# Eulerian multiphase models for biomass mixing and reactions in bidisperse gas-solid flows

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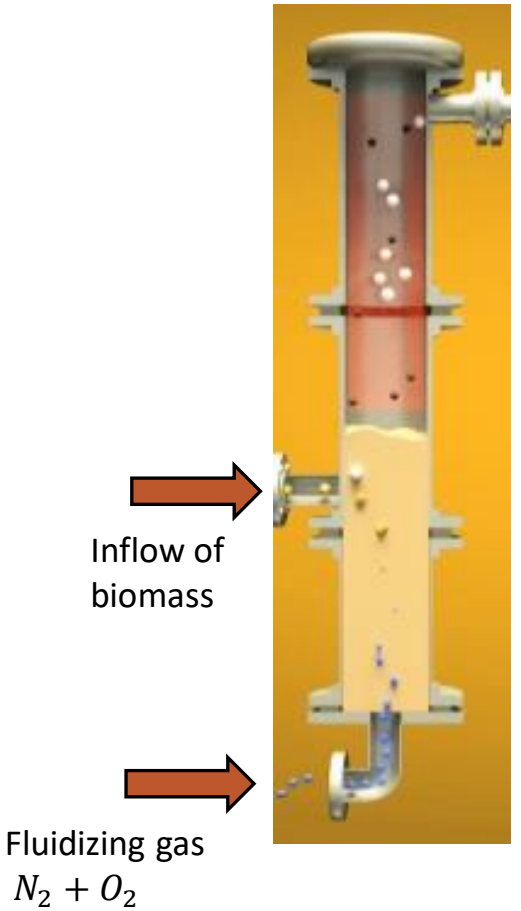
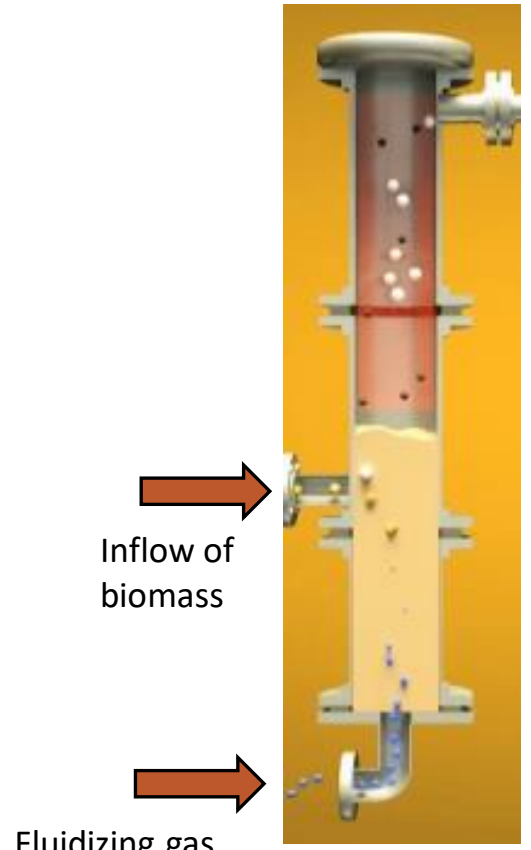
# Autothermal pyrolysis

- Thermochemical conversion of biomass for production of bio-fuels
- Conventional pyrolysis is done in the absence of oxygen
- Pyrolysis of biomass is an endothermic process
- Heat is supplied to the walls of the reactor
- Feasible for small scale reactors
- Not feasible for plant-scale reactors due to the reduced surface area to volume ratio of the reactor
- Heat transfer becomes a bottleneck for scale-up of the conventional biomass pyrolysis process.
- Autothermal pyrolysis aims at addressing this limitation
- Small amounts of oxygen is injected into the reactor to allow partial oxidation of pyrolysis products.
- The exothermic reactions supply heat for the endothermic reactions.



# Important aspects

- Important aspects:
  - Char combustions is one of the major contributors of heat
  - Retention of char is essential for its reaction with oxygen
  - The quick release of volatile gases from biomass is important for  bio-oil yields
  - The performance of the reactor may be affected by the geometric configurations of the fluidized bed reactor
  - The quality of mixing of biomass and sand may be influenced by point of injection of biomass, affecting the yields
- Hydrodynamics
  - Eulerian multi-fluid model
  - Investigation mixing in the fluidized bed reactor.
- Chemistry
  - What are the relevant chemistry mechanism for this process?
  - Chemistry solver: chemFoam

