Multiscale/Multiphysics simulations for multiphase gas-solids flow reactors

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Sponsors: DOE OASCR, FE, NE and EERE
Outline

- Multiscale/multiphysics simulations for multiphase reacting flows
  - Specific issues for biomass pyrolysis/gasification
- Current set of ORNL models used at various scales
- Example simulation results
  - Biomass pyrolysis
  - Fluidized bed CVD coater for nuclear fuel particles
  - Coal gasifier simulation with 1000s of processors
- Importance of multiphysics coupling
- Compound wavelet matrix method (CWM), dynamic CWM, time parallel CWM
- Summary
Role of multiphase flow reactors in Energy Security and Sustainability

- **Fuel Production and Processing**
  - Refineries: catalytic crackers, H₂ production, S removal, …
  - Coal gasification, clean-up (SOx, NOx, Hg, CO₂)
  - Biomass (cellulosic) pyrolysis and gasification
  - Nuclear fuel production

- **Energy Production**
  - Fuel cells
  - Coal and biomass combustion
  - Nuclear reactors, separation etc.
  - Silicon production and coating for photovoltaic applications
  - Novel combustion technologies:
    - Oxycombustion
    - Chemical looping combustion
      - Higher efficiency with lower entropy losses
      - No thermal NOx
      - Separated CO₂ stream for sequestration
      - Potential carbon-negative technology

- **Energy Utilization and Efficiency**
  - Polymerization reactors
  - Catalytic reactors

Multiphase flows occur in most energy-intensive industrial processes
Biomass gasification

• ~ mm particles
  • Complex flow: gas phase, gas phase in char, pyrolysis front, unreacted biomass
  • Wide range of species
  • Surface processes at nm length scale and ns time scales

• ~ m in size
  • Gasification/pyrolysis at high temperatures (~1000°C) in reactor with large residence times ~10 s
  • Biomass particles cycle thru wide range of conditions where complex chemistry occurs

Design challenge:
Maintain optimal temperatures, species, residence times in each zone to attain right gasification/pyrolysis

Truly multiscale problem:
~O(13) time scales, ~O(10) length scales

Materials challenge:
Design/understand material properties for the biomass pellets/particles at μm/nm scale
  – Size
  – Porosity
  – Integrity
  – Composition
  – Binders?

SP et al. (CFD in CRE, 2008; Chapter in a book edited by Mark Nimlos)
What is being done and what can be done differently...

- New technologies take decades
  - Lab scale → pilot scale → production scale
  - Resistance to adopting new ideas
  - Current models have limited quantitative predictability/credibility
  - Cultural barrier

- Why we need to do things differently
  - Energy crisis is current and growing
  - We need tomorrow’s technology today
  - Economic opportunity

- What can be done differently
  - Development of integrated and scalable MSMP predictive models
  - Component and lab-scale experiments targeted to validate computational models
  - Integrate lab scale experiments along with simulations to design new plants and devices
Multiphysics heterogeneous chemically reacting flows for energy systems

Goal: Building a suite of models for unprecedented capability to simulate multiphase flow reactors

- Through support from various DOE offices (FE, EERE, and NE) we have developed suite of models for unprecedented capability to simulate heterogeneous chemically reacting flows
- Hybrid methods to couple two physical models (e.g. MFIX DEM)
- Uncertainty quantification to probe only quantities of interest at smaller scales
MACROSCELE CFD SIMULATIONS
MFIX simulation package

- General multiphase flow CFD code which couples hydrodynamics, heat & mass transfer and chemical reactions
- SMP, DMP and Hybrid Parallel code which runs on many platforms including Beowulf clusters
- Open-source code and collaborative environment (http://www.mfix.org or http://mfix.netl.doe.gov)
- Over 1500 researchers from over 500 institutions around the world
Multiphase formulation

• Two Phases
  - Fluid
  - Solids

• Three phases
  - Fluid
  - Solids
    - Solids - 1
    - Solids - 2

- Details of flow field and particle interaction have been averaged out.
- Account for the information lost due to averaging through the use of constitutive equations

Continuity Equation
\[
\frac{\partial}{\partial t} (\varepsilon_m \rho_m) + \nabla \cdot (\varepsilon_m \rho_m \mathbf{v}_m) = \sum_{l=1}^{M} R_{ml}
\]

