Computational study on biomass fast pyrolysis:

Hydrodynamic effects on the performance of a laboratory-scale fluidized bed reactor

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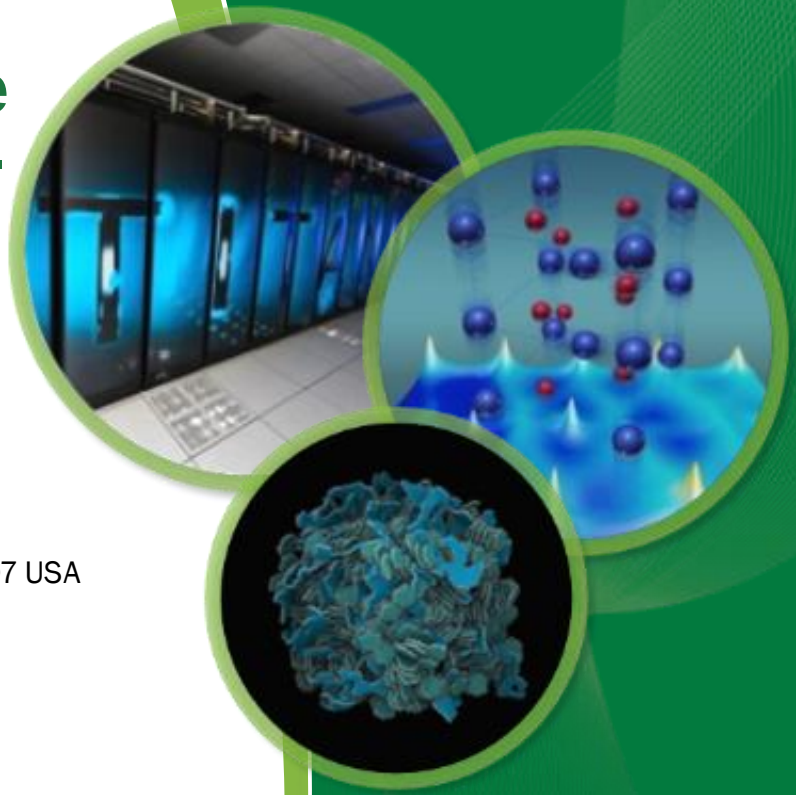

ChemCatBio Chemical Catalysis for Bioenergy

CCPC

Presented at the 2019 U.S. Department of Energy, National Energy Technology Laboratory's (NETL) Workshop on Multiphase Flow Science
Morgantown, West Virginia, August 7, 2019

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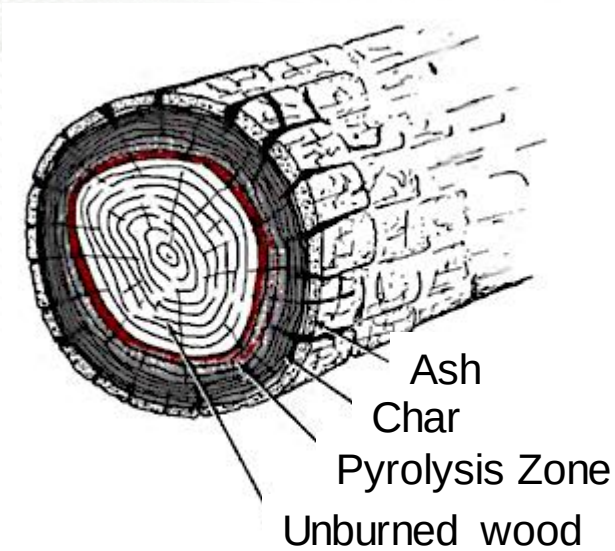
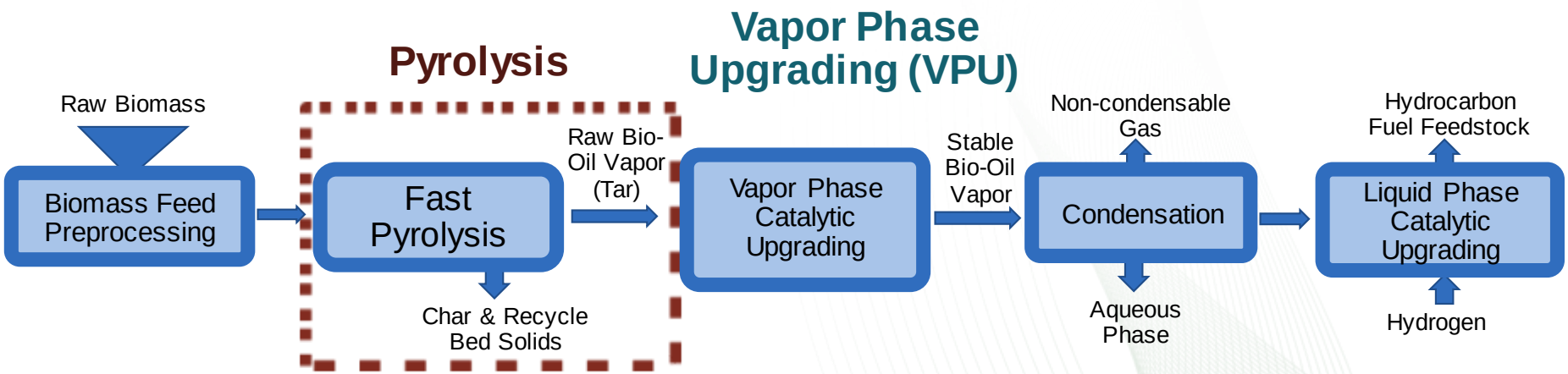
Thermochemical conversion of biomass via fast pyrolysis



Source: Heat-Its Role in Wildland Fire by Clive M. Countryman

- High yield and composition of raw oil are key, so commercial risk and economics depend on accurate performance predictions.
- Most available basic lab data are from bubbling fluidized bed reactors (FBRs).
- Good physics-based models are necessary for interpreting and scaling up lab experiments.



How do bubbling-bed hydrodynamics affect raw oil yield & composition?

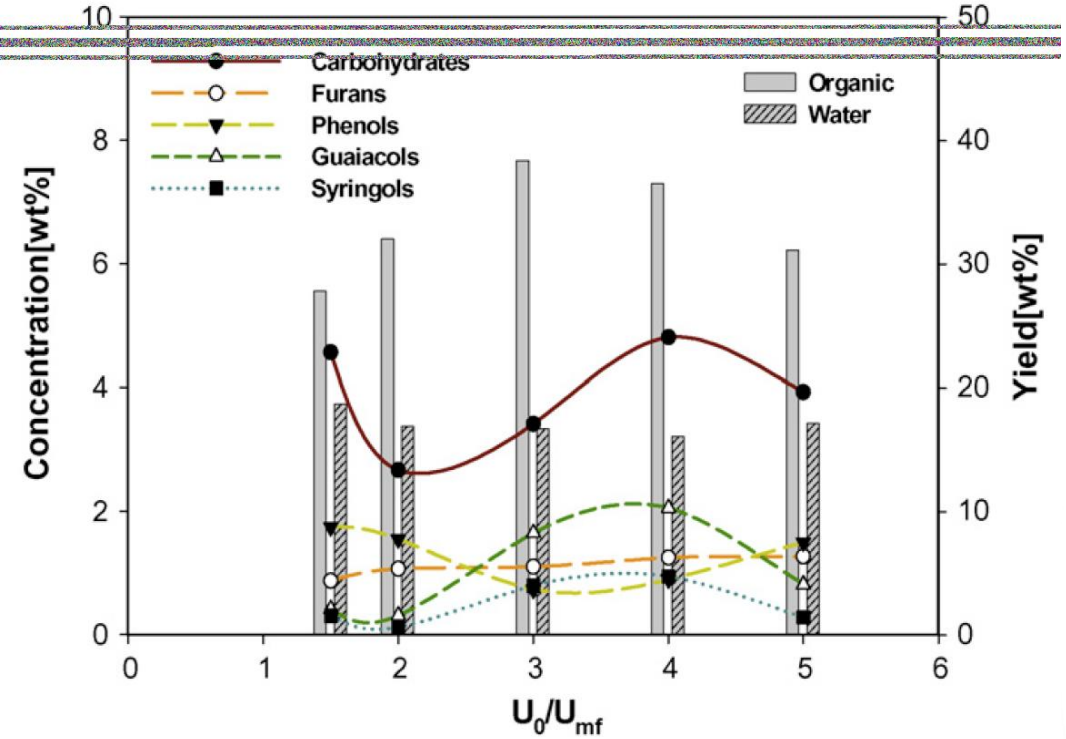


Figure: S.-H. Lee, M.-S. Eom, K.-S. Yoo, N.-C. Kim, J.-K. Jeon, Y.-K. Park, B.-H. Song, S.-H. Lee, The yields and composition of bio-oil produced from *quercus acutissima* in a bubbling fluidized bed pyrolyzer, J. Anal. Appl. Pyrolysis 83 (2008) 110-114. http://dx.doi.org/10.1016/j.jaap.2008.06.006

Hydrodynamics directly impact:

1. Particle residence time
2. Gas residence time
3. Particle heating rate
4. Particle attrition/fragmentation
5. Particle and ash elutriation
6. Particle segregation

All the above significantly impact raw oil yield and composition.