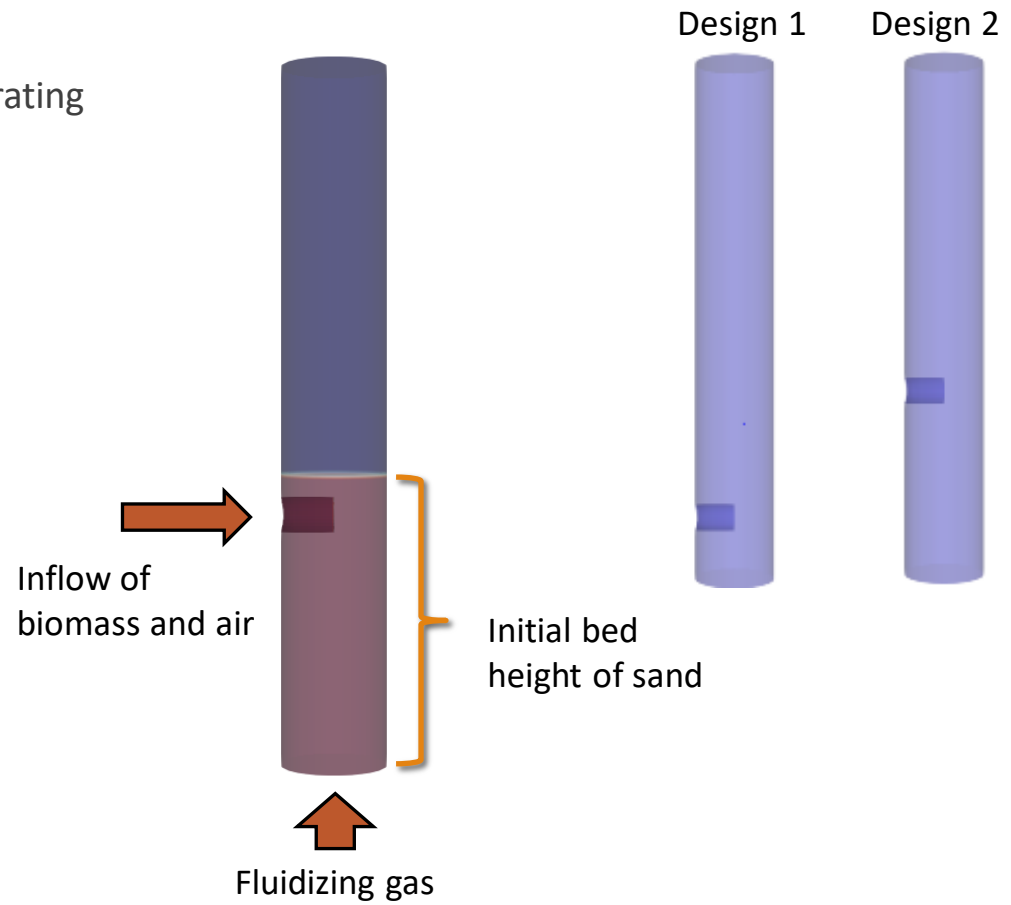


# Hydrodynamics:

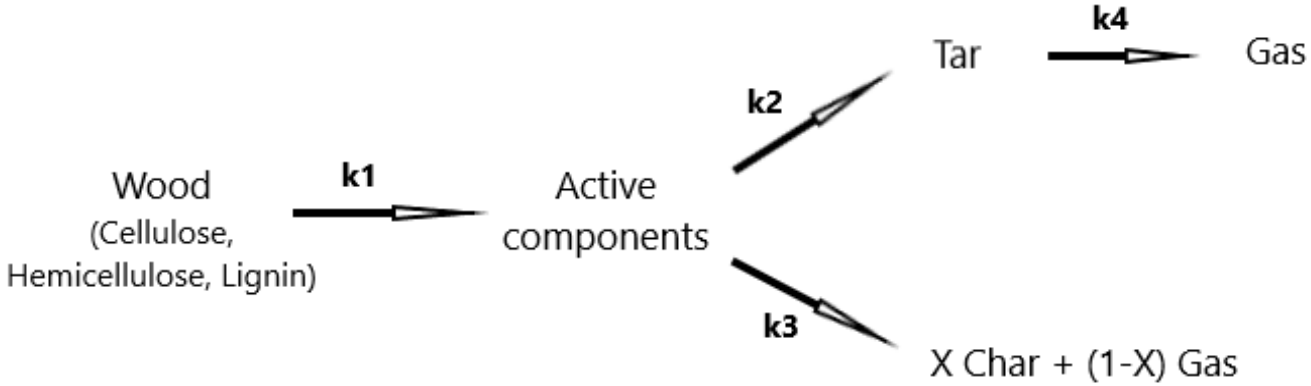
- Mixing of biomass in sand is important in biomass pyrolysis
- Biomass at room temperature injected into a bed of sand at the desired operating temperature
- Properties of the particles in question

| *Solid particles* | *Size (μm)* | *Density (kg/m$^3$)* |
|---|---|---|
| Silica sand | 600 | 2650 |
| Biomass | 1587 | 700 |

- The reactor dimensions
  - Diameter: 3.81 cm
  - Height: 42. 7 cm
  - Biomass auger diameter: 1.27 cm
  - Biomass injection height: 6.81 cm
- At what height should we inject biomass into the reactor?



# Chemistry




| | |
|---|---|
| Devolatilization | Ranzi 2008, Ranzi 2017<br>Multi-components and is a multi-step process. |
| Char combustion | Kinetic rate obtained from experiments done at the Bioeconomy institute, ISU |
| Secondary gas phase reactions | CRECK model |

R.S. Miller, J. Bellan, A generalized biomass pyrolysis model based on superimposed cellulose, hemicellulose and lignin kinetics, Combust. Sci. Technol. 126 (1997) 97–137. https://doi.org/10.1080/00102209708935670.