Momentum Equation
\[
\frac{\partial}{\partial t} (\varepsilon_m \rho_m \mathbf{v}_m) + \nabla \cdot (\varepsilon_m \rho_m \mathbf{v}_m \mathbf{v}_m) = \nabla \cdot \mathbf{S}_m + \sum_{l=1}^{M} \mathbf{I}_{ml} + \mathbf{f}_m
\]

Granular Stresses are modeled by the kinetic theory of granular material in the viscous regime and plasticity theory in the plastic regime

Drag law describes the interaction between the gas and the particles
BIOMASS PYROLYSIS REACTOR
Prototype case

- Lathouwers and Bellan, IJMF 2001
- Good test as the kinetics for a continuum model are available
- The geometry and flow conditions simulated are similar to those in this paper for qualitative comparison
  - Fluidizing gas velocity: 0.5 m/s
  - Biomass feed (0.5 kg/s) – Bagasse – Cellulose (0.36), Hemicellulose (0.47) and Lignin (0.17)
  - Gas temperature – 700 K and biomass temperature – 400K
Chemical thermodynamics and kinetics

$\text{virgin (s)} \xrightarrow[K_1]{ } \text{active (s)}$

$\text{active (s)} \xrightarrow[K_2]{ } \text{tar (g)} \xrightarrow[K_3]{ } \text{gas (g)}$

$\text{active (s)} \xrightarrow[K_3]{ } \text{char (s)} + (1 - X) \text{gas (g)}$

$\Delta h_1 = 0 \text{ kJ/kg}$

$\Delta h_2 = 255 \text{ kJ/kg}$

$\Delta h_3 = -20 \text{ kJ/kg}$

$\Delta h_4 = -42 \text{ kJ/kg}$

Rate constants and activation energy for the biomass pyrolysis kinetics scheme above:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A (1/s)</th>
<th>E (J/kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1^c$</td>
<td>$2.8 \times 10^{16}$</td>
<td>$242.4 \times 10^6$</td>
</tr>
<tr>
<td>$K_2^c$</td>
<td>$3.28 \times 10^{14}$</td>
<td>$196.5 \times 10^6$</td>
</tr>
<tr>
<td>$K_3^c$</td>
<td>$1.3 \times 10^{10}$</td>
<td>$150.5 \times 10^6$</td>
</tr>
<tr>
<td>$K_1^h$</td>
<td>$2.1 \times 10^{16}$</td>
<td>$186.7 \times 10^6$</td>
</tr>
<tr>
<td>$K_2^h$</td>
<td>$8.75 \times 10^{15}$</td>
<td>$202.4 \times 10^6$</td>
</tr>
<tr>
<td>$K_3^h$</td>
<td>$2.6 \times 10^{11}$</td>
<td>$145.7 \times 10^6$</td>
</tr>
<tr>
<td>$K_1^l$</td>
<td>$9.6 \times 10^{8}$</td>
<td>$107.6 \times 10^6$</td>
</tr>
<tr>
<td>$K_2^l$</td>
<td>$1.5 \times 10^{9}$</td>
<td>$143.8 \times 10^6$</td>
</tr>
<tr>
<td>$K_3^l$</td>
<td>$7.7 \times 10^{6}$</td>
<td>$111.4 \times 10^6$</td>
</tr>
<tr>
<td>$K_4$</td>
<td>$4.28 \times 10^6$</td>
<td>$108 \times 10^6$</td>
</tr>
</tbody>
</table>

The char formation ratios for reaction $K_3$ are: $X^c = 0.35$, $X^h = 0.6$, and $X^l = 0.75$

The species properties are taken from Lathowers and Bellan, 2001
Solids distribution and gas flow

- Fluidization gas levitates the particles and the biomass
- The reactor operates in the bubbling bed regime
- The gas undergoes local acceleration and deceleration depending on the flow of the solids
- The flow of solids and gas is transient and highly dynamic
- The reactor geometry causes recirculation near the top of the reactor
- The fluidizing and product gas leave the domain through the exit

Void fraction with gas velocity vectors at two different instants
Solids distribution and gas flow

- The gas flow is perturbed slightly to accommodate the injection of the biomass.
- Fluidization gas and the bed particles exert axial force on the incoming biomass into the reactor.
- The biomass accumulates closer to the inlet but quickly disperses and also undergoes pyrolysis in contact with the high temperature gas and solids.

