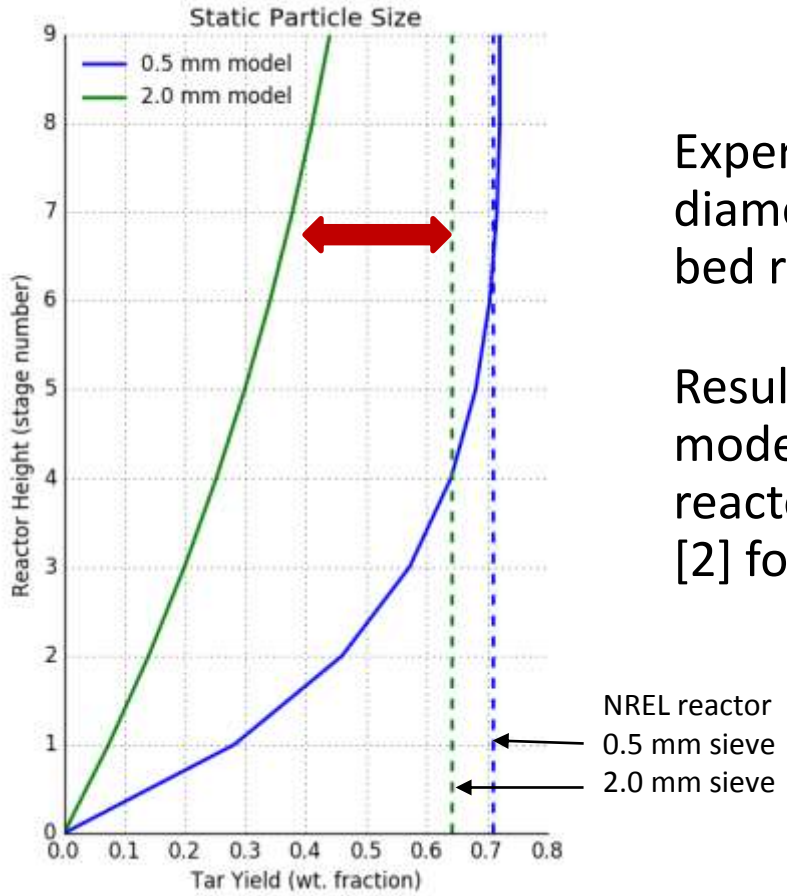
Models often assume all biomass particles are similar to sieve size.

Particle size distributions from various biomass feedstocks as produced from a Thomas Model 4 Wiley mill. Source: NREL Milestone Completion Report.

Reactor models must account for size distributions

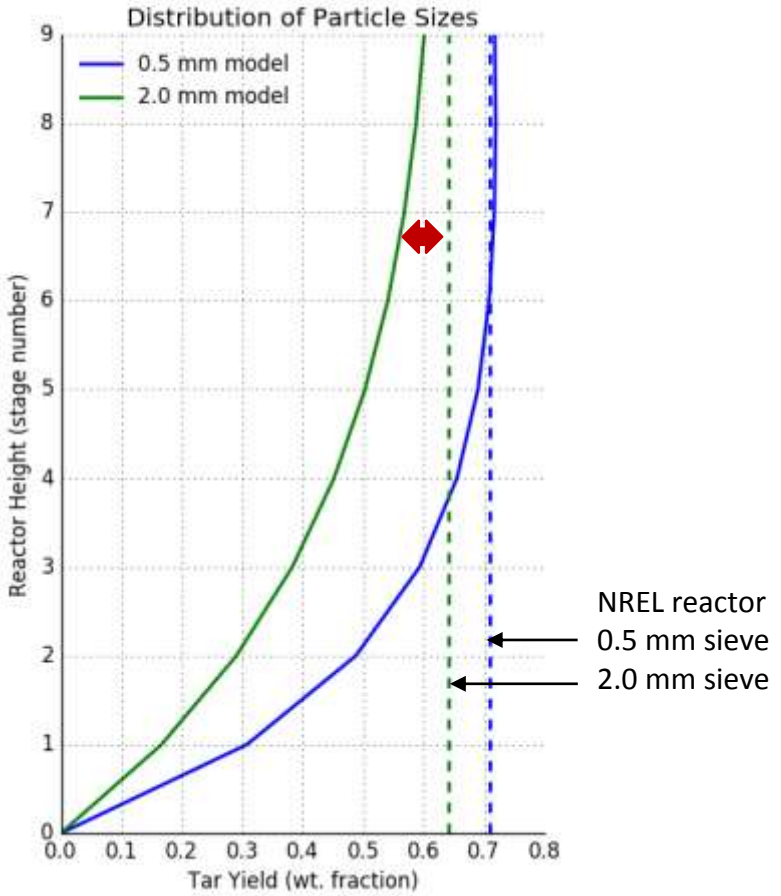
Products (wt. %)	0.5 mm sieve		2.0 mm sieve	
	Experiment	Model	Experiment	Model
Total liquids	**70.8 ± 1.1**	**72.1**	**63.5 ± 1.9**	**44.0**
Char	9.5 ± 0.1	13.7	11.7 ± 1.3	8.2
Gas	15.5 ± 0.6	12.3	18.7 ± 0.8	6.5