# Eulerian model

- The gas phase is considered as the primary phase, and the solid phases are considered as the secondary phases.
- Phase volume fractions are used to track phases in the finite volume frame.
- The volume fraction of the phases sum to unity.

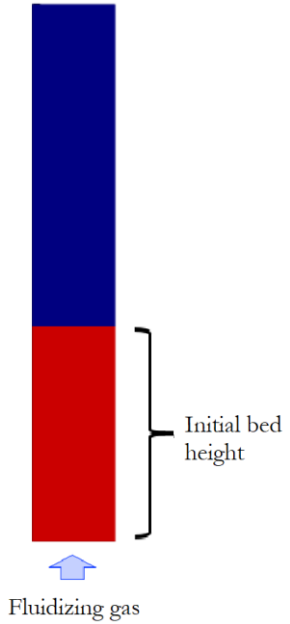
$$\phi_g + \sum_{k=1}^{K} \phi_{s,k} = 1$$

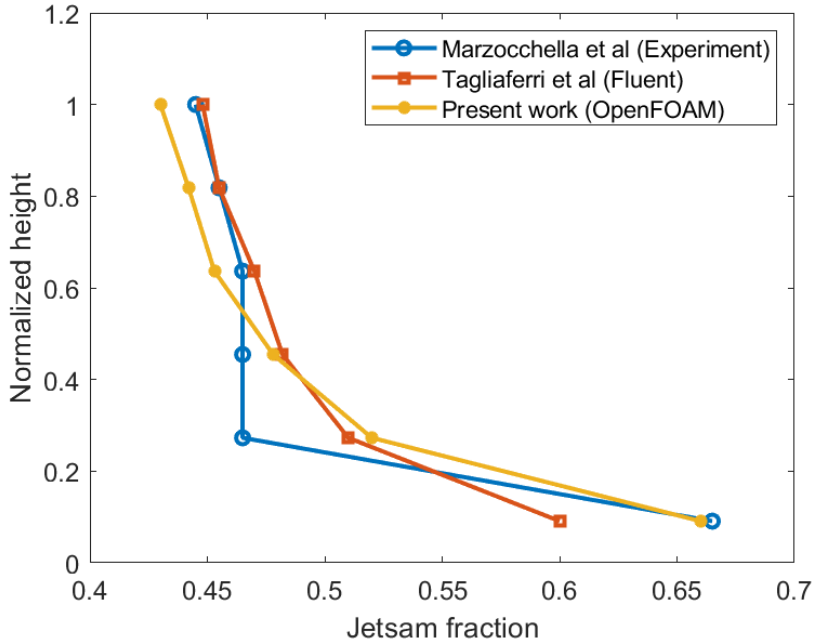
- Each phase has an equations for continuity and momentum and **energy.**
- **Heat and mass transfer between phases**
- **Transport equations for species.**
- Closures for momentum exchange between phases: gas-particle drag, and particle-particle drag
- **Momentum exchange due to mass transfer between phases**
- Kinetic theory closures granular flows ( granular temperature, particle pressure, solid viscosity, solid conductivity)
- Frictional stress model

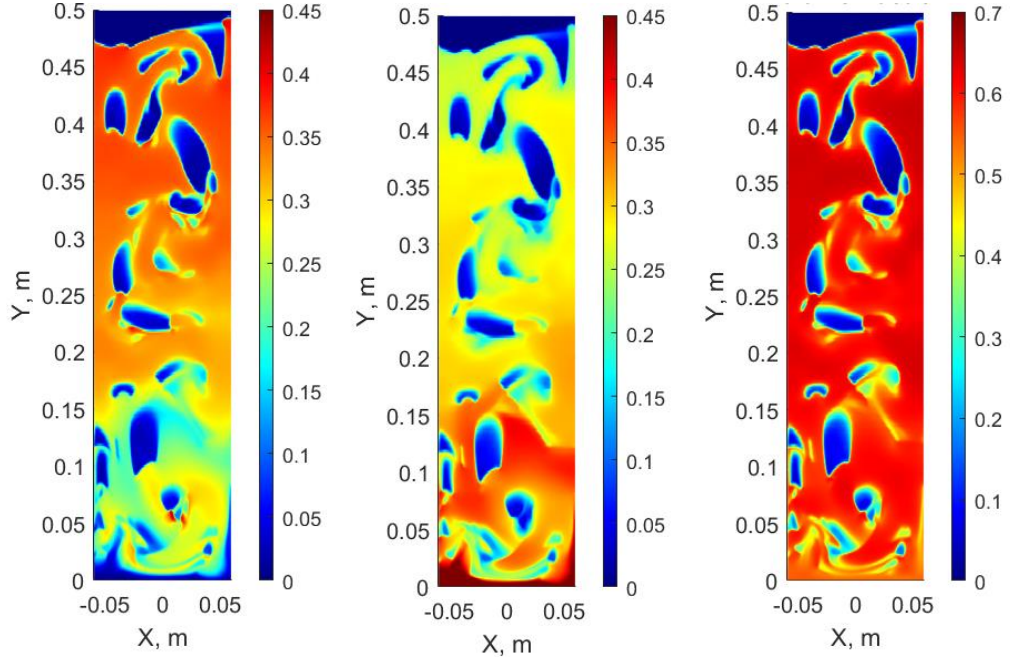
# Eulerian model: validation

| *Solid particles* | *Size (μm)* | *Density (kg/m³)* |
|---|---|---|
| Flotsam: Silica sand | 125 | 2600 |
| Jetsam: Glass beads | 500 | 2540 |