MFiX simulations of FBR pyrolysis

Two-Fluid Model

- Version and assumptions:
  - Eulerian-Eulerian (Two-Fluid Model)
  - Syamlal-O'Brien drag model
  - Kinetic theory of granular flow
    - Schaeffer frictional stress tensor formulation
    - Sigmoidal stress blending function
  - Modified SIMPLE integration with variable time stepping
  - Jackson and Johnson partial-slip wall boundary condition
  - 3D cylindrical
  - Constant biomass density (char)
  - Liden reduced kinetics for biomass
  - DLSODA ODEPACK chemistry solver
    - First-order irreversible Arrhenius rates
    - Liden 1988 biomass pyrolysis kinetics

MFiX TFM

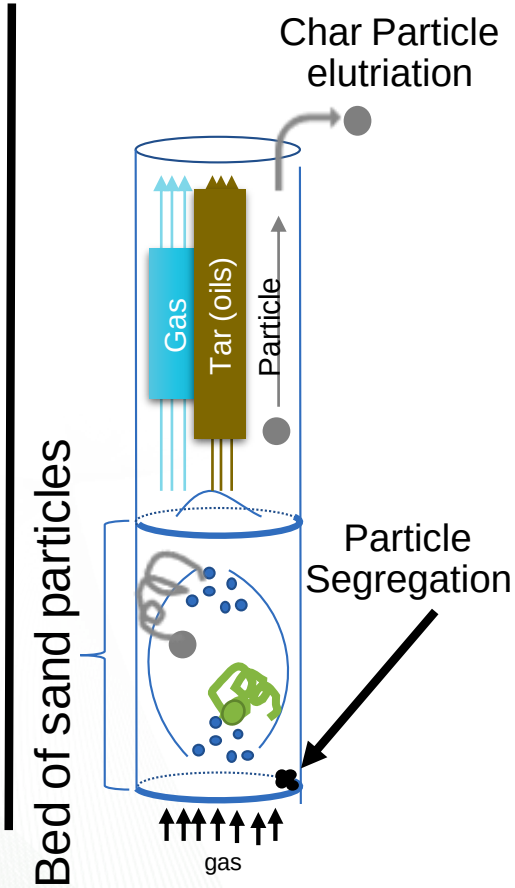
$$\text{wood} \xrightarrow{k1} \text{tar} \xrightarrow{k3} \text{gas}$$

$$\text{wood} \xrightarrow{k2} \text{gas} + \text{char}$$

$$\frac{dm_i}{dt} = -mk_i$$

$$k_i = A_i \exp(-E_i / RT)$$

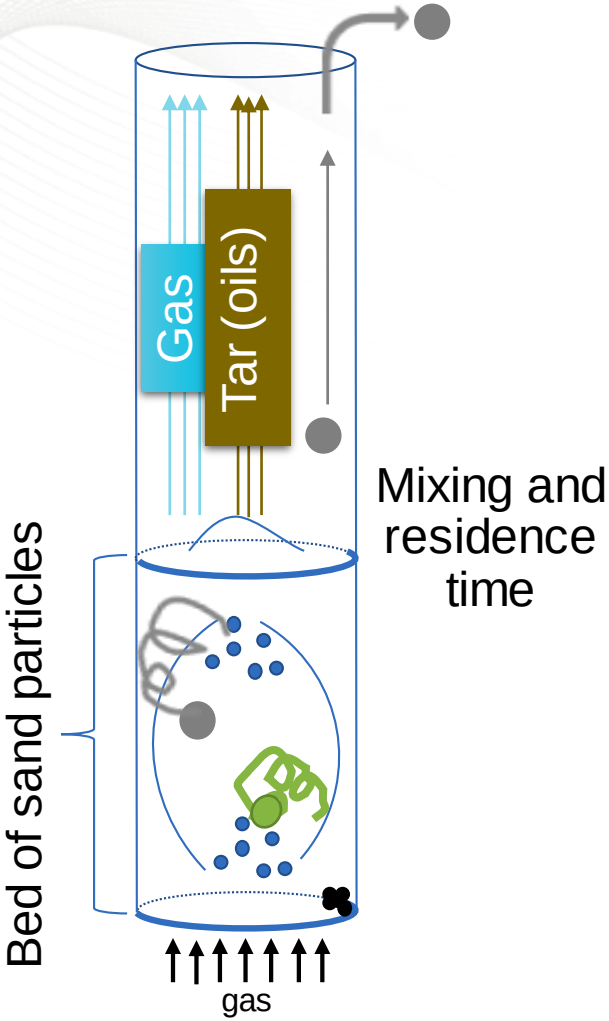
Pyrolysis reactor physics



CADES

Ramirez, E., Finney, C. E. A., Pannala, S., Daw, C. S., Halow, J., & Xiong, Q. (2017). Computational study of the bubbling-to-slugging transition in a laboratory-scale fluidized bed. Chemical Engineering Journal, 308, 544-556. doi:https://doi.org/10.1016/j.cej.2016.08.113

Interpret MFIX Results with Low-Order Models

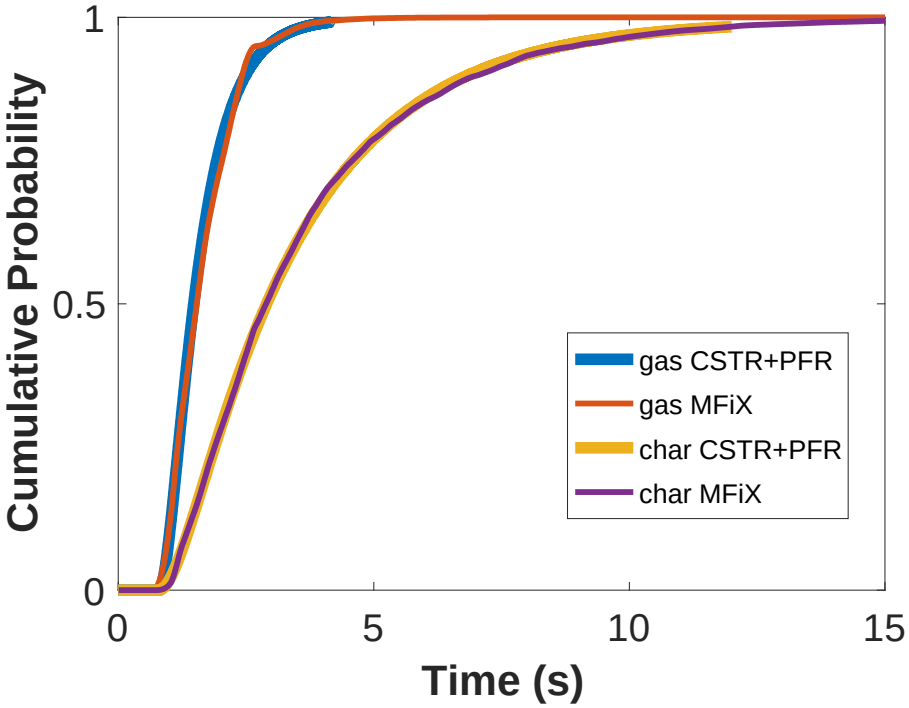


Use simplified reactor models to 'compress' essential hydrodynamic information from MFIX and combine it with pyrolysis chemistry

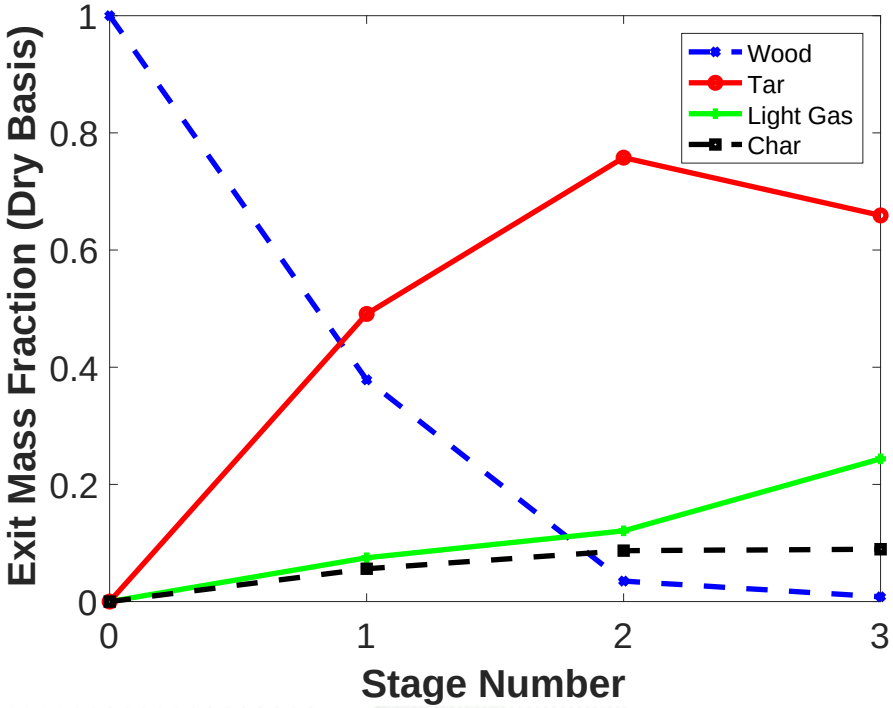
- Quantify impact of bubbles and bed solids circulation on biomass solids and pyrolysis vapor residence time distributions (RTDs)
- Identify major reaction/mixing zones needed to understand/approximate performance trends
- Relate solids and gas RTDs to predict trends for how biomass particle properties and reaction chemistry impact overall yields
- Utilize low-order models for rapid studies of operating/design parameter sweeps