Products (wt. %)	0.5 mm sieve		2.0 mm sieve	
	Experiment	Model	Experiment	Model
Total liquids	**70.8 ± 1.1**	**72.1**	**63.5 ± 1.9**	**60.1**
Char	9.5 ± 0.1	13.7	11.7 ± 1.3	11.3
Gas	15.5 ± 0.6	12.3	18.7 ± 0.8	9.6



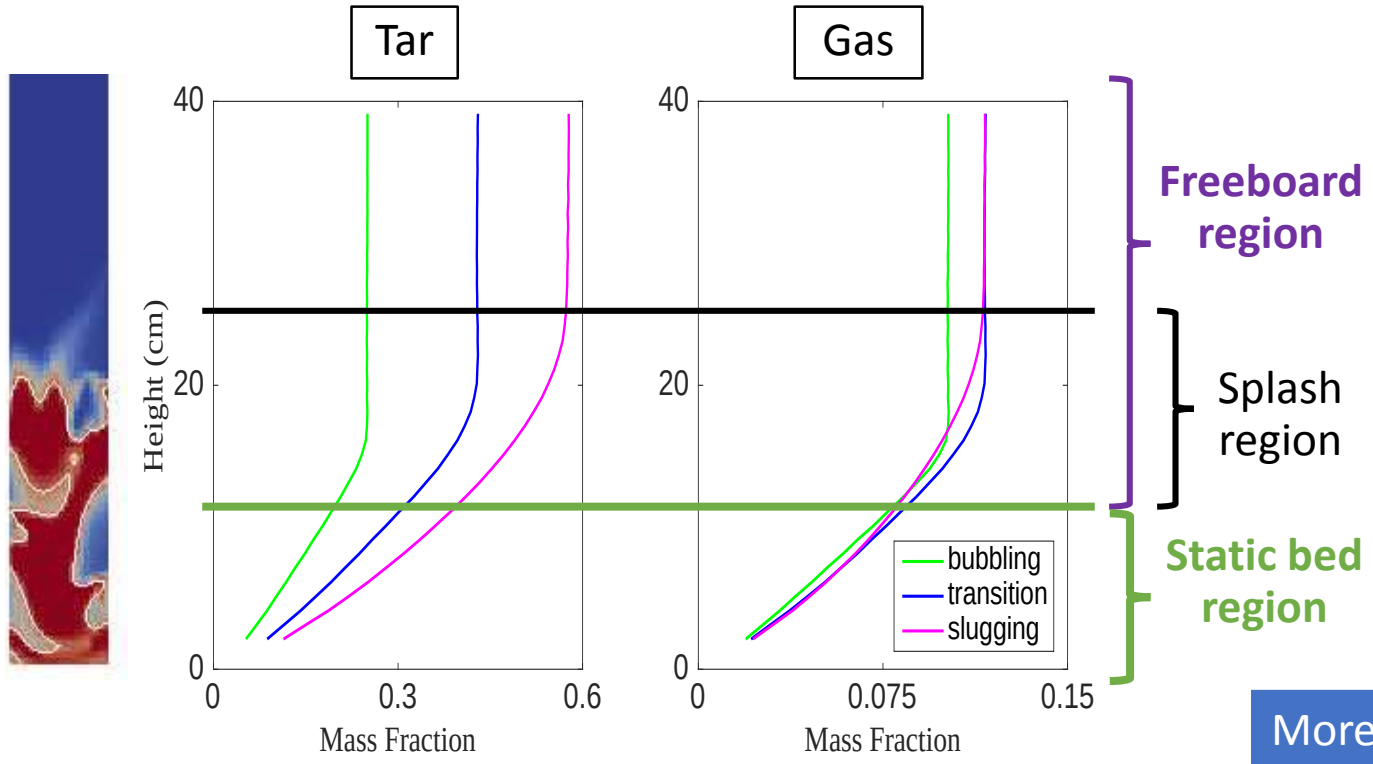
Experimental data from 2-inch diameter bubbling fluidized bed reactor at NREL.