- Segregation of binary mixture of particles starting at a perfectly mixed condition
- Particles segregate as the bed is fluidized




*Flotsam* *Jetsam* *Total Particle*

Tagliaferri C, Mazzei L, Lettieri P, Marzocchella A, Olivieri G, Salatino P. CFD simulation of bubbling fluidized bidisperse mixtures: Effect of integration methods and restitution coefficient.
*Chem Eng Sci*. 2013;102:324-334. doi:10.1016/j.ces.2013.08.015

# Local solid mixing

$$M_{\xi_A} = \begin{cases} \dfrac{\xi_A}{2\bar{\xi}_A}, & 0 \le \xi_A < \bar{\xi}_A \\ 1 - \dfrac{1}{2}\left(\dfrac{1-\xi_A}{1-\bar{\xi}_A}\right), & \bar{\xi}_A \le \xi_A \le 1 \end{cases}$$

- Compute the solid fraction for biomass, $\xi_A$
- Then compute the local solid mixing index
- How well does sand mix with biomass

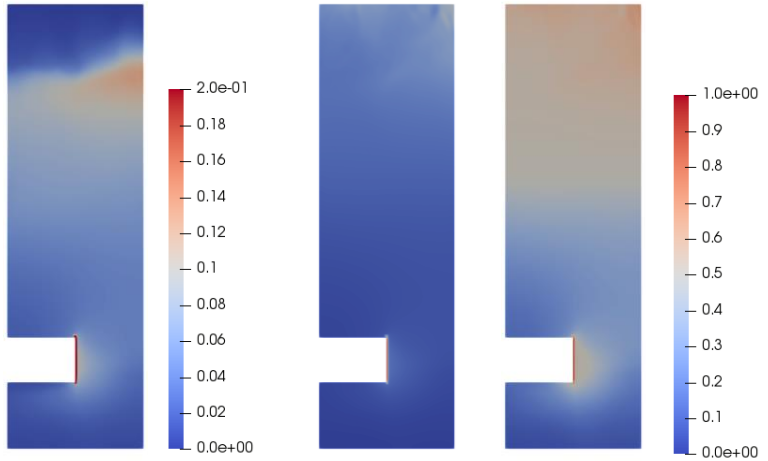
$$\{0 \le \xi_A \le 1\} \rightarrow \{0 \le M_{\xi_A} \le 1\}, with\ \overline{\xi_A} \rightarrow 0.5$$

$M_{\xi_A} = 0.5$ corresponds to perfectly mixed state

$$\xi_A = \frac{\phi_A}{\phi_A + \phi_B}$$

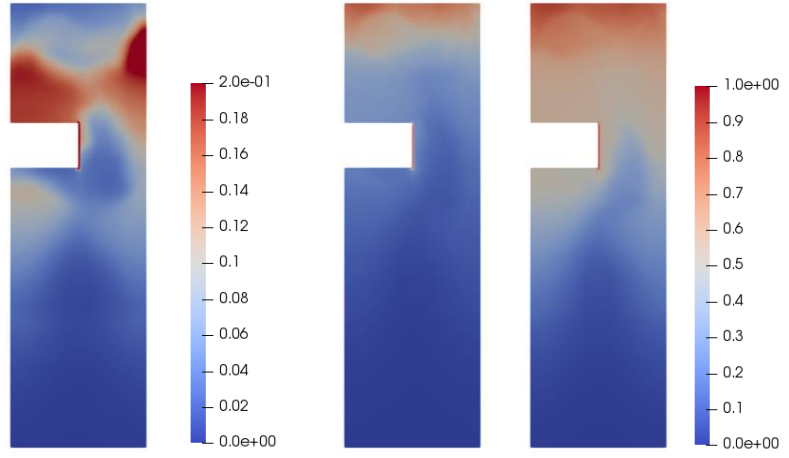
Can identify regions of rich and lean mixing unlike the conventional mixing indices

