Computational study on biomass fast pyrolysis oil yield: effects of the bubbling-to-slugging transition in a laboratory-scale fluidized bed

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Background and Motivation (1)

Basic steps in thermochemical conversion of biomass via pyrolysis

• Efficient generation of the raw oil is a key step for all versions of catalytically upgraded pyrolysis oil production.

• Good control of the raw oil yield and composition is essential to achieving acceptable process risk and economics.

• Reliable planning, interpretation, and scale-up of lab and pilot-scale experimental demonstrations requires good physically-based models.
Background and Motivation (2)

Why model biomass fast pyrolysis in bubbling fluidized beds?

Bubbling beds are widely used in industry for biomass conversion because they provide:

1. Uniform temperatures
2. High heating rates
3. Efficient mass transfer
4. Relatively low particle attrition
5. Low pumping energy requirements

The majority of experimental fast pyrolysis studies in the literature are based on bubbling fluidized bed reactors.

Background and Motivation (3)

Why should computational fluid dynamics (CFD) be included in modeling for fluidized bed biomass fast pyrolysis?

- The dominant gas-solids mixing and turbulent multiphase transport processes are highly complex and difficult to scale.
- CFD provides the most comprehensive way to account for the nonlinear coupling between hydrodynamics, heat and mass transfer, and chemistry.
- Changes in physical and chemical feedstock properties can be explicitly included at high levels of detail.

Not getting overwhelmed by the complex physics and chemistry while still maintaining an acceptable computational overhead is the greatest challenge.
Objective: Assist experimental demonstrations and scale-up studies to optimize raw oil production

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

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.

Approach (1): Model impact of hydrodynamic regime transitions

How does the bubbling-to-slugging transition (BTST) impact pyrolyzer performance?

<table>
<thead>
<tr>
<th>Fixed</th>
<th>Bubbling</th>
<th>Slugging</th>
</tr>
</thead>
</table>

BTST varies widely with design and operation (not easily predicted):
- bed H/D ratio
- temperature
- pressure
- particle properties
- fluidizing gas properties

Slugging is generally bad because of poor mixing, high attrition, high elutriation.

Focus of study: Geldart B particle fluidization

Figure: S. Shaul, E. Rabinovich, H. Kalman, Generalized flow regime diagram of fluidized beds based on the height to bed diameter ratio, Powder Technol. 228 (2012) 264-271. http://dx.doi.org/10.1016/j.powtec.2012.05.029
Approach (2): Simulate relevant lab experiments

- Target: NREL bubbling bed lab pyrolyzer used to study biomass feedstock impact
- Key questions:
  - Can observed bio-oil yield variations with flow, biomass type be explained?
  - How does performance relate to the bubbling-to-slugging transition?

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Experiment</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle diameter</td>
<td>m</td>
<td>$500 \times 10^{-6}$</td>
<td>$500 \times 10^{-6}$</td>
</tr>
<tr>
<td>Particle density (Sand)</td>
<td>kg/m³</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>Particle density (Wood)</td>
<td>kg/m³</td>
<td>540</td>
<td>540</td>
</tr>
<tr>
<td>Particle density (Char)</td>
<td>kg/m³</td>
<td>-</td>
<td>180</td>
</tr>
<tr>
<td>Temperature</td>
<td>K</td>
<td>773</td>
<td>773</td>
</tr>
<tr>
<td>Pressure (inlet)</td>
<td>kPa</td>
<td>101</td>
<td>101</td>
</tr>
<tr>
<td>Fluidizing $\text{N}_2$ (range)</td>
<td>kg/s</td>
<td>$6.64 - 28.3 \times 10^{-5}$</td>
<td>$6.64 - 51.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Minimum fluidization</td>
<td>kg/s</td>
<td>-</td>
<td>$8.85 \times 10^{-5}$</td>
</tr>
<tr>
<td>Minimum fluidization</td>
<td>m/s</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>Coefficient of restitution</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
</tr>
<tr>
<td>Angle of repose</td>
<td>°</td>
<td>-</td>
<td>30</td>
</tr>
</tbody>
</table>

Assumptions:
- Minimum fluidization – Richardson correlation
  - $\text{N}_2$ density – ideal gas temperature and pressure corrected
  - $\text{N}_2$ viscosity – NASA 7-coefficient polynomial, temperature corrected
Methods (1): Fast pyrolysis CFD model details

• DOE-supported MFiX simulation tool
• Version and assumptions:
  • Eulerian-Eulerian (Two-Fluid Model)
  • Gidaspow drag model
  • Granular flow parameters
    – Schaeffer frictional stress tensor formulation
    – Hyperbolic tangent stress blending function
  • Modified SIMPLE integration with variable time stepping
  • Jackson and Johnson partial-slip wall boundary condition
  • 2D Cartesian mesh (initial, later 3D)
• Variable biomass density
• Miller and Bellan reduced kinetics for biomass
Methods (2): Miller and Bellan pyrolysis kinetics

