Modeling Fast Biomass Pyrolysis in a Gas/Solid Vortex Reactor

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ISCRE-22, Maastricht, 04 Sept. 2012
History and Description
Vortex Reactor Development Timeline

Kerrebrock et al., 1961, “Vortex containment for the gaseous-fission rocket”

Kochetov et al., 1969, Vortex drying chambers

Anderson et al., 1971, Colloid core nuclear rocket

Folsom, 1974, Annular fluidized beds

Loftus et al., 1992, Flue gas scrubbing

Volchkov et al., 1993, Fluid dynamics in vortex chambers

Haldipure et al., 1999, Liquid/solid vortex contactor

Kuzmin et al., 2005, Vortex centrifugal bubbling reactor

Recent Work:
• De Broqueville
• De Wilde
• Kuzmin
• Marin
• Parmon
• Ryazantsev
• Trachuk

➢ Hydrodynamics
➢ Mass & Heat Transfer
➢ FCC
➢ Biomass gasification
➢ Adsorption
Gas/Solid Vortex Reactor (GSVR)

GSVR Characteristics:
• Gas injection forces bed rotation & induces fluidization
• Centrifugal forces resist drag
  ➢ Dense bed
  ➢ High radial slip velocity
Rotating Bed Reactors in a Static Geometry (RBR-SG)

Gas/Solid Fluidization Reactors

Conventional Fluidized Bed

Riser/Circulating Fluidized Bed

Conventional Rotating Fluidized Bed

Gas/Solid Vortex Reactor

2. http://www.fluidcodes.co.uk/fbed.html
3. adapted from Watano et al., Powder Tech. 131 (2003) 250-255

gravitational technologies

centrifugal technologies
Gas/Solid Fluidization Reactors

- Improved gas/solid mass transfer
- Larger surface area per reactor volume
- Larger potential for intensification

### Gas/Solid Slip Velocity vs. Solid Volume Fraction

- **GSVR & Rotating Fluidized Bed Reactors**
  - Terminal velocity

- **Risers & Circulating Fluidized Beds**

- **Fluidized Beds**

#### Centrifugal technologies
- Shorter gas/solid contact time

#### Gravitational technologies
- Longer gas/solid contact time

Experimental

with Jelena Kovacevic
Experimental GSVR Set-up
0.9 mm polyvinylidene fluoride particles ($\rho = 1800 \text{ kg/m}^3$)
~1 kg/s air flow
~5 kg bed mass
High-Speed Video – Small Particles

70 micron particles
(5000 FPS)

~1.6 mm particles
(10000 FPS)
Non-reacting Flow Modeling
Computational Fluid Dynamics

- Computational fluid dynamics $\rightarrow$ Fluent 13.0
- Eulerian/Eulerian two-fluid model, granular solid phase
- Gidaspow drag model \(^1\)

\[
\beta = \begin{cases} 
150 \frac{\alpha_p(1 - \alpha_g)\mu_g}{\alpha_g d_p^2} + 1.75 \frac{\rho_g\alpha_p}{d_p} |\tilde{u}_p - \tilde{u}_g| & \text{for } \alpha_g \leq 0.8 \\
\frac{3}{4} C_D \frac{\alpha_p\alpha_g\rho_g}{d_p} |\tilde{u}_p - \tilde{u}_g| \alpha_g^{-2.65} & \text{for } \alpha_g > 0.8
\end{cases}
\]

\[C_D = \begin{cases} 
\frac{24}{Re_p} (1 + 0.15 Re_p^{0.687}) & (Re_p \leq 1000) \\
0.44 & (Re_p > 1000)
\end{cases}\]

Model geometries tested:

(a) (b) (c)

General Non-reacting Flow Results

**Bed Mass:** 2.1 kg – 4.4 kg

**Air Flow Rate:** 0.5 kg/s – 1.0 kg/s

**Bed ΔP:** 2 kPa – 8 kPa

**Solids VF:** 0.4 – 0.6

**Solids Velocity:** 4 – 9 m/s
2D (with gravity), 0.74 kg/s air, 3250 g bed
3D, 0.74 kg/s air, 3250 g bed
(iso-surfaces = 0.40 and 0.01 solids volume fraction)
Model Validation
Bed Pressure Drop and Bed Thickness

\[ \Delta P_{\text{bed}} \]

Pressure Field (Pa)

Bed Thickness
Experimental data: (+) signs

Bed Pressure Drop (kPa) vs Bed Thickness (mm)