Fast pyrolysis model using low-order chemistry + MFiX-based hydrodynamics ('Hybrid' modeling approach)

Step 1. Use MFiX gas and biomass RTDs to create zone reactor model approximation

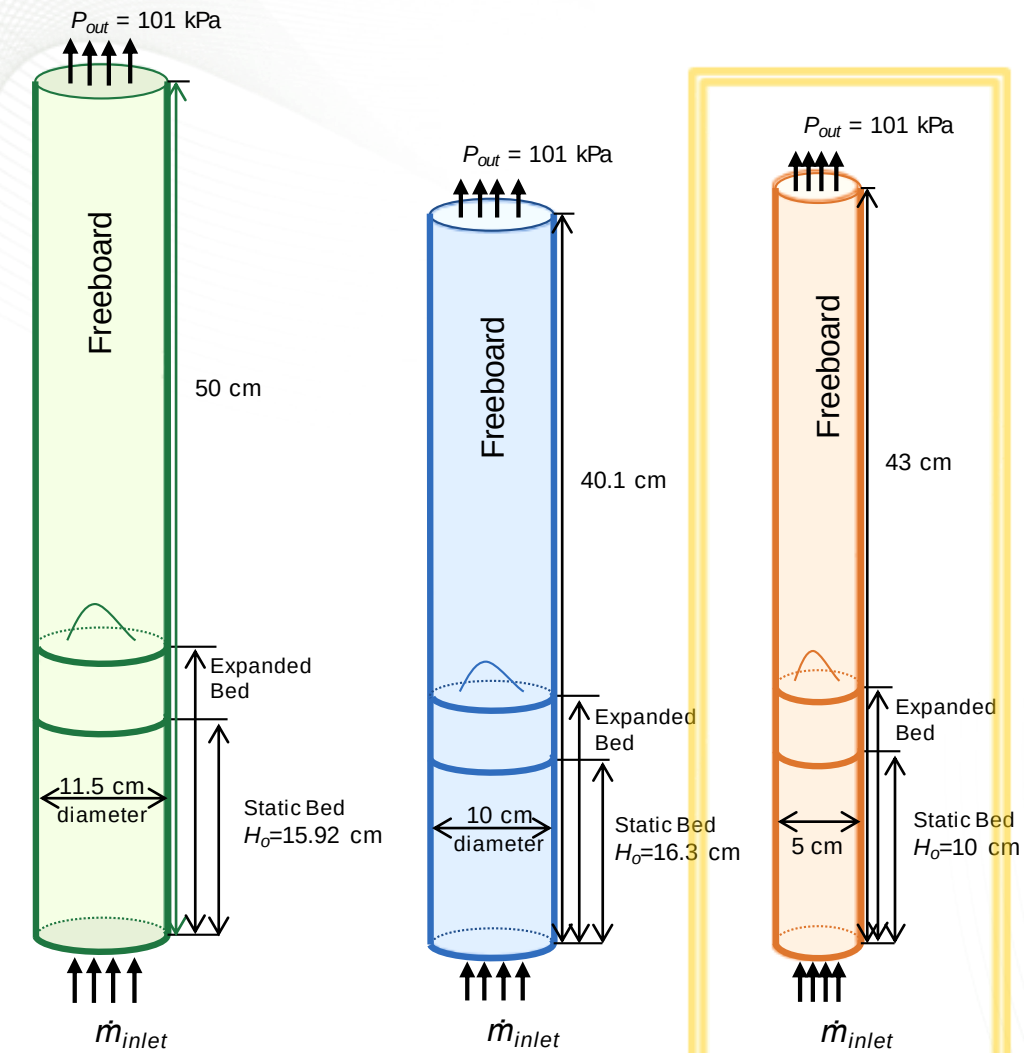


Step 2. Use zone model + Liden kinetics to predict yields



E. Ramirez, Tingwen Li, Mehrdad Shahnam, C. Stuart Daw, Computational study on biomass fast pyrolysis: Hydrodynamic effects on the performance of a laboratory-scale fluidized bed reactor, **Manuscript in preparation**.

Compare MFiX predictions with target reactor data



Mixing biomass char
Park and Choi 2013

RTD study
Berruti 1988

NREL Pyrolysis Experiment

Key steps:

- Simulate expected particle and gas RTDs with MFiX including segregation and elutriation

Questions:

- Are MFiX mixing patterns consistent with the literature?
- Can existing FB correlations capture MFiX predicted RTD trends?
- When chemistry is added, do predicted bio-oil yields agree with experiments?
- Are MFiX improvements needed?

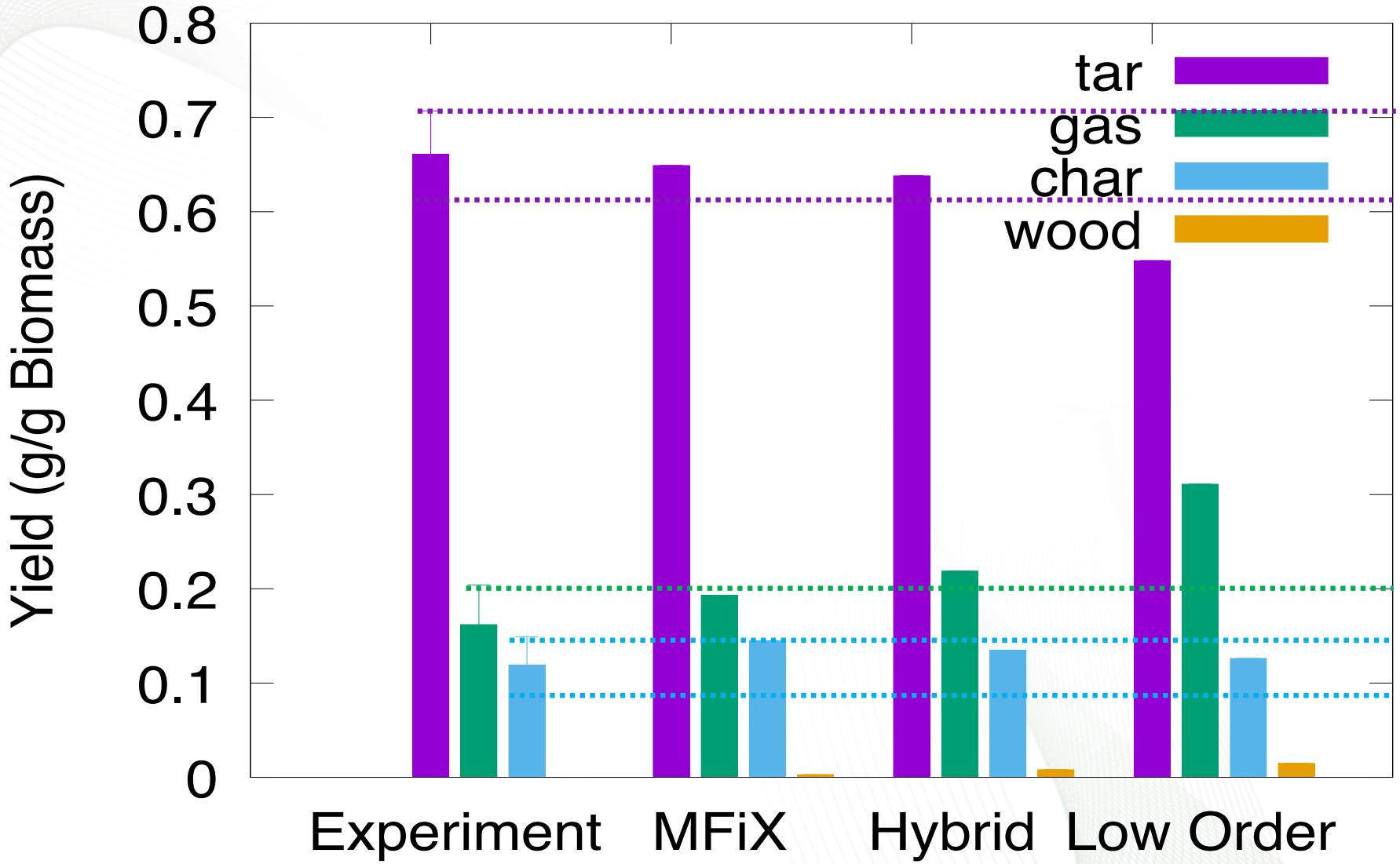
H.C. Park, H.S. Choi, The segregation characteristics of char in a fluidized bed with varying column shapes, Powder Technology 246 (2013) 561-571.

F. Berruti, A.G. Liden, D.S. Scott, Measuring and modelling residence time distribution of low density solids in a fluidized bed reactor of sand particles, Chemical Engineering Science 43 (1988) 739-748.