Results are from Dsv particle model coupled to a low-order reactor model, see reference [2] for more information.

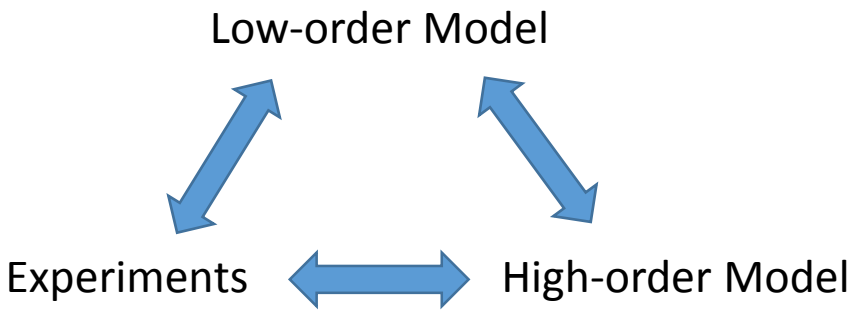


CFD can provide details not available from low-order models or experiments

Preliminary MFiX results: hydrodynamic effects on kinetics



- Flow dynamics through the reactor
- Bubble effects
- Oscillatory dynamics
- Statistical analysis
- Validation using pressure taps



Bubbling = 3.50 U_o/U_{mf}
Transition (BTST) = 5.00 U_o/U_{mf}
Slugging = 7.50 U_o/U_{mf}

Most tar and gas conversion occurs inside the bed and splash region.

More information on MFiX CFD work:
465429 Computational Study of the Bubbling-to-Slugging Transition in a Laboratory-Scale Fluidized Bed

When: Wednesday, November 16, 2016: 8:49 AM
Location: Peninsula (Hotel Nikko San Francisco)

Summary

- Residence time distributions combined with kinetic reactions and simple mass balances provide a low-order approximation of fluidized bed pyrolysis reactors
- Computational models can provide information about hydrodynamics and pyrolysis conditions within reactors
- Particle size distributions must be accounted for to accurately predict pyrolysis yields in reactor models
- Low-order models can help inform high-order (CFD) simulations

Acknowledgements

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Questions?

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GitHub
github.com/pyrolysis

Related Talk:
465429 Computational Study of the Bubbling-to-Slugging Transition in a Laboratory-Scale Fluidized Bed

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[1] Daw, C. Stuart, Gavin Wiggins, Qingang Xiong, and Emilio Ramirez. **Development of a Low-Order Computational Model for Biomass Fast Pyrolysis: Accounting for Particle Residence Time**. ORNL/TM-2016/69 (2016).

[2] Wiggins, Gavin M., Peter N. Ciesielski, and C. Stuart Daw. **Low-Order Modeling of Internal Heat Transfer in Biomass Particle Pyrolysis**. *Energy & Fuels* 30, no. 6 (2016): 4960-4969.

Supplemental Material

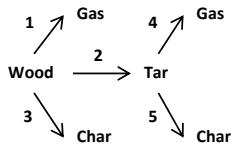
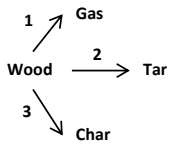
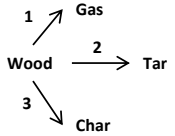
Kinetic schemes for wood

Some schemes account for secondary reactions which degrade tar yield while other schemes only focus on primary reactions.

Experimental setup varies.

Some parameters derived from experiment while others use literature data.

Broad range of sample materials, some do not report type of biomass.