- Bed mass: 4.38 kg
- Bed mass: 3.25 kg
- Bed mass: 2.12 kg

Air flow:
- 0.5 kg/s
- 0.75 kg/s
- 1.0 kg/s

ISCRE-22, Maastricht, 04 Sept. 2012
Model Deficiencies & Refinement

- Pressure Field
  - Gas-phase properties
  - Gas flow rate
  - GSVR geometry
  - CFD model parameters
  - Wall interactions
  - Particle properties
  - Bed mass

- Solids Velocity
  - Bed Thickness (Bulk Solids Fraction)
Particle Image Velocimetry (PIV)
On-going Model Refinement - PIV

Raw image collection

Processed velocity field

Goal:
Compare time-averaged data over many image pairs

Average Solids Velocity

PIV data

CFD

r = 0
Radius →
r = R
Modeling Biomass Pyrolysis
Biomass Pyrolysis in a GSVR

Traditional Static Fluidized Bed

GSVR

D = 54 cm (solids region)
L = 10 cm

Biomass feed zone (300 K)

N₂ (923 K)

Sand

Products

1. http://www.pyne.co.uk
Pyrolysis Modeling in a GSVR

- 2D periodic GSVR simulations
- Heterogeneous reactions (solid $\rightarrow$ gas + char):
  - 10-reaction network with pseudo-components $^1$
- Continuous feeding of biomass
  - Cellulose, hemicellulose, and lignin
  - Different rates for each biomass component
- 4-phase Eulerian multiphase simulation (3 granular)
  - Gas, biomass, char, and sand
  - Sand and biomass retained in reactor
  - Char leaves with gas flow due to lower density

Virgin Biomass $\rightarrow$ Active Biomass

Tar (g) $\rightarrow$ Pyrolysis Gases

Char (s) + Pyrolysis Gases

Volume fraction

## Base GSVR Operating Variables

<table>
<thead>
<tr>
<th>Volume (m³)</th>
<th>0.023</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow rate (kg/s)</td>
<td>0.22</td>
</tr>
<tr>
<td>Biomass feed rate (kg/s)</td>
<td>0.035</td>
</tr>
<tr>
<td>Biomass moisture content (wt%, dry basis)</td>
<td>10</td>
</tr>
<tr>
<td>Sand mass in reactor (kg)</td>
<td>5</td>
</tr>
<tr>
<td><strong>Gas-to-biomass ratio</strong> (kg&lt;sub&gt;gas&lt;/sub&gt;/kg&lt;sub&gt;biomass&lt;/sub&gt;)</td>
<td>6.4</td>
</tr>
<tr>
<td>Gas feed temperature (K)</td>
<td>923</td>
</tr>
<tr>
<td>Biomass feed temperature (K)</td>
<td>300</td>
</tr>
<tr>
<td>Biomass feed rate/volume (kg/m³·s)</td>
<td>1.5</td>
</tr>
</tbody>
</table>

→ **Biomass composition (wt% dry):**
  - 36% cellulose
  - 47% hemicellulose
  - 17% lignin
Volume Fraction and Temperature

(a) Biomass VF
(b) Char VF
(c) Sand VF

(b) Gas
(d) Biomass
(e) Char
(f) Sand

0.030 biomass
0.065 char
0.55 sand
Volume Fraction Animation

Biomass

Char

Total solids (biomass, char, sand)
Comparison – GSVR vs Fluidized Bed

**Static Fluidized Bed**

- D = 3.81 cm
- H = 34.3 cm

- Dry biomass feed zone (300 K)
- N₂ (923 K)
- 8 cm of heated wall (800 K)

**GSVR**

- D = 54 cm (solids region)
- L = 10 cm

- Dry biomass feed zone (300 K)
- N₂ (923 K)

Comparison – GSVR vs Fluidized Bed

<table>
<thead>
<tr>
<th></th>
<th>GSVR</th>
<th>Static FB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (m$^3$)</td>
<td>0.023</td>
<td>0.00039</td>
</tr>
<tr>
<td><strong>Gas-to-biomass ratio</strong> (kg$<em>{\text{gas}}$/kg$</em>{\text{biomass}}$)</td>
<td>6.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Sand mass in reactor/volume (kg/m$^3$)</td>
<td>217</td>
<td>322</td>
</tr>
<tr>
<td>Supplementary heating</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Outlet Temperature (K)</td>
<td>784</td>
<td>790</td>
</tr>
<tr>
<td>Gas-phase residence time (s)</td>
<td>~0.05</td>
<td>~0.75</td>
</tr>
</tbody>
</table>