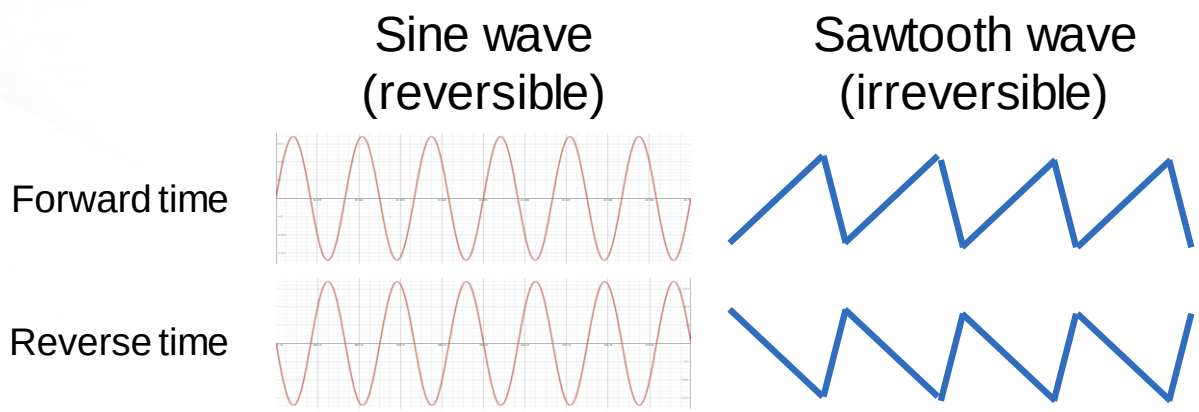
NREL pyrolyzer conditions

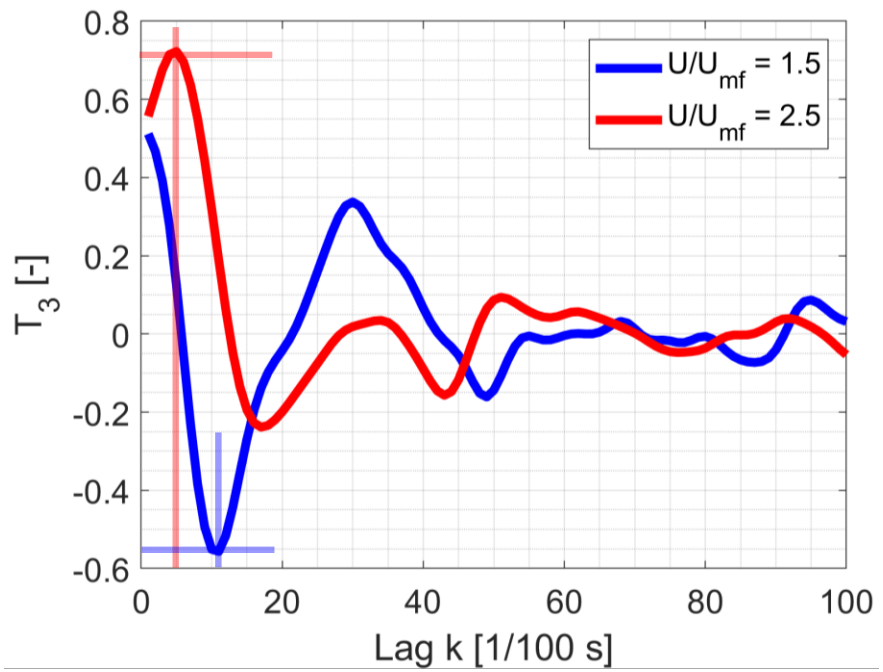
Property	Units	Values
Particle diameter (sand)	µm	500
Particle density (sand)	kg/m^3	2500
Particle diameter (styrofoam/char)	µm	278
Particle density (styrofoam)	kg/m^3	-
Particle density (char)	kg/m^3	80
Temperature	K	773
Pressure (inlet)	kPa	133
Fluidizing N_2 (range)	m/s	0.13 – 0.47
Minimum fluidization (at 773 K)	m/s	0.0565
Coefficient of restitution	—	0.9
Angle of repose	°	30
Friction coefficient	—	0.1

Comparison of the three models with experimental yields



Time-irreversibility functions show change in bubble passage profiles





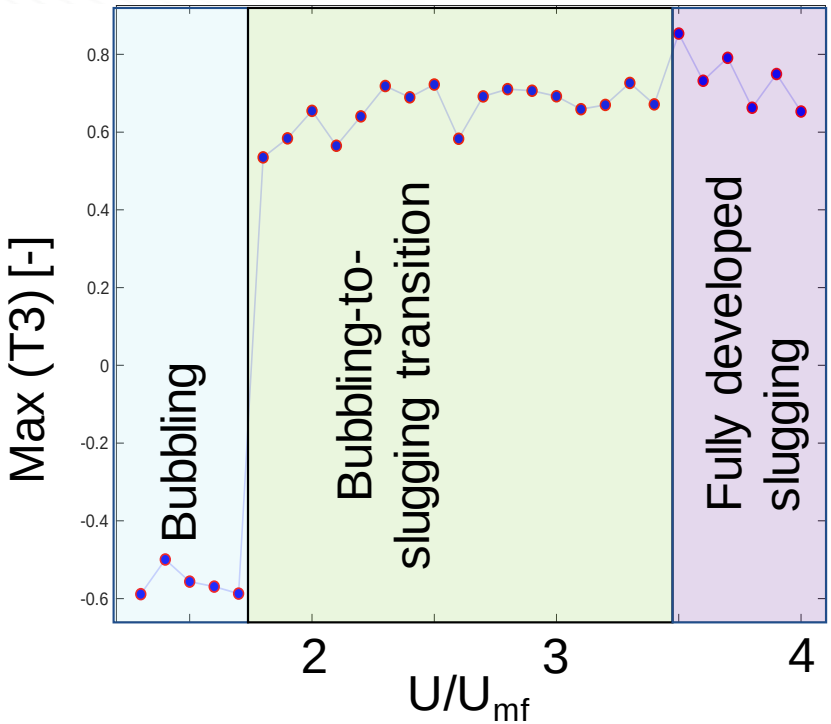
$$T_3(k) = \sqrt{N-k}\,\frac{\sum_i^{N-k}(x_{i+k}-x_i)^3}{\left[\sum_i^{N-k}(x_{i+k}-x_i)^2\right]^{3/2}}$$

Summary metrics: magnitude and location (lag) of maximum T_3

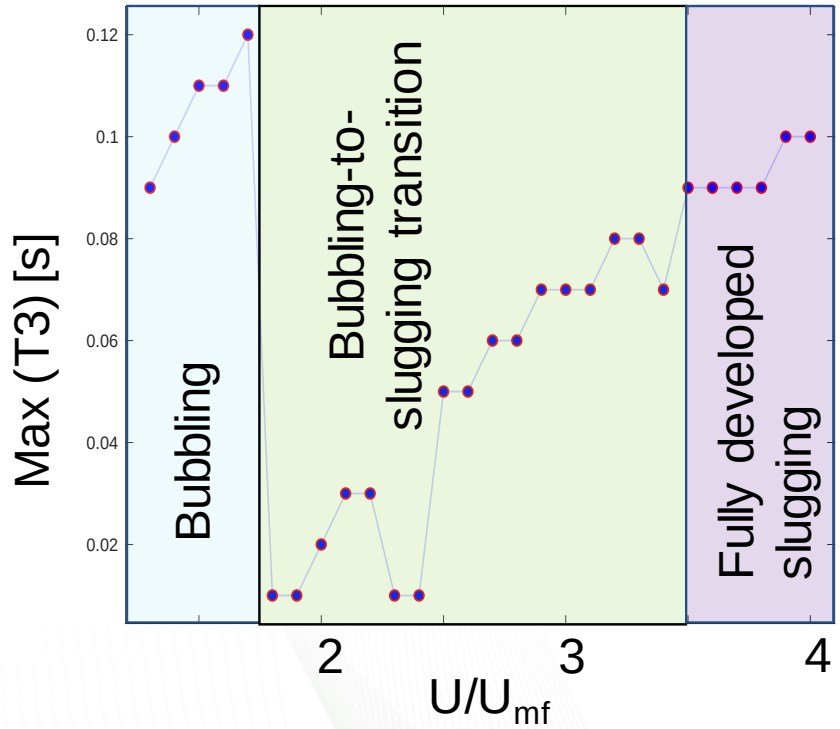
Observable: time series of a variable at a chosen location

Time-irreversibility metric captures bubbling-to-slugging transition

Maximum time irreversibility



Location of maximum time irreversibility



- Observable: time series of bed pressure averaged over slice of 0.9–1.0 · H_0
- "Jitter" due to finite-sample effects (limited observation time of ~30–40 s)

Char mixing changes with fluidization regime

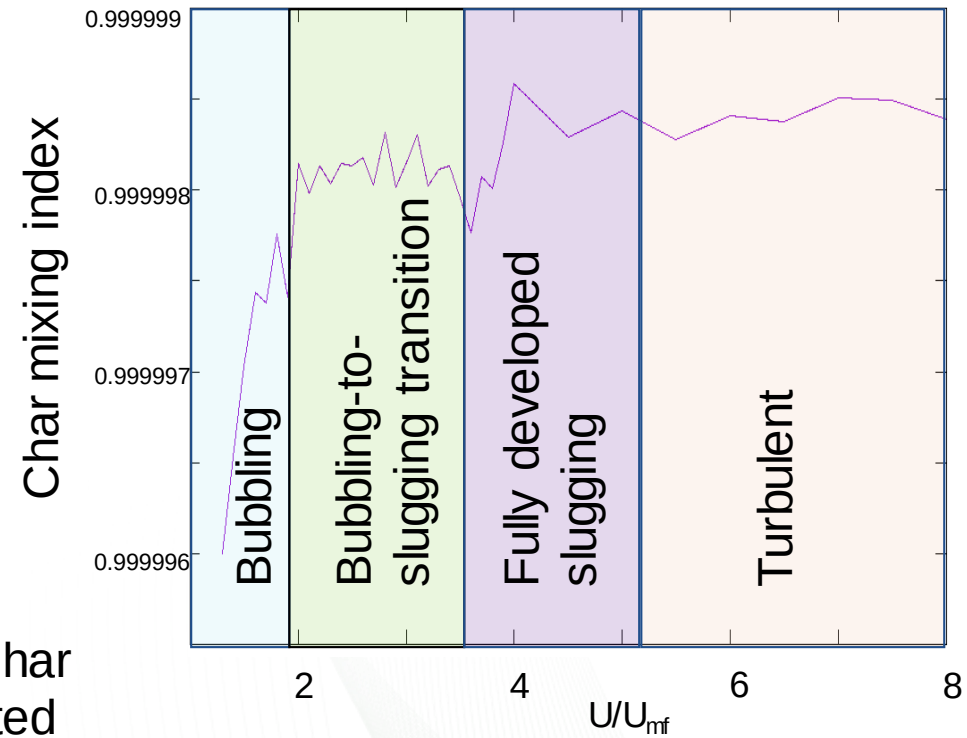
Fluidization regime affects char particle mixing intensity
Hydrodynamics must be considered