					Kinetic Parameters		
Reference	**Biomass**	**Experimental Setup**	**Temperature**	**Kinetic Scheme**	**A (1/s)**	**E (kJ/mol)**	**Source**
Blasi 1993	dry wood slab 0.025 m thick	84 kW/m^2	300 - 1200 K		A1 = 5.16 × 10^6 A2 = 1.48 × 10^{10} A3 = 2.66 × 10^{10} A4 = 4.28 × 10^6 A5 = 1.0 × 10^6	E1 = 88.6 E2 = 112.7 E3 = 106.5 E4 = 108 E5 = 108	Thurner, Mann 1981 Thurner, Mann 1981 Liden, Berruti, Scott 1988 Liden et al. 1988 estimated
Blasi 2001	beech wood size < 80 µm	tube furnace 1000 K / min N_2 gas flow isothermal	573 - 708 K		A1 = 4.38 × 10^9 A2 = 1.08 × 10^{10} A3 = 3.27 × 10^6	E1 = 152.7 E2 = 148 E3 = 111.7	experiment experiment experiment
Chan 1985	lodgepole pine 1 cm cylinder 0.5 - 1.5 cm thick	pyrex reactor xenon arc lamp 16.7 W/cm^2	273 - 1173 K		A1 = 1.3 × 10^8 A2 = 2.0 × 10^8 A3 = 1.08 × 10^7 A4 = 5.13 × 10^6 A5 = 1.48 × 10^6	E1 = 140 E2 = 133 E3 = 121 E4 = 87.9 E5 = 144	Hajaligol, Peters, et al. 1982 Hajaligol, Peters, et al. 1982 Shafizadeh 1977-1983 Hajaligol, Peters, et al. 1982 Sakai 1971, Froment 1981
Font 1990	almond shells 0.297 - 0.5 mm	pyroprobe 100 20 °C / ms	733 - 878 K		A1 = 1.521 × 10^7 A2 = 5.851 × 10^6 A3 = 2.981 × 10^3	E1 = 139 E2 = 119 E3 = 73	experiment experiment experiment
Font 1990	almond shells 0.297 - 0.5 mm	fluidized bed sand 0.105-0.210 mm	673 - 733 K		A1 = 6.803 × 10^8 A2 = 8.229 × 10^8	E1 = 156 E2 = 148	experiment experiment

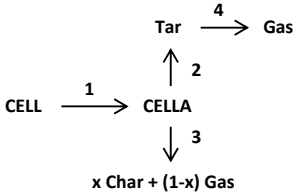
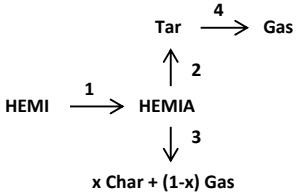
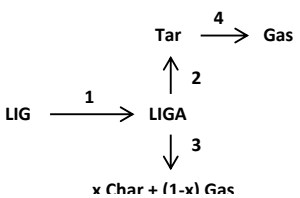
Kinetic schemes for cell., hemi., lignin

Schemes such as Miller and Bellan 1997 and Ranzi 2014 provide kinetic parameters based on cellulose, hemicellulose, and lignin composition.

Ability to estimate product yields for different wood species based on composition.

Some parameters derived from experiment while others taken from literature.

Experimental setup varies, Ranzi 2014 scheme developed for biomass gasification (no secondary reactions).