Biomass mass distribution along with gas velocity vectors at two different instants.
Biomass composition

- The fast reacting hemicellulose is primarily found near the inlet contrary to the cellulose.
- The distribution of the various species is related to the physical/thermodynamic/transport properties along with the chemical reactivity as functions of local temperature.
- This in turn influences the variation of the product gas both in space and time.
Fluidizing gas bypasses through the bed to the outlet.

Product species have higher residence time in the reactor.
Temporal variation of exit gases

The product gas and tar gas are still in the transient regime after 5 seconds of the biomass injection → function of the reaction kinetics, the temperature distribution, the solids and gas contacting etc.
Conclusions from biomass study

- The detailed CFD simulations can provide spatio-temporal variations of the solids, biomass, gas, gas and solid species, reaction rates etc.

- The MFIX simulation software used here can run on 1000s of processors and can be employed for detailed 3D simulations of realistic pyrolyzers and gasifiers.

- The model is quite well validated for various fluidized bed reactors.

- However, reaction kinetics and thermodynamics conducive to continuum multiphase flows need to be determined through experiments.

- The models still need to be systematically validated to improve confidence levels.

- Once validated models are available, the reactors can be optimized by simulations and reduce the design space for experiments.
FLUIDIZED BED CVD COATER FOR NUCLEAR FUEL PARTICLES
Simulation objectives:

- Demonstrate simulations with sufficient detail to capture known effects of coater operation and design on quality
- Develop analytical tools that aid coater scale-up and design
- Develop improved nuclear fuel coaters with unprecedented levels of product quality
- Develop improved fundamental understanding of the controlling mechanisms for both C and SiC chemical vapor deposition
- Develop improved fundamental understanding of the dynamics of spouted bed reactors
Observation (1): MFIX can predict correct dynamic time scales

- Gas pulsations are directly measurable
- Pulsations contain important information on solids circulation
- The circulation times also relate to particle-coating gas contact time

500 μm ZrO$_2$ at 300 K in air for UTK 2-inch mockup
Observation (2): Standard heat transfer correlations in MFIX appear to work well for this application

- Gunn (1978) heat & mass transfer correlations used
- Large effects of temperature due to
  - Density and viscosity change
  - Sudden radial and axial expansion
- Two different example cases
  - 500 µm ZrO2 in 30.06 m/s air at 298 K
  - 536 µm buffer coated UCO in 14.6 m/s Argon/Acetylene/Propylene mixture at 1523K
- Jet expansion is much more dramatic at higher T
- At higher T, spouting also becomes more vigorous and pulsation frequency drops by ~1/2
- Consistent with experiments
  - indicates proper coupling between heat transfer and hydrodynamics
Observation (3): We see very high spatial & temporal gradients at coating conditions

- Experimental observations indicate core zone is the most important (location of 'snow' formation during C deposition)

- Inlet gas heats very quickly to furnace temperature with solids (unlike pure gas flow)

- Very large absolute fluctuations in velocities, temperatures & concentrations during pulsation cycle

- Characteristics of these gradients, fluctuations expected to be major factors for design, scaling
Observation (4): Injector design very critical to overall spouting behavior

Side View (Translucent)
[Contour surface corresponds to 0.99 void fraction] Similar to peering into a glass bed with marbles

3D Multi-hole (6 holes: 1 + 5) Reference NUCO IPyC condition 3D Single-hole
Observation (5): MFIX simulation predicts surface ‘sloshing’ observed in experiments
Discriminating characteristics (DCs) have been proposed as generic quantitative indicators