Design 1



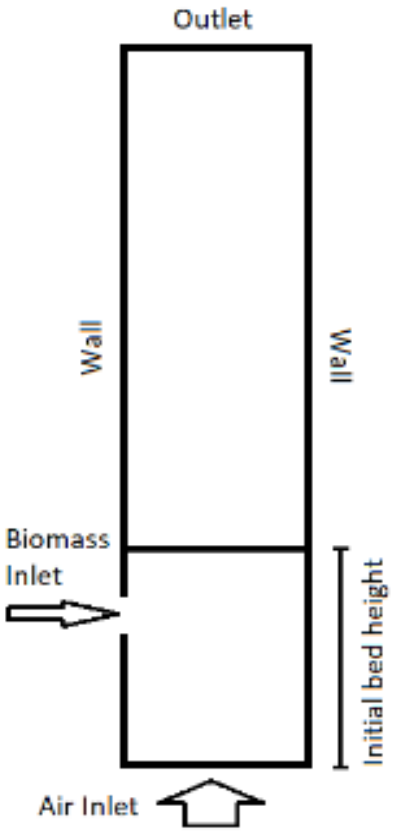

$\phi_A$ $\xi_A$ $M_{\xi_A}$

Design 2




$\phi_A$ $\xi_A$ $M_{\xi_A}$

# Coupling hydrodynamics and reactions



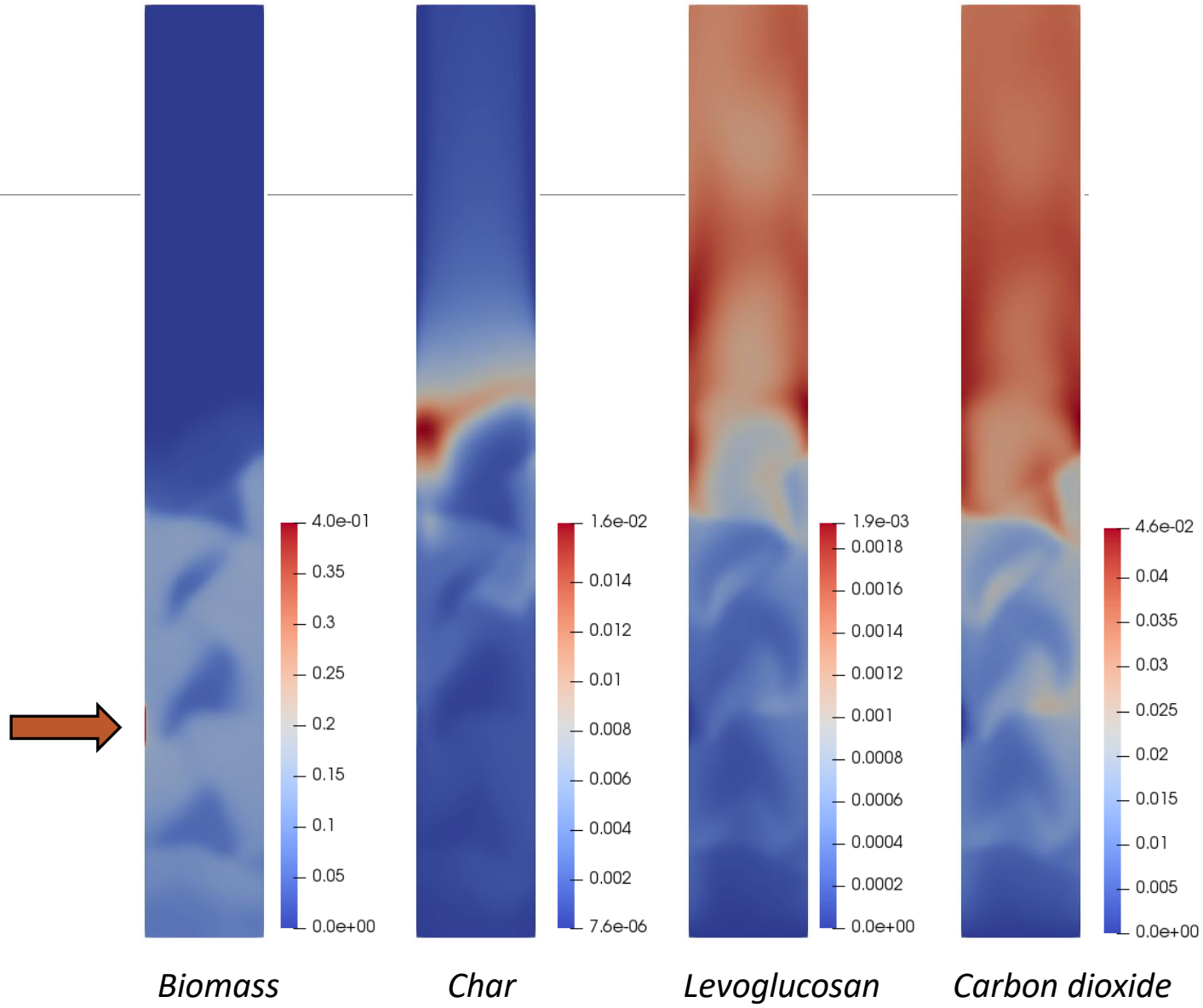

- Domain
  - Reactor diameter: 3.81 cm
  - Height: 42.7 cm
  - Initial bed height: 10.5 cm
  - Biomass inlet diameter: 1.27 cm
  - Biomass inlet height: 6.81 cm
- Operating conditions
  - Air flow rate: 20 SLPM
  - Biomass feed rate: 1 kg/hr
  - Air inlet temperature: 773K
  - Biomass inlet temperature: 300K
  - Silica sand diameter: 600 µm
  - Biomass size 1587 µm