Kramer's mixing index

$$M = \frac{\sigma_0^2 - \sigma^2}{\sigma_0^2 - \sigma_r^2}$$

$$\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(X_i - \bar{X})^2}$$

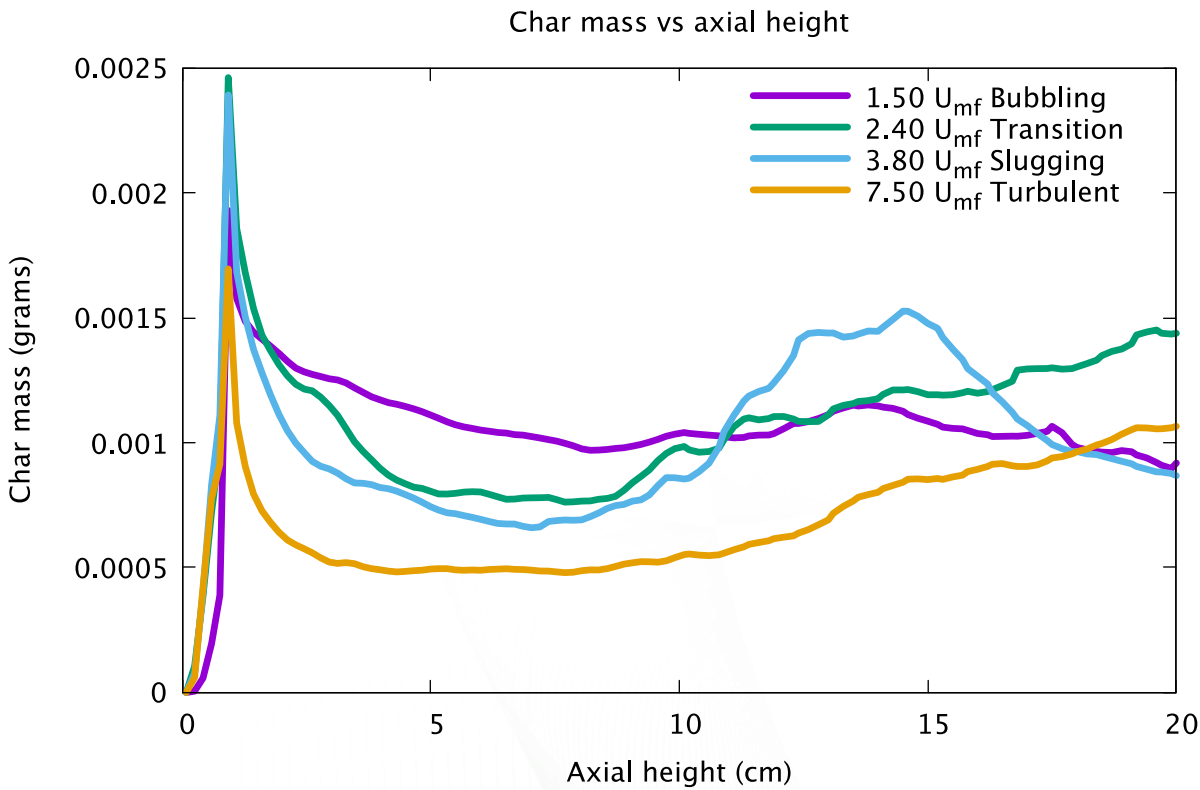
σ_0^2= standard deviation mass fraction of char when sand and char completely segregated
σ_r^2= standard deviation mass fraction of char when sand and char completely mixed

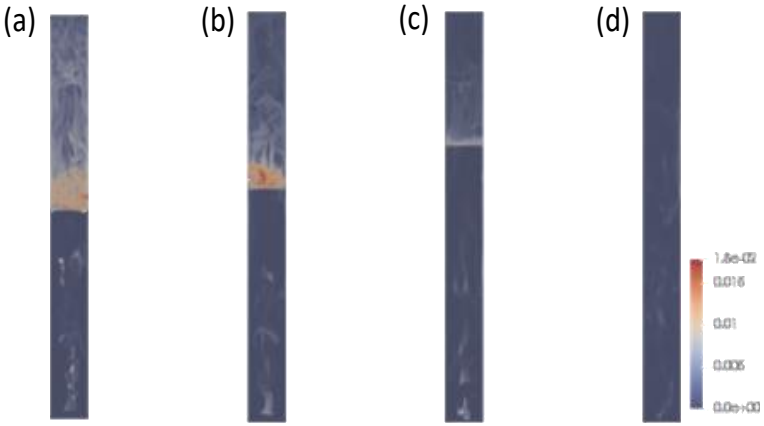


Gyenis, J. (1999). Assessment of mixing mechanism on the basis of concentration pattern. *Chemical Engineering and Processing: Process Intensification*, *38*(4), 665-674. doi:10.1016/S0255-2701(99)00066-5

Char spatial distribution changes with fluidization regime

- At bubbling-to-slugging transition char concentration at bottom decreases, but increase in top
- At slugging more char in top region
- At turbulent least char in the bed



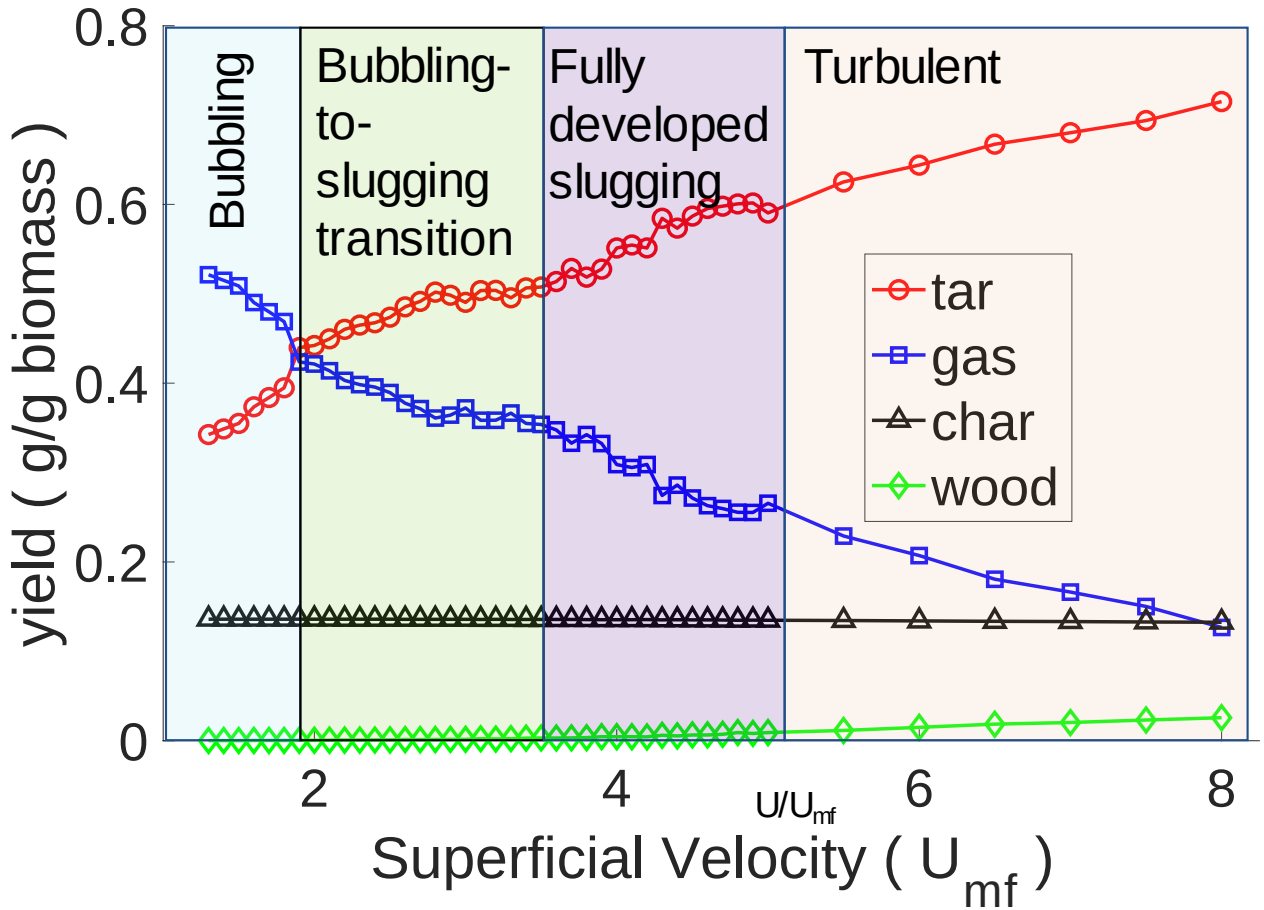


Note: this considers up to H_0 and does not include freeboard.