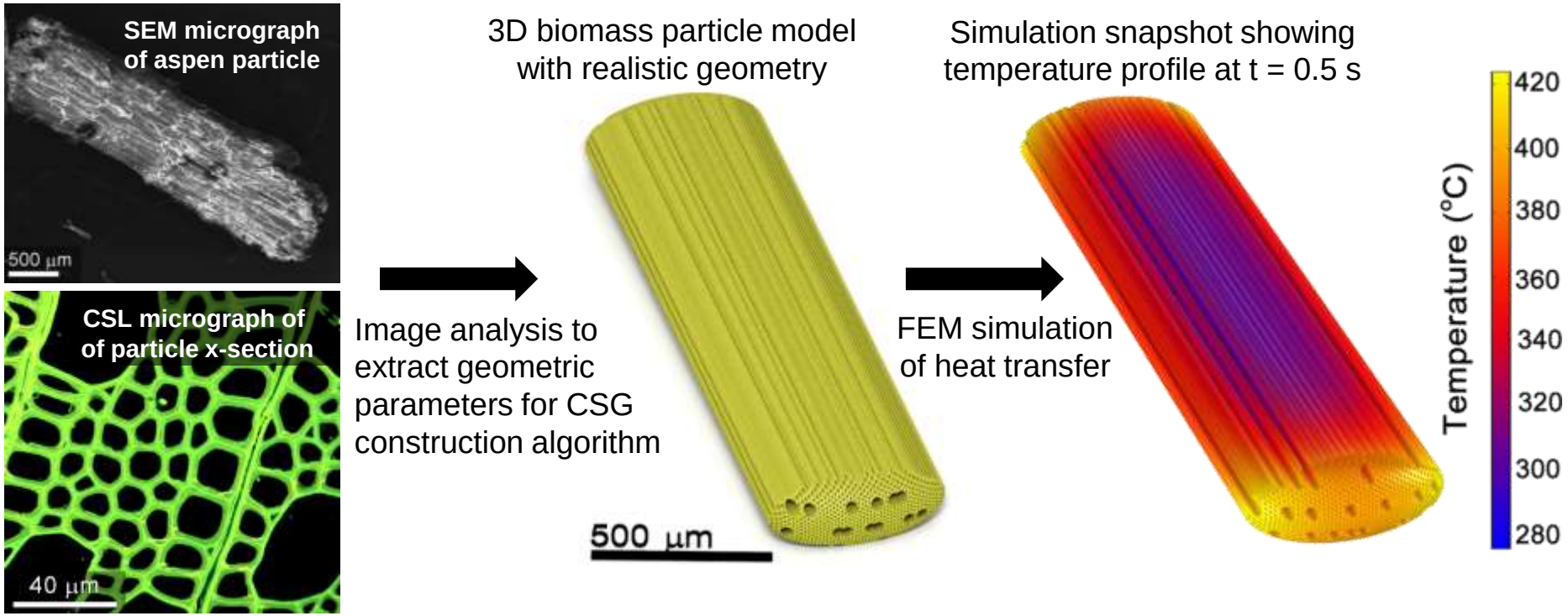
					Kinetic Parameters			
Reference	**Biomass**	**Experimental Setup**	**Temperature**	**Kinetic Scheme**	**A (1/s)**	**E (kJ/mol)**	**Source**	**Notes**
Miller 1997	cellulose hemicellulose lignin beech, cherry pine, poplar bagasse, oak olive husk 0.5 - 20 mm size 2 - 5.2 cm size	5 - 80 K/min 1000 K/s	500 - 1200 K		A1 = 2.8 × 10^{19} A2 = 3.28 × 10^{14} A3 = 1.3 × 10^{10} A4 = 4.28 × 10^{6} x = mass ratio	E1 = 242.4 E2 = 196.5 E3 = 150.5 E4 = 108	Blasi, Russo 1994 Blasi, Russo 1994 Blasi, Russo 1994 Blasi, Russo 1994	Kinetic parameters from other sources. Model compared to other experiments. Micro and macro particle sizes.
					A1 = 2.1 × 10^{16} A2 = 8.75 × 10^{15} A3 = 2.6 × 10^{11} A4 = 4.28 × 10^{6} x = mass ratio	E1 = 186.7 E2 = 202.4 E3 = 145.7 E4 = 108	Ward, Braslaw 1985 Blasi, Russo 1994 Blasi, Russo 1994 Blasi, Russo 1994	
					A1 = 9.6 × 10^{8} A2 = 1.5 × 10^{9} A3 = 7.7 × 10^{6} A4 = 4.28 × 10^{6} x = mass ratio	E1 = 107.6 E2 = 143.8 E3 = 111.4 E4 = 108	Ward, Braslaw 1985 Koufopanos 1989 Koufopanos 1989 Blasi, Russo 1994	

Realistic 3-D particle models with microstructure

Detailed microscopy providing highly resolved species-specific microstructure.

Allows assessment of microstructure on heat/mass transfer during pyrolysis.

Enables simulations of oil yield and composition at the particle scale as functions of feedstock species, particle size distribution, and moisture.



Images courtesy of Peter Ciesielski of NREL.

Low-order particle model

Approximate heat-up as 1-D conduction with bulk properties and simple boundary conditions.