- OpenFOAM
  - Reacting multiphase solver
  - Eulerian multi-model
  - Kinetic theory closures
  - Particle-particle drag (Syamlal)
- Boundary conditions
  - Superficial velocity inlet
  - Pressure inlet-outlet
  - No-slip wall condition for gas
  - J&J wall conditions for particle velocity and granular energy at the wall
  - Neumann boundary for volume fractions at the wall
  - Neumann boundary condition for heat flux at walls to ensure no heat loss

Syamlal M, Rogers W, O`Brien TJ. *MFIX Documentation Theory Guide*. USDOE Morgantown Energy Technology Center, WV (United States); 1993. doi:10.2172/10145548

# CFD results

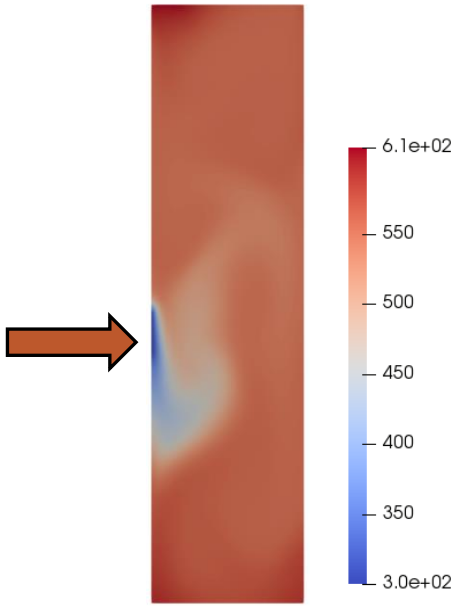
- Results with only the Ranzi devolatilization mechanism
- Biomass injected at the side of the wall as shown by arrow
- Instantaneous fields at 15 s
- Few products of the Ranzi devolatilization:
  - Char
  - Levoglucosan ($C_6H_{10}O_5$)
  - Carbon dioxide ($CO_2$)



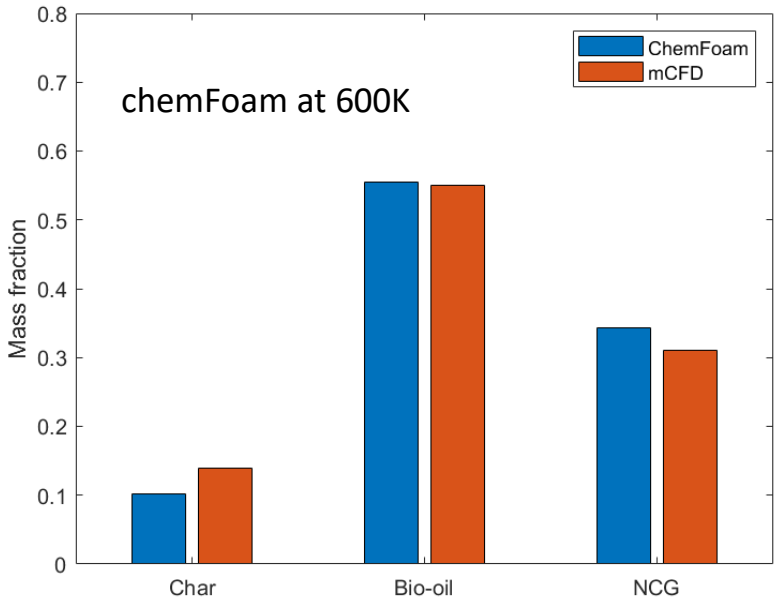
# Yields

Polin JP, Peterson CA, Whitmer LE, Smith RG, Brown RC. Process intensification of biomass fast pyrolysis through autothermal operation of a fluidized bed reactor. *Appl Energy*. 2019;249:276-285. doi:10.1016/j.apenergy.2019.04.15

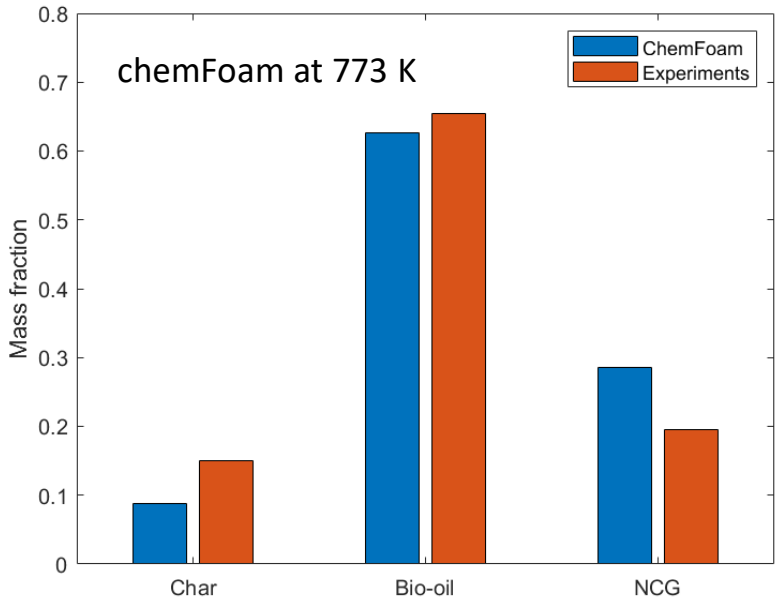
- Comparison of yields for Ranzi devolatilization
- Unlike the chemistry solver biomass has a distribution of temperature associated with CFD
- Note: The CFD is not truly conventional pyrolysis! Wouldn't be right to compare to the experiments