**Product Yields** (wt% of fed biomass):

<table>
<thead>
<tr>
<th></th>
<th>GSVR</th>
<th>Static FB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tar</td>
<td>76.0</td>
<td>63.4</td>
</tr>
<tr>
<td>Pyrolysis gas</td>
<td>8.9</td>
<td>21.5</td>
</tr>
<tr>
<td>Char</td>
<td>14.5</td>
<td>14.4</td>
</tr>
<tr>
<td>Biomass (unconverted)</td>
<td>0.0</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>Biomass conversion rate / reactor volume (kg/m$^3$·s)</strong></td>
<td>1.5</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Process Intensification
Increase gas and biomass feed rates proportionately

- Base feed rates:
  - 0.22 kg/s gas
  - 0.035 kg/s biomass

→ Reactor performance and product yields ~ the same (but increased ΔP)
→ Plus, shorter gas residence time and higher heat transfer coefficients

Typical range for static fluidized beds and risers/CFBs: $1\text{,}2$

$\sim 100 - 200 \text{ W/(m}^2\text{ K)}$
Operating the reactor with biomass as the only solid
- Much larger char mass accumulates
- Product distribution the same as in cases with sand
- Char removal occurs in pulsing, oscillatory pattern

Biomass

Char

Contours of Volume fraction (biomass)  (Time=3.1750e+02)  Apr 30, 2012
ANSYS FLUENT 13.0 (2d, dp, pbns, eulerian, apa, rks, transient)

Contours of Volume fraction (char)  (Time=3.1750e+02)  Apr 30, 2012
ANSYS FLUENT 13.0 (2d, dp, pbns, eulerian, apa, rks, transient)
GSVRs have the potential to intensify processes

- High intrinsic mass/heat transfer can yield improved overall rates
- High solid volume fractions can reduce equipment size

Biomass Pyrolysis Example

- Stratification of solid phases to retain sand & unreacted biomass
- Comparison to a static fluidize bed
  - Comparable degree of char formation
  - Increased tar and reduced pyrolysis gas formation
- Significantly opportunity for intensification in GSVR
  - 3x – 5x larger heat and mass transfer coefficients
  - Ability to increase feed rates without biomass loss, but more ΔP

Future Projects

- Direct measurement of solid velocities using PIV
- Experimental GSVR to examine heat transfer and reacting flows
Acknowledgements

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Ghent University Resources
- High-Performance Computing Cluster

Funding
- Methusalem grant - Flemish government
- ERC Advanced Grant - MADPII
Flow Paths and Heat Transfer

- gas flow path
- solid velocity

(a) Convective Heat Trans. Coef. (W/m²·K)

(b) Heat Flux to Biomass (W/m²)

Radius (m)
### Table 1
Pyrolysis reaction mechanism and related data [9.47–49].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H_{\text{rxn}} ) (kJ/kg)</th>
<th>( A_f ) (1/s)</th>
<th>( E_A ) (kJ/mol)</th>
<th>( k_{\text{rxn}} @ 773 \text{ K}(1/\text{s}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>CL(_v) → CL(_a)</td>
<td>0</td>
<td>2.80 \times 10^{19}</td>
<td>242.4</td>
</tr>
<tr>
<td>1b</td>
<td>HC(_v) → HC(_a)</td>
<td>0</td>
<td>2.10 \times 10^{16}</td>
<td>186.7</td>
</tr>
<tr>
<td>1c</td>
<td>LG(_v) → LG(_a)</td>
<td>0</td>
<td>9.60 \times 10^{8}</td>
<td>107.6</td>
</tr>
<tr>
<td>2a</td>
<td>CL(_a) → Tar</td>
<td>255</td>
<td>3.28 \times 10^{14}</td>
<td>196.5</td>
</tr>
<tr>
<td>2b</td>
<td>HC(_a) → Tar</td>
<td>255</td>
<td>8.75 \times 10^{15}</td>
<td>202.4</td>
</tr>
<tr>
<td>2c</td>
<td>LG(_a) → Tar</td>
<td>255</td>
<td>1.50 \times 10^{9}</td>
<td>143.8</td>
</tr>
<tr>
<td>3a</td>
<td>CL(_a) → 0.35 Char(_c) + 2.6 Pgas</td>
<td>−20</td>
<td>1.30 \times 10^{10}</td>
<td>150.5</td>
</tr>
<tr>
<td>3b</td>
<td>HC(_a) → 0.6 Char(_f) + 1.6 Pgas</td>
<td>−20</td>
<td>2.60 \times 10^{11}</td>
<td>145.7</td>
</tr>
<tr>
<td>3c</td>
<td>LG(_a) → 0.75 Char(_f) + Pgas</td>
<td>−20</td>
<td>7.70 \times 10^{6}</td>
<td>111.4</td>
</tr>
<tr>
<td>4</td>
<td>Tar → 4Pgas</td>
<td>−42</td>
<td>4.25 \times 10^{6}</td>
<td>108.0</td>
</tr>
</tbody>
</table>

\(^a\) Fractional char formation for CL, HC, and LG are 0.35, 0.60, and 0.75 kg char/kg, respectively.