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

intra-particle heat conduction

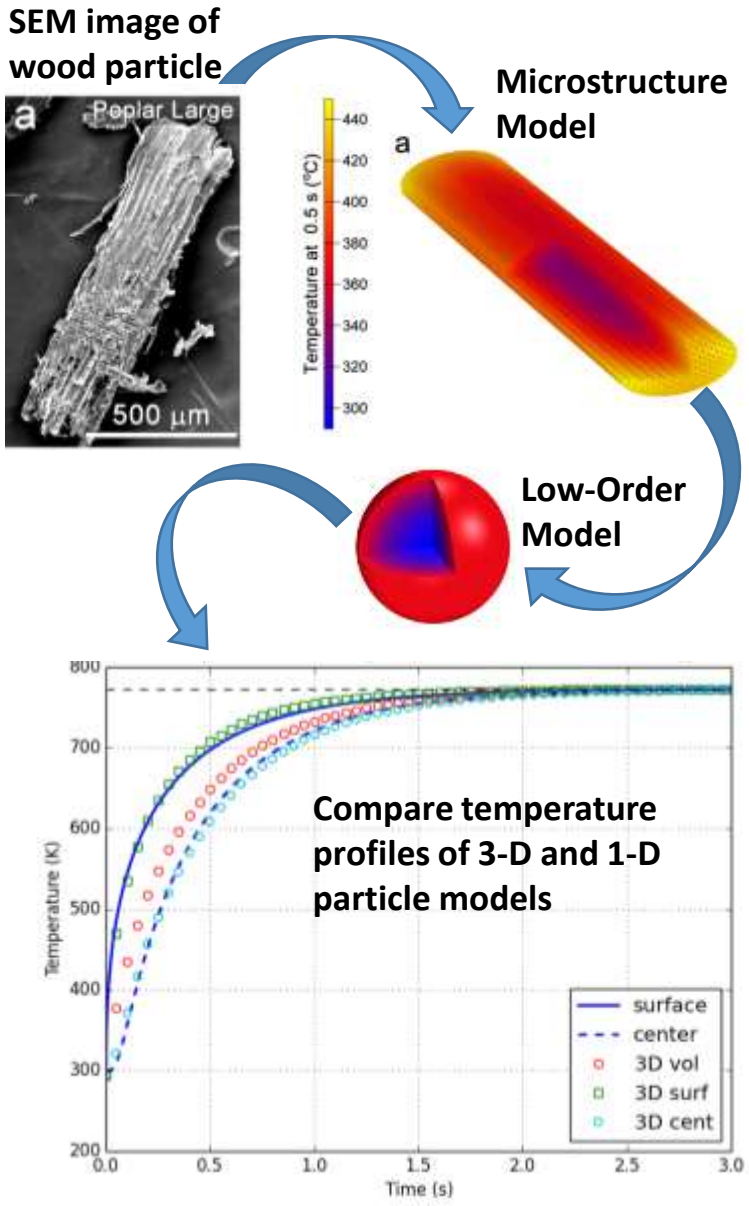
$$k\left.\frac{\partial T}{\partial r}\right|_{r=R} = h\left(T_\infty - T_R\right)$$

boundary condition with convection at particle surface

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

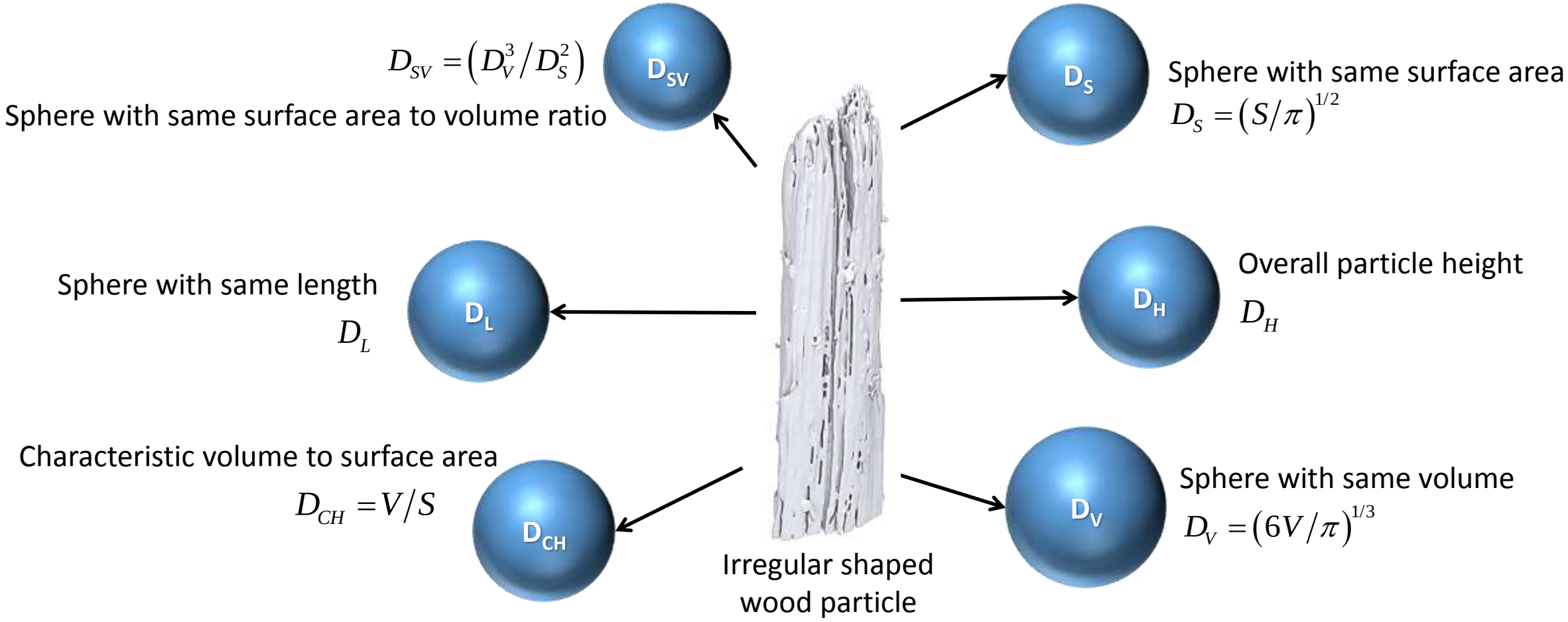
boundary condition with symmetry at particle center