Bubbles/mixing/elutriation affect pyrolysis yield

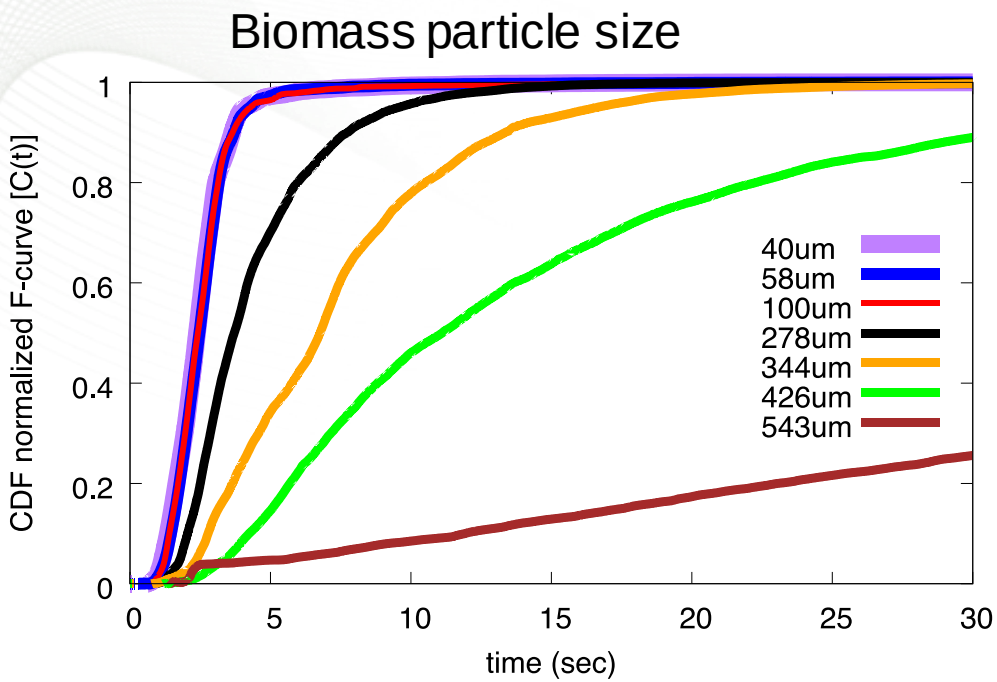
Slugging beds reach a maximum in tar (oil) yield in the bubbling-to-slugging transition

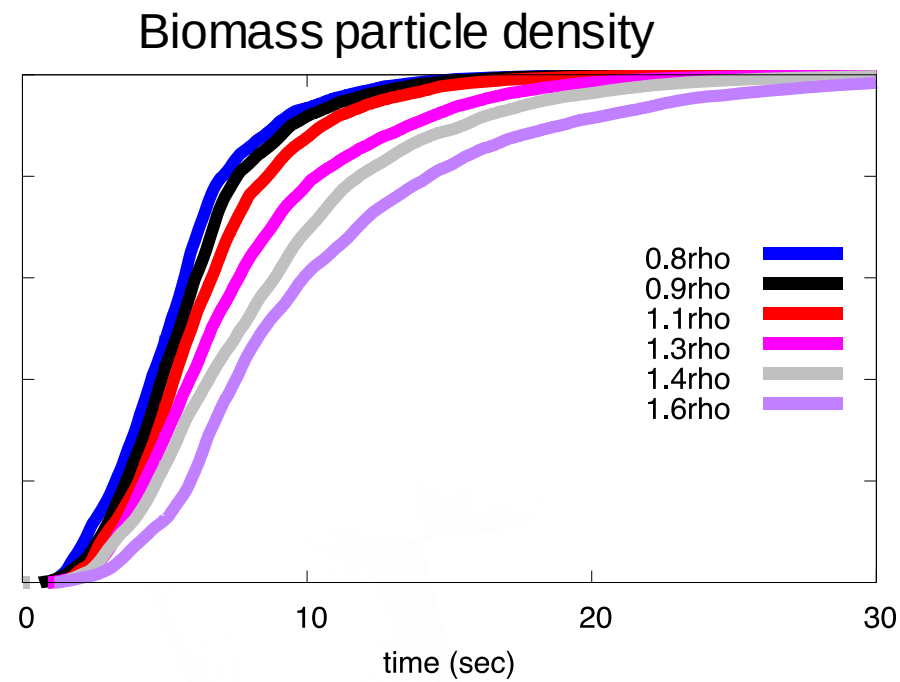
Maximum tar (oil) yield occur at turbulent fluidization where slip velocity between gas and particles is high with a very short residence time

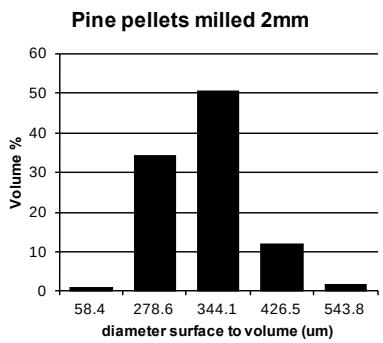


- "Jitter" due to finite-sample effects (limited bubble events seen during tracing)

Particle size and density affect residence time distribution





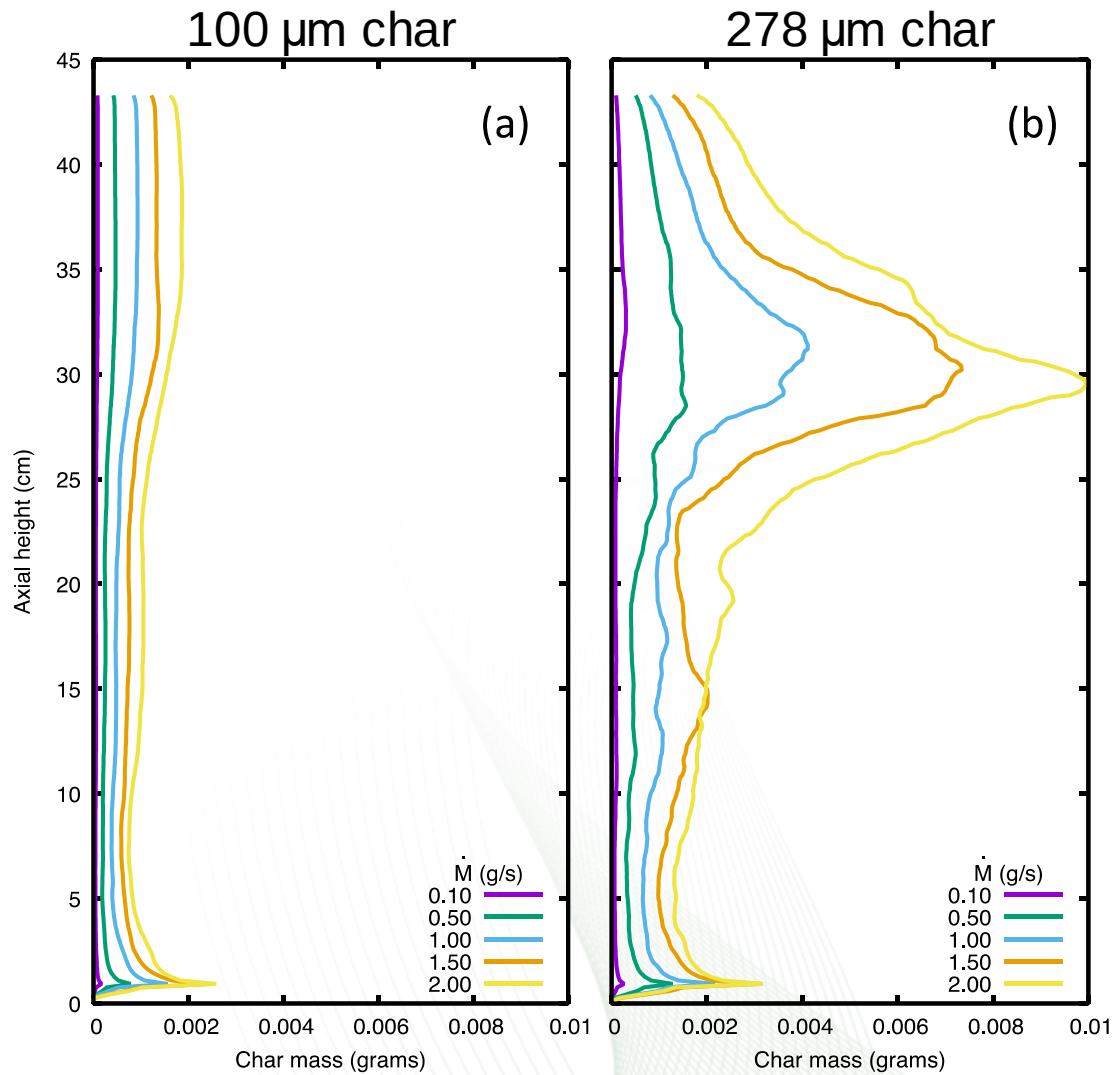


Particle size and density must be selected carefully such that elutriation will occur

Pecha, M. B., Ramirez, E., Wiggins, G. M., Carpenter, D., Kappes, B., Daw, S., & Ciesielski, P. N. (2018). "Integrated Particle- and Reactor-Scale Simulation of Pine Pyrolysis in a Fluidized Bed." Energy & Fuels, 32(10), 10683-10694.