*Biomass temp*



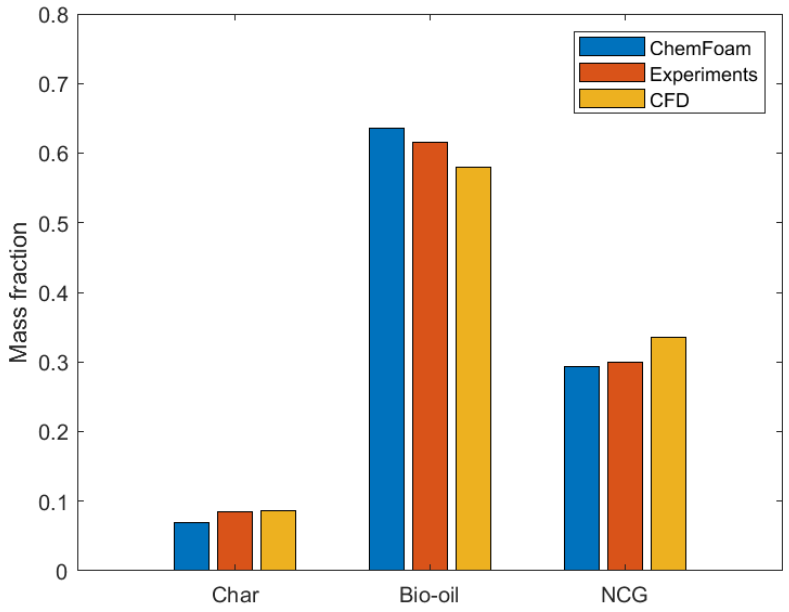

*Comparison of models*

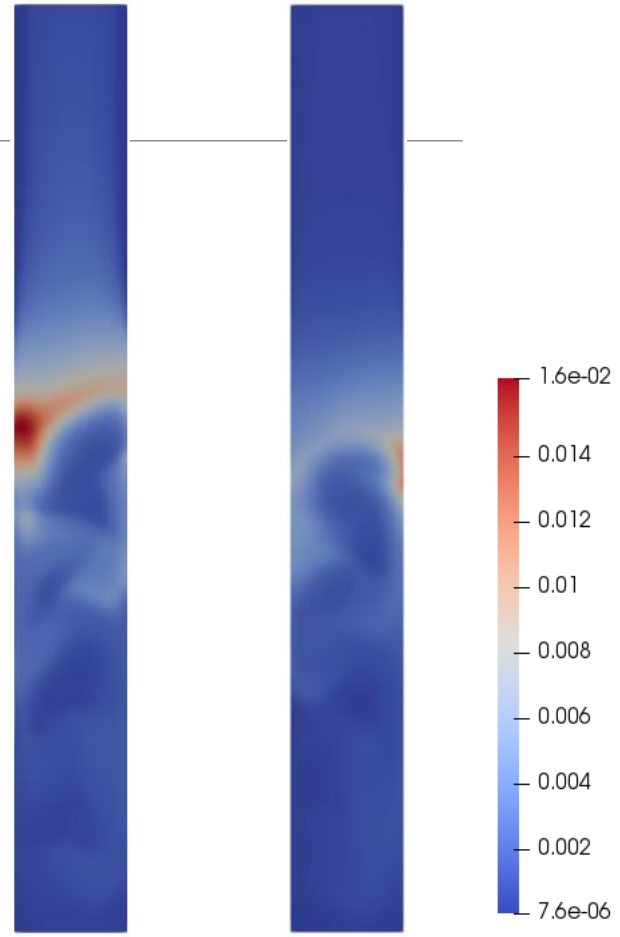



*Conventional pyrolysis*

# Char combustion

- Addition of char combustion with the Ranzi devolatilization mechanism
- Some char consumption visible at the end of 15 seconds
- The char left over matches the experimental results
- Early stage of autothermal pyrolysis
- Need longer simulations runs to get to autothermal operating conditions