\(^b\) Subscripts “\(v\)” and “\(a\)” indicate the virgin and activated forms of biomass, respectively.

### Table 2
Pyrolysis species and relevant thermochemical and physical properties.

<table>
<thead>
<tr>
<th>Component</th>
<th>Phase</th>
<th>MW (^a) (g/mol)</th>
<th>( \Delta H_f ) (kJ/mol)</th>
<th>( \rho_f ) (dry kg/m(^3))</th>
<th>( C_p ) (J/(kg K))</th>
<th>( \lambda ) (W/(m K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CL(_a)</td>
<td>Biomass</td>
<td>100</td>
<td>0</td>
<td>500</td>
<td>1400</td>
</tr>
<tr>
<td>2</td>
<td>HC(_a)</td>
<td>Biomass</td>
<td>100</td>
<td>0</td>
<td>500</td>
<td>1400</td>
</tr>
<tr>
<td>3</td>
<td>LG(_a)</td>
<td>Biomass</td>
<td>100</td>
<td>0</td>
<td>500</td>
<td>1400</td>
</tr>
<tr>
<td>4</td>
<td>Char(_c)</td>
<td>Char</td>
<td>100</td>
<td>−45.27</td>
<td>175</td>
<td>1100</td>
</tr>
<tr>
<td>8</td>
<td>Char(_f)</td>
<td>Char</td>
<td>100</td>
<td>−17.53</td>
<td>300</td>
<td>1100</td>
</tr>
<tr>
<td>9</td>
<td>Char(_f)</td>
<td>Char</td>
<td>100</td>
<td>−9.77</td>
<td>375</td>
<td>1100</td>
</tr>
<tr>
<td>10</td>
<td>Tar</td>
<td>Gas</td>
<td>100</td>
<td>25.5</td>
<td>−</td>
<td>Phenol</td>
</tr>
<tr>
<td>11</td>
<td>Pgas</td>
<td>Gas</td>
<td>25</td>
<td>5.33</td>
<td>−</td>
<td>Ethylene</td>
</tr>
<tr>
<td>12</td>
<td>H(_2)O</td>
<td>Gas</td>
<td>18.02</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>13</td>
<td>N(_2)</td>
<td>Gas</td>
<td>28.02</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>14</td>
<td>Sand</td>
<td>Sand</td>
<td>−</td>
<td>2650</td>
<td>800</td>
<td>0.75</td>
</tr>
</tbody>
</table>

\(^a\) The molecular masses of the biomass, char, and gas-phase pseudo-components are arbitrary and only affect the as-written stoichiometry of the reactions.

The emissivity of all particulate phases was assumed to be 0.75.
<table>
<thead>
<tr>
<th>Case name</th>
<th>Air Feed Rate (kg/s)</th>
<th>Biomass Feed Rate (kg/s)</th>
<th>Biomass Water %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>0.22</td>
<td>0.035</td>
<td>10</td>
</tr>
<tr>
<td>No-H$_2$O (high-T)</td>
<td>0.22</td>
<td>0.035</td>
<td>0</td>
</tr>
<tr>
<td>1.5x-flow</td>
<td>0.33</td>
<td>0.052</td>
<td>10</td>
</tr>
<tr>
<td>2x-flow</td>
<td>0.44</td>
<td>0.070</td>
<td>10</td>
</tr>
<tr>
<td>No-sand</td>
<td>0.22</td>
<td>0.035</td>
<td>10</td>
</tr>
<tr>
<td>No-sand/No-H$_2$O (high-T)</td>
<td>0.22</td>
<td>0.035</td>
<td>0</td>
</tr>
</tbody>
</table>

→ Inlet Gas Temperature = 923 K  
→ Biomass Feed Temperature = 300 K
Typical range for static fluidized beds and risers/CFBs: $1,2$

$\sim 100 - 200 \text{ W/(m}^2\text{K)}$

No-Sand Cases Results

(a) Volume Fraction vs Radius (m)

(b) Convective Heat Trans. Coef. (W/m²K) vs Radius (m)