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)



Characterizing irregular shaped particles

An equivalent diameter or characteristic length can be used to represent a measured parameter (surface area, volume, etc.) of an irregularly shaped particle.

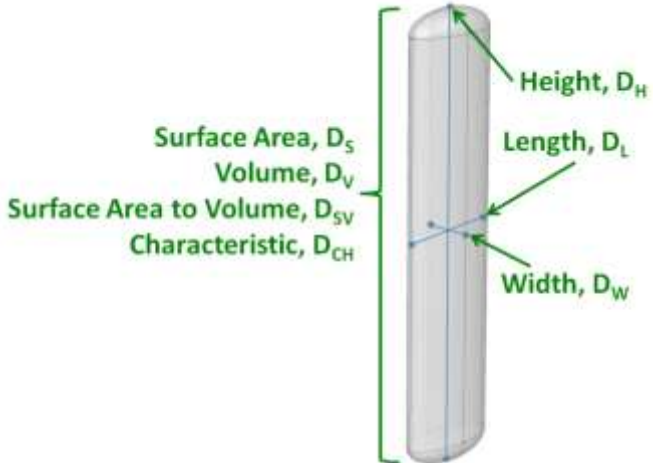


Dsv model reproduces 3-D temperature profiles

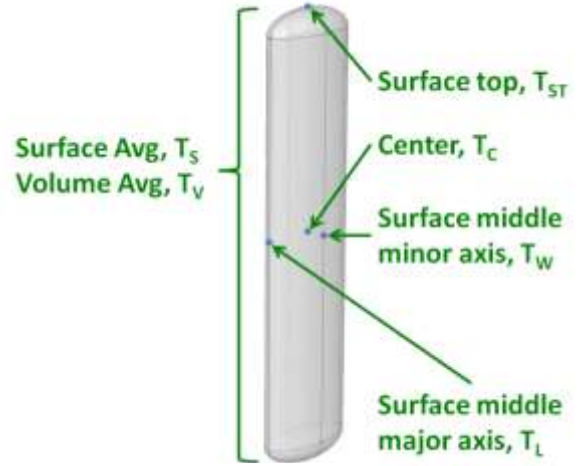
Bulk properties from Wood Handbook used for 3-D and 1-D particle model comparison for pure heat conduction (no kinetics).