- Initially use simple kinetics to identify issues; transition later to more complex kinetics
- Challenge to implement kinetics coupled with hydrodynamics

Figure: Model of Polysaccharide. (Source: DOE Genome Programs. Courtesy of the U.S. Department of Energy)

Kinetic scheme

Biomass
- Cellulose
- Hemicellulose
- Lignin

Tar → k1

k2: gas + char

k3: gas

First-order irreversible Arrhenius rate

\[
\frac{dm_i}{dt} = mk_i
\]

\[
k_i = A_i \exp\left( \frac{E_i}{RT} \right)
\]

Methods (3): Characterize and quantify pyrolysis hydrodynamics

Simulated pressure and bubble probes at multiple locations

Pressure Statistics

- MFiX simulated dynamic output:
  - pressure time series

Dynamic properties:

- void fraction time series

Derived bubble statistics with MS3DATA:

- probability distributions
- standard statistics
- temporal analysis
- information metrics

Potential on-line diagnostics


Bubble Statistics

- MFiX simulated dynamic output:
  - size distribution
- time scales
- critical transition analysis

Provides physical interpretations

Example Results: Pressure amplitude statistics track the bubbling-to-slugging transition (BTST)

Fully developed slugging ~5.5 $U_o/U_{mf}$

BTST 4.5 – 5.5 $U_o/U_{mf}$

Onset of BTST ~5 $U_o/U_{mf}$

Mean P (Pa)

$\sigma_p$

Mean

Standard deviation

Skewness

Kurtosis

MFiX results imply that on-line diagnostics should be possible
Example Results: Simulated tar and bubble patterns

<table>
<thead>
<tr>
<th>$U_0/U_{mf}$</th>
<th>Gas (blue)</th>
<th>Sand (red)</th>
<th>Tar Conc. (brown)</th>
<th>Bubbles and tar (oil) generation are highly correlated</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td></td>
<td></td>
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<tr>
<td>4.5</td>
<td></td>
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<tr>
<td>5.0</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>5.5</td>
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</tr>
<tr>
<td>6.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.5</td>
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<td></td>
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</tr>
</tbody>
</table>

Bubbles and tar (oil) generation are highly correlated.
Example Results: Are there maximum yields at reactor outlet?

Tar, no maximum in regime transition, needs further analysis.
Example Results: Predicted pyrolyzer conversion profiles

Fluidized bed appears to be in transient state
Highest tar and gas yield at Slugging
Most tar and gas conversion occurs inside the bed and splash region

Bubbling = 3.50 Uo/Umf
Transition (BTST) = 5.00 Uo/Umf
Slugging = 7.50 Uo/Umf

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Results: Why is char accumulating in reactor?

• Char elutriation depends on particle shape and volume
• Char particle morphology must be measured to correctly determine char and gas residence time

Terminal velocity depends on area and volume

Terminal velocity
\[ V_T = \sqrt{\frac{4d_p(\rho_p - \rho_g)g}{\rho_g C_D}} \]

Reynolds number
\[ Re_p = \frac{\rho_g V_p D_p}{\mu_g} \]

Char particle elutriation depends on particle terminal velocity

\[ U_{T, \text{sphere}} = 42.3 \text{ cm/s} \]
\[ \sim 4.8 U_o/U_{mf} \]

\[ U_{T, \phi=0.5} = 14.9 \text{ cm/s} \]
\[ \sim 1.7 U_o/U_{mf} \]

This study 2 – 8 U_o/U_{mf}

Char sphericity must be accounted in simulation

Char particle elutriation

\[ C_D = \frac{24}{Re_p} \left[ 1 + (8.1716e^{-4.0655 \times \phi_s}) Re_p^{0.0964 + 0.5565 \phi_s} \right] + \frac{73.69 Re_p e^{-5.0748}}{Re_p + 5.378 e^{6.2122 \phi_s}} \]

Haider and Levenspiel 1989

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Conclusions and future plans

• Need experimental measurements of elutriated and non-elutriated biomass/char
  – Role of particle morphology
  – Role of ash components
  – Role of fragmentation/attrition

• Effects of particle size distributions
  – See Gavin Wiggins’ talk on particle-scale modeling and heat transfer

• Impact of more detailed pyrolysis kinetic mechanisms
  – More reactions and product species
  – Better heats of reaction

• Evaluation of more sophisticated dynamic information metrics

• Testing and validation of on-line diagnostics derived from simulations
Questions:

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Computational Pyrolysis Consortium

http://cpcbiomass.org

Transitioning to Consortium for Computational Physics and Chemistry (CCPC)