Char concentration varies with particle size and feed rate

- Larger particles create char layer at top of sand bed and freeboard region
- Tar vapors may be reduced through the char layer
- Char particle concentration changes bed particle size distribution and possibly fluidization
- 0.1181 g/s particle feed rate
- Monodisperse cases from among 100–500 µm PSD



Concluding remarks

- Quantifying the combined effects of hydrodynamics and chemistry is essential in utilizing lab-scale biomass pyrolysis reactor data for scale up
- Biomass particle properties and fluidization intensity have major impacts on product yields
- Two-fluid codes like MFiX can yield useful details about pyrolyzer hydrodynamics and gas and solid RTDs but improvements to the physics are still needed
- Combining MFiX hydrodynamics with low-order chemistry models appears to offer potential benefits
- Biomass pyrolysis reactor geometry and operating conditions must be designed in conjunction with a model that can capture the physics of interest
- **Biomass particle properties and feed rate have the potential to negatively affect pyrolysis yield and composition**
- **Char mixing and concentration in the bed and freeboard should be considered at the reactor design stage**

Acknowledgements

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SABIC – Sreekanth Pannala

University of Tennessee – Nourredine Abdoulmoumine and Biomass convErsion And Modeling (BEAM) team, Bredesen Center for Interdisciplinary Research and Graduate Education

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Questions?

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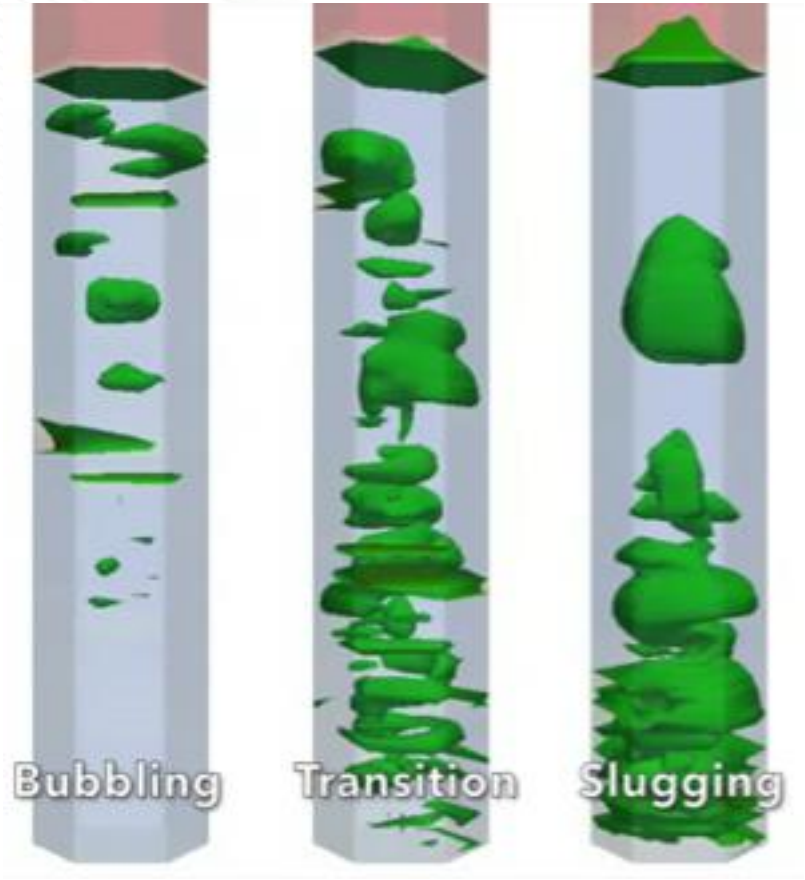
Consortium for Computational Physics and Chemistry
http://cpcbiomass.org

Extra slides if there are questions

Background and Motivation (3)

How should lab FBR data be interpreted/analyzed?



FB Hydrodynamics directly impact:

1. Particle residence time
2. Gas residence time
3. Particle heating rate
4. Particle attrition/fragmentation
5. Particle and ash elutriation
6. Particle segregation

All the above significantly impact raw oil yield and composition.

Note: Bubble boundary depicted where void fraction > 0.65

E. Ramirez, C.E.A. Finney, S. Pannala, C.S. Daw, J. Halow, Q. Xiong, Computational study of the bubbling-to-slugging transition in a laboratory-scale fluidized bed, Chemical Engineering Journal 308 (2017) 544-556. http://dx.doi.org/10.1016/j.cej.2016.08.113

Kramer's mixing index for char mixing

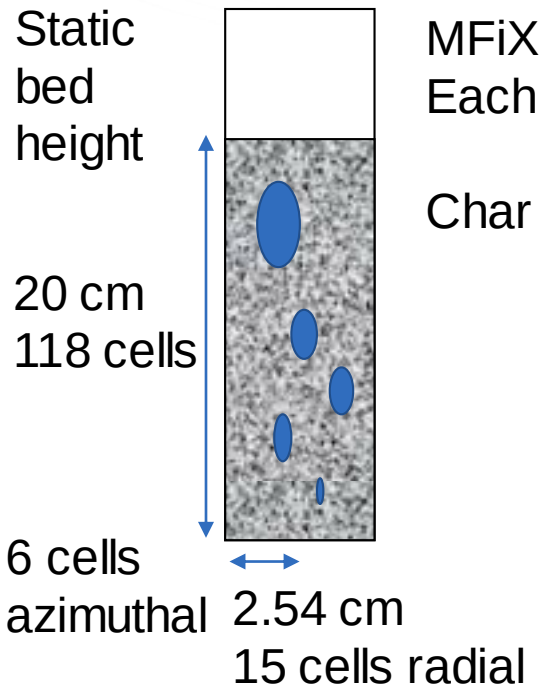
- $M = \frac{\sigma_0^2 - \sigma^2}{\sigma_0^2 - \sigma_r^2}$ m=1 complete mixing, m=0 complete segregation
- $\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(X_i - \bar{X})^2}$

Created segregated and complete mixed case for analysis

- σ_0^2= standard deviation mass fraction of char when sand and char completely segregated (heterogeneous)
- σ_r^2= standard deviation mass fraction of char when sand and char completely mixed (homogeneous)

Guo, J. (1999). A new theory of mixing and its application on the basis of concentration fluctuation. *Chemical Engineering and Processing: Process Intensification, 38*(4), 665-674. doi:10.1016/S0255-2701(99)00066-5
Pu, W., Zhao, C., Xiong, Y., Liang, C., Chen, X., Lu, P., & Fan, C. (2010). Numerical simulation on dense phase pneumatic conveying of pulverized coal in horizontal pipe at high pressure. *Chemical Engineering Science, 65*(8), 2500-2512. doi:10.1016/j.ces.2009.12.025

Complete mixing case (Homogeneous)



MFiX has multiple cells 10620 cells in static bed height
Each cell char and sand mass measured (time averaged time 15-19 s

Char fraction in each cell used for stats (standard deviation)

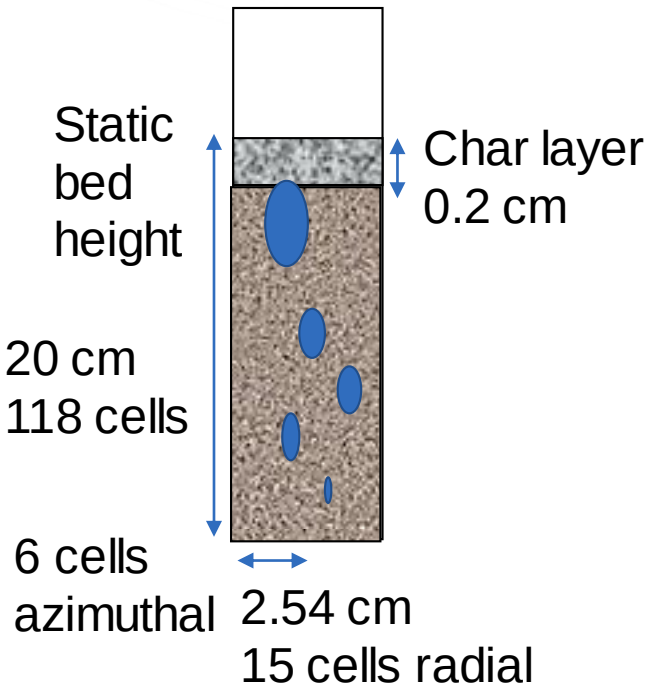
σ_r^2=0 (standard deviation)

Assumption for fully mixed:
Bed region emulsion and bubbles have the same char fraction throughout

Complete segregated case (Heterogenous)

MFiX has multiple cells 10620 cells in static bed height
Each cell char and sand mass measured (time averaged time 15-19 s)

Char fraction in each cell used for stats (standard deviation)
Char layer volume based on 0.51 void fraction (expanded bed-fluidized).