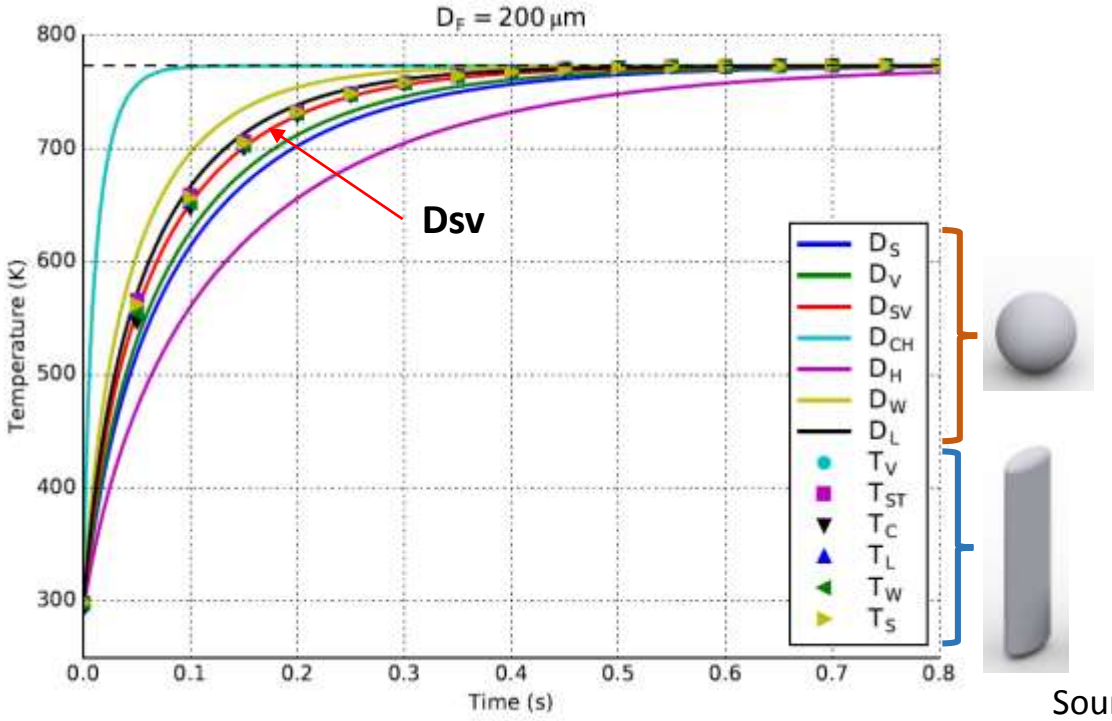
Property	Loblolly Pine	White Oak
ρ (kg/m^3)	540	720
k (W/m·K)	0.12	0.16
h (W/m^2·K)	350	350
C_p (J/kg·K)	103.1 + 3.867 T	103.1 + 3.867 T
T_o (K)	293	293
T_f (K)	773	773

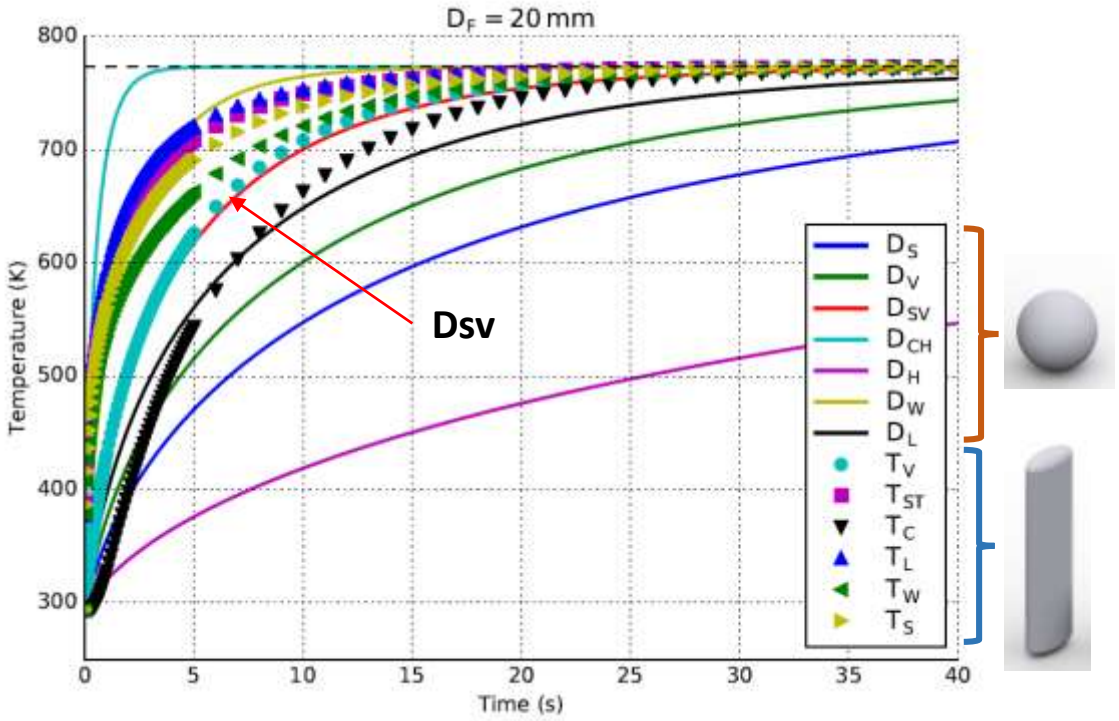
Geometry for calculating equivalent diameters.



Locations of temperature profiles.







Source: [2].