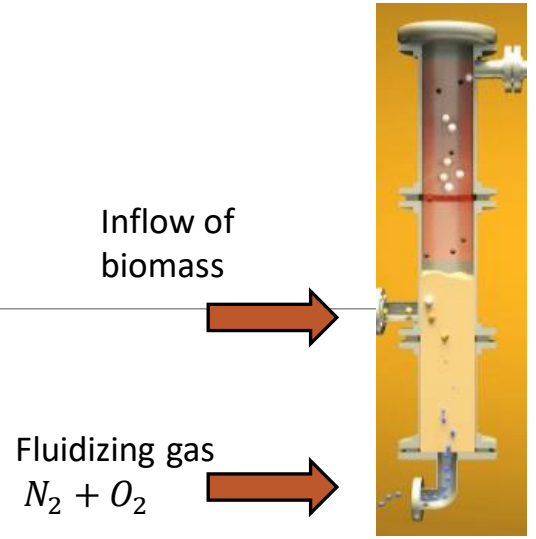



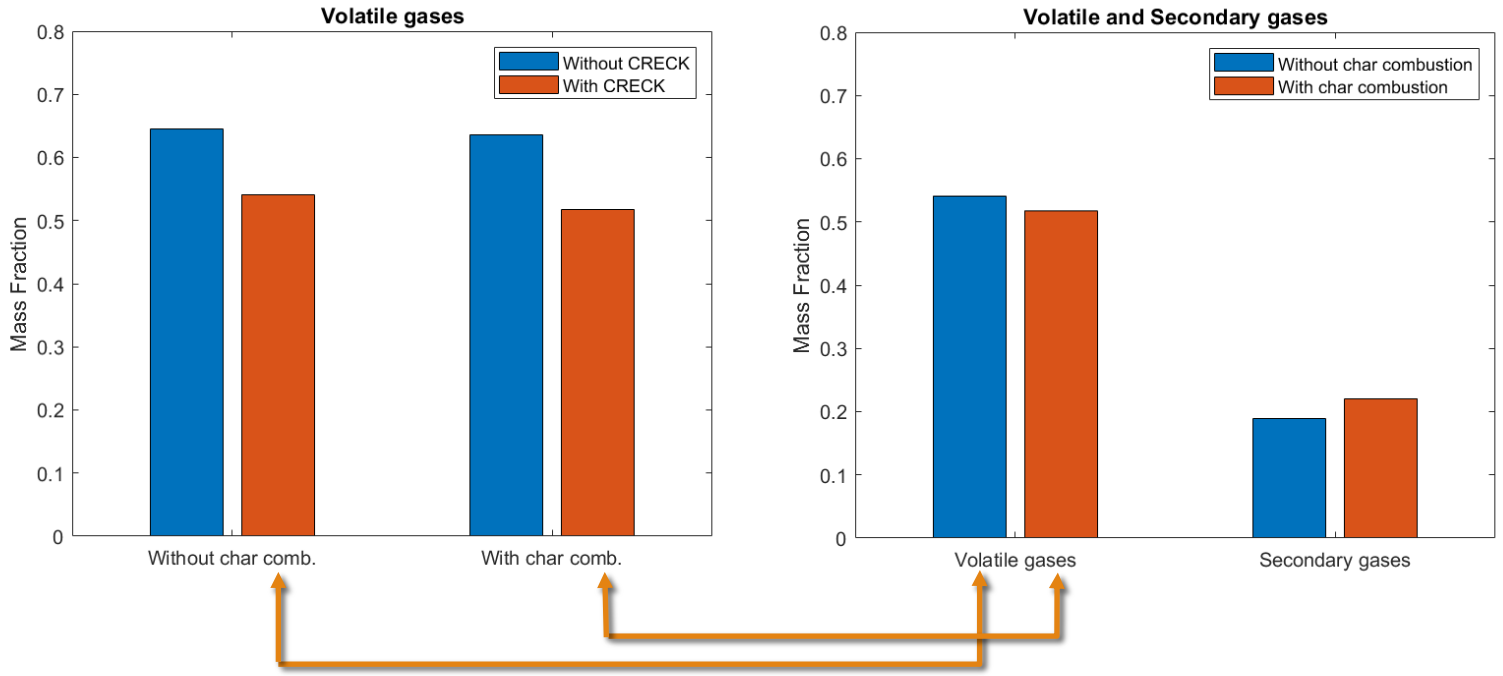

*Without oxygen* *With oxygen*

# Secondary gas phase

- CRECK:
  - 137 species
  - 4533 reactions
- Residence time
  - Estimated to 1-2 seconds
- Importance
  - May be neglected for small case reactors, but will be crucial for large, plant scale reactors
  - Computational overhead with including in CFD: 15-20 times
- Alternatives?

| Bio-oil | |
|---|---|
| Levoglucosan | Propanoic acid |
| Hydroxy acetaldehyde | Xylofuranose |
| Glyoxal | Furfural |
| Acetaldehyde | Ethanol |
| 5-(hydroxy methyl)-furfural | Acetic acid |
| Propionaldehyde | Coumaryl alcohol |
| Methanol | Phenol |
| Formaldehyde | Sinapyl aldehyde |
| Formic acid | Anisole |
| Acrolein | |



# Summary: Biomass pyrolysis

- Chemical kinetic mechanism: Devolatilization, char combustion, secondary gas phase
- The zero-dimensional chemistry can be used to estimate yields based on the feedstock.
- The Ranzi devolatilization mechanism and char combustion was coupled with the hydrodynamics in mCFD demonstrating simulation capabilities.
- Secondary gas phase reactions may be superfluous for small scale reactors, meaning that the mechanism including Ranzi devolatilization and char combustion may be adequate for predicting yields.
- For longer residence times, the secondary gas phase reactions will be needed.
- Incorporating CRECK mechanism in mCFD is computationally expensive
- Alternative methods, such as a reduces chemical mechanism or decoupling chemistry from hydrodynamic simulations may be required.

# Acknowledgements

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