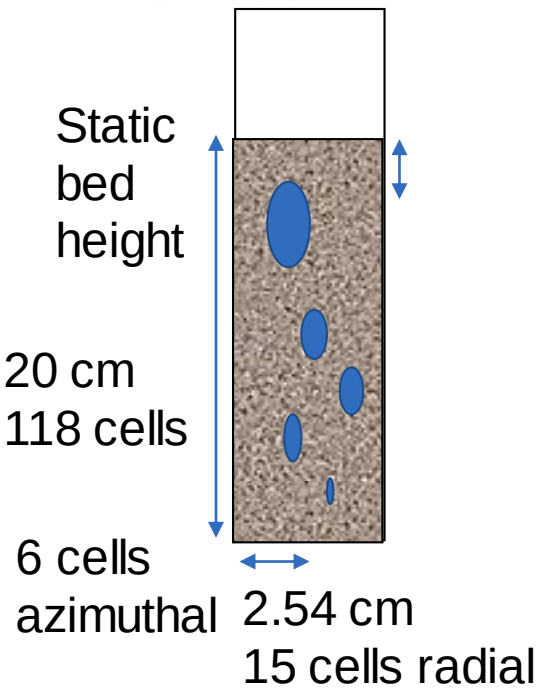
σ_0^2=0.312996541687 (standard deviation)

Assumption for fully segregated:
Char layer above bed of sand is just char. Bubbles and emulsion in char layer have the same char fraction =1.

Mixing cases (1.3 – 8.0 U_{mf})

MFiX has multiple cells 10620 cells in static bed height
Each cell char and sand mass measured (time averaged time 15-19 s)

Char fraction in each cell used for stats (standard deviation)



σ_r^2 (standard deviation)

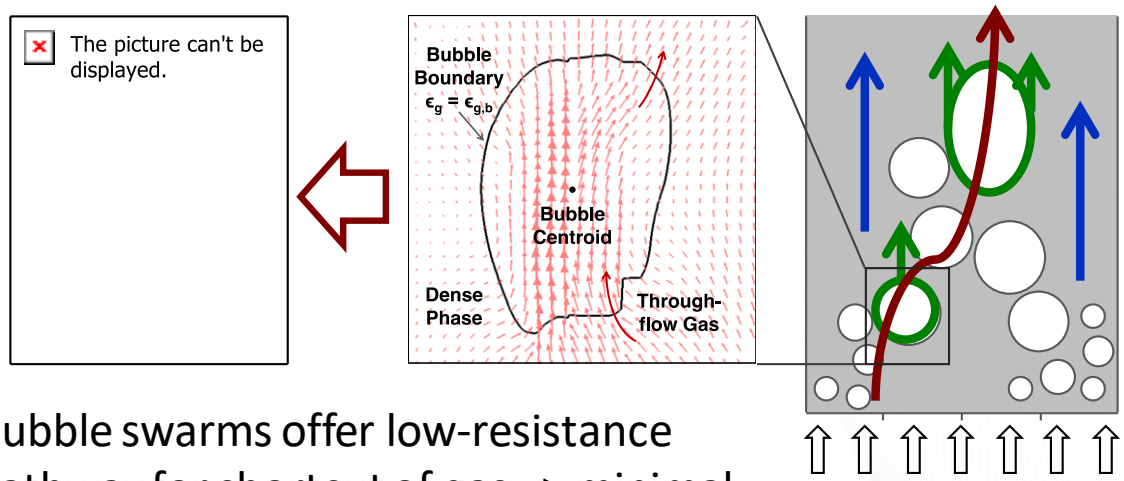
Assumption for mixing cases:
Char mass fraction=
char mass/(char mass + sand mass)

Averaged of 15.0 – 19.0 seconds
Bubbling bed at stationary state

Phase 3: Preliminary Work

What is unique about bubbles that affects RTD and yields?

Total Gas Flow = dense flow + visible bubble flow + through-flow

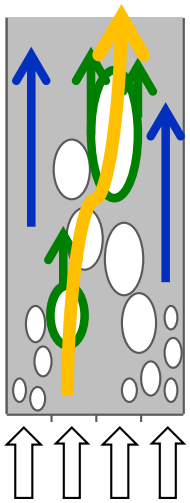


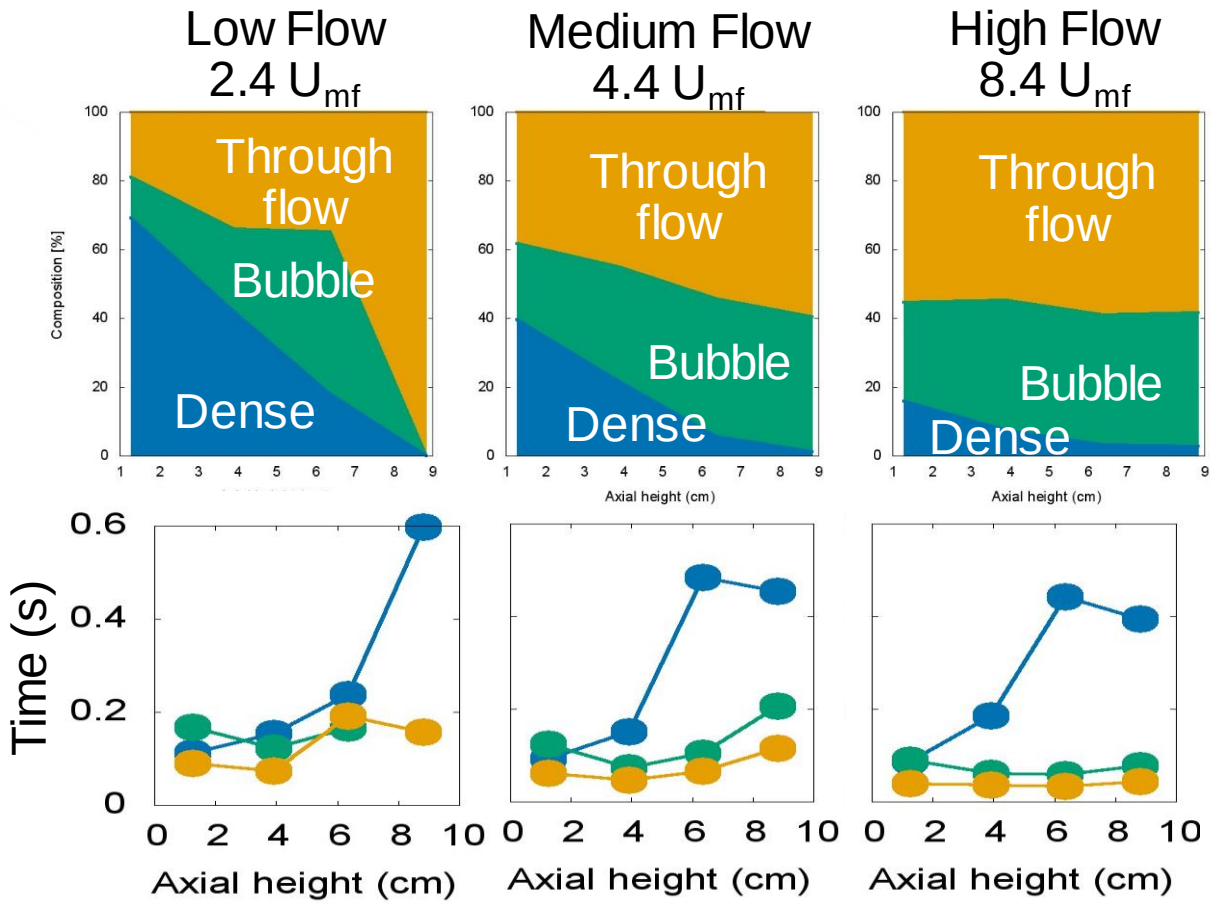
Bubble swarms offer low-resistance pathway for shortcut of gas => minimal contact with dense phase

A. Bakshi, C. Altantzis, R.B. Bates, A.F. Ghoniem, Multiphase-flow statistics using 3d detection and tracking algorithm (ms3data): Methodology and application to large-scale fluidized beds, Chemical Engineering Journal 293 (2016) 355-364. http://dx.doi.org/10.1016/j.cej.2016.02.058

Phase 3: Preliminary: Pyrolysis chemistry + CFD

Bubbles affect residence time along reactor height





Peer reviewed publications

Ramirez, E., Li, T., Shahnam, M., & Daw, C. S. (**In Preparation**). “Computational study on biomass fast pyrolysis: Hydrodynamic effects on the performance of a laboratory-scale fluidized bed reactor.” Chemical Engineering Journal.

Ramirez, E., Finney, C.E.A., Daw, C. S. (**In Preparation**). “Computational study on biomass fast pyrolysis: Design considerations for a laboratory-scale fluidized bed.” Chemical Engineering Journal.

Pecha, M. B., Ramirez, E., Wiggins, G. M., Carpenter, D., Kappes, B., Daw, S., & Ciesielski, P. N. (2018). “Integrated Particle- and Reactor-Scale Simulation of Pine Pyrolysis in a Fluidized Bed.” Energy & Fuels, 32(10), 10683-10694.

Ramirez, E., Finney, C.E.A., Pannala, S., Daw, C.S., Halow, J., Xiong, Q. (2017). "Computational study of the bubbling-to-slugging transition in a laboratory-scale fluidized bed." Chemical Engineering Journal, **308**: 544-556.

Xiong, Q., et al. (2016). "Modeling the impact of bubbling bed hydrodynamics on tar yield and its fluctuations during biomass fast pyrolysis." Fuel **164**: 11-17.

Daw, C.S., Wiggins, G., Xiong, Q., Ramirez, E. (2016) “Development of a Low-Order Computational Model for Biomass Fast Pyrolysis: Accounting for Particle Residence Time.” ORNL/TM-2016/69.

Clark, E., Griffard, C., Ramirez, E., & Ruggles, A. (2015). Experiment attributes to establish tube with twisted tape insert performance cooling plasma facing components. Fusion Engineering and Design, **100**, 541-549.