<table>
<thead>
<tr>
<th>Case name</th>
<th>$m_{\text{sand}}^{\text{ss}}$ (kg)</th>
<th>$m_{\text{bio}}^{\text{ss}}$ (kg)</th>
<th>$m_{\text{char}}^{\text{ss}}$ (kg)</th>
<th>$T_{\text{bio}}^{\text{avg}}$ (K)</th>
<th>$T_{\text{char}}^{\text{avg}}$ (K)</th>
<th>$T_{\text{sand}}^{\text{avg}}$ (K)</th>
<th>$T_{\text{gas}}^{\text{outlet}}$ (K)</th>
<th>$m_{\text{char}}^{\text{out}}$ (kg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>5.0</td>
<td>0.056</td>
<td>0.119</td>
<td>721</td>
<td>753</td>
<td>761</td>
<td>751</td>
<td>0.0056</td>
</tr>
<tr>
<td>No-sand</td>
<td>0.0</td>
<td>0.056</td>
<td>1.939</td>
<td>727</td>
<td>751</td>
<td>–</td>
<td>750</td>
<td>0.0060</td>
</tr>
<tr>
<td>No-H₂O</td>
<td>5.0</td>
<td>0.036</td>
<td>0.123</td>
<td>734</td>
<td>787</td>
<td>794</td>
<td>784</td>
<td>0.0050</td>
</tr>
<tr>
<td>No sand/No-H₂O</td>
<td>0.0</td>
<td>0.036</td>
<td>1.938</td>
<td>741</td>
<td>784</td>
<td>–</td>
<td>783</td>
<td>0.0056</td>
</tr>
</tbody>
</table>
## Biomass Pyrolysis Product Distribution

<table>
<thead>
<tr>
<th>Case name</th>
<th>Char (%)</th>
<th>Tar (%)</th>
<th>Pyrolysis gas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>16.1</td>
<td>73.8</td>
<td>9.5</td>
</tr>
<tr>
<td>973 K</td>
<td>14.6</td>
<td>75.6</td>
<td>8.9</td>
</tr>
<tr>
<td>No-H₂O</td>
<td>14.5</td>
<td>76.0</td>
<td>8.9</td>
</tr>
<tr>
<td>1.5x-flow</td>
<td>16.3</td>
<td>73.8</td>
<td>9.2</td>
</tr>
<tr>
<td>2x-flow</td>
<td>16.8</td>
<td>73.3</td>
<td>9.1</td>
</tr>
<tr>
<td>No-sand</td>
<td>17.1</td>
<td>73.6</td>
<td>9.3</td>
</tr>
<tr>
<td>No sand/No-H₂O</td>
<td>16.0</td>
<td>75.6</td>
<td>8.7</td>
</tr>
</tbody>
</table>

*a* Char production fraction necessary to achieve a perfect mass balance over the reactor; mass balance errors ranged from −0.9% to +0.3%.
“Full” 2D Simulations – Effect of Gravity

- 0.4 m³/s air flow @ 1.225 kg/m³ and 4.375 kg bed mass
- Run without gravity for 10 seconds
- Run 10 more sec. with/without gravity
- Quadrant view of solids VF:

![Graph showing solid volume fraction vs. radius and bed thickness](image-url)

- Avg. Solid Vol. Fraction for last 28 timesteps
“Full” 2D Simulations – Effect of Gravity

- 0.8 m³/s air flow @ 1.225 kg/m³ and 4.375 kg bed mass
0.49 kg/s air, no gravity

0.49 kg/s air, with gravity

0.98 kg/s air, no gravity

0.98 kg/s air, with gravity
Bed ΔP (2D, ϕ = 0.10)

Total ΔP (2D, ϕ = 0.10)

Bed ΔP (3D, ϕ = 0.05 & 0.05)

Total ΔP (3D, ϕ = 0.05 & 0.05)
On-going Model Refinement - PIV

Particle Image Velocimetry (PIV)
- Allows for 2D particle velocity field near end-wall
- Final “major” observable for bulk validation

Raw image collection

Processed velocity field
2x-Flow VF Animation (back-up slide)

Biomass

Char

Total solids (biomass, char, sand)
Scaled Bed Pressure Drop

\[ \Delta \Pi = \frac{\Delta P_{\text{bed}}}{\rho_s g H_{\text{bed}} \varepsilon_s} \]

Deviation due to differences in solid velocity

Slope indicates increasing solid velocity
CFD Example Movies

3D, 0.74 kg/s air, 3250 g bed

Contours of Volume fraction (polymer)  (Time=1.3002e+01)  Aug 05, 2011
ANSYS FLUENT 13.0 (3d, pbn5, eulerian, rke, transient)