<table>
<thead>
<tr>
<th>Discriminating Characteristic</th>
<th>Multi-hole</th>
<th>Single-hole</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensionless Solids Circulation Time (DSCT)</td>
<td>20.75</td>
<td>35.34</td>
<td>40% reduction</td>
</tr>
<tr>
<td>Ballistic Particle Profile (BPP) (10%) (cm)</td>
<td>8.56</td>
<td>10.97</td>
<td>Significant reduction in fountain height</td>
</tr>
<tr>
<td>Net Solids Impact Rate (NSIR) (g/s)</td>
<td>32.77</td>
<td>17.83</td>
<td>90% increase in wall impacts</td>
</tr>
<tr>
<td>Core Diameter (CD) (cm)</td>
<td>2.96</td>
<td>2.18</td>
<td>Significant increase in core diameter</td>
</tr>
<tr>
<td>Gas Velocity at center line at initial bed height (VG@CH) (cm/s)</td>
<td>346</td>
<td>949</td>
<td>Significant decrease in gas velocity</td>
</tr>
<tr>
<td>Solids Velocity at center line at initial bed height (VS@CH) (cm/s)</td>
<td>39.8</td>
<td>80.4</td>
<td></td>
</tr>
<tr>
<td>Gas T at center line at initial bed height (TG@CH) (K)</td>
<td>1371</td>
<td>1000</td>
<td>Gas heats up quickly</td>
</tr>
<tr>
<td>Solids T at center line at initial bed height (TS@CH) (K)</td>
<td>1516</td>
<td>1486</td>
<td></td>
</tr>
<tr>
<td>H2 concentration at center line at initial bed height (H2@CH)</td>
<td>0.0393</td>
<td>0.0243</td>
<td>Significant product formation at bed height</td>
</tr>
<tr>
<td>Acetylene concentration at center line at initial bed height (C2H2@CH)</td>
<td>0.0221</td>
<td>0.0788</td>
<td>Significant decrease in the reactant species</td>
</tr>
<tr>
<td>Propylene concentration at center line at initial bed height (C3H6@CH)</td>
<td>0.0179</td>
<td>0.0639</td>
<td>Significant decrease in the reactant species</td>
</tr>
<tr>
<td>GRADT (K/cm)</td>
<td>857.87</td>
<td>249.37</td>
<td>Huge difference in the gas heat-up rate</td>
</tr>
<tr>
<td>T@GRADT (K)</td>
<td>434.5</td>
<td>461.9</td>
<td></td>
</tr>
<tr>
<td>Y@GRADT (cm)</td>
<td>0.25</td>
<td>1.382</td>
<td>Gas heats up very close to the inlet</td>
</tr>
</tbody>
</table>
## Geometries and gas distributors

<table>
<thead>
<tr>
<th>Run</th>
<th>Geometry</th>
<th>Distributor</th>
<th>Diluent gas partition Center</th>
<th>ring</th>
<th>Total gas mass flow rate [kg/hr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cardioid</td>
<td>Ring+center</td>
<td>0.908</td>
<td>0.092</td>
<td>10.7</td>
</tr>
<tr>
<td>2</td>
<td>Cardioid</td>
<td>Ring+center</td>
<td>0.938</td>
<td>0.062</td>
<td>16.1</td>
</tr>
<tr>
<td>3A</td>
<td>Cardioid</td>
<td>Multiport</td>
<td>0.908</td>
<td>0.092</td>
<td>10.7</td>
</tr>
<tr>
<td>3B</td>
<td>Cardioid</td>
<td>Multiport</td>
<td>0.908</td>
<td>0.092</td>
<td>10.7</td>
</tr>
<tr>
<td>4</td>
<td>Cardioid</td>
<td>Multiport</td>
<td>0.908</td>
<td>0.092</td>
<td>10.7</td>
</tr>
<tr>
<td>5</td>
<td>Cone</td>
<td>Center</td>
<td>N/A</td>
<td></td>
<td>10.7</td>
</tr>
</tbody>
</table>
Reference cone design
Ring + center (Design #1)
Multiport injector (Design #3)
Conclusions from FBCVD scale-up studies

- Cardioid chalice with the multi-port design appears to have the best gas-solids mixing and heat transfer rates
  - Conical spouted beds cannot be scaled from 2” to 6”
  - Impact of swirl is minimal
  - Coater hydrodynamics and heat transfer are only minimally affected by mass transfer and chemical reactions.

- Design time reduced by order of magnitude at a fraction of cost
COAL GASIFIER
Carbonaceous Chemistry for Continuum Modeling (C3M)

- **Devolatilization**
  
  \[ HF: \text{Volatile Matter} \rightarrow \alpha_d \text{Tar} + \beta_d \text{CO} \text{CO} \beta_d \text{CO}_2 \text{CO}_2 + \beta_d \text{CH}_4 \text{CH}_4 + \beta_d \text{H}_2 \text{H}_2 + \beta_d \text{H}_2 \text{O} \text{H}_2 \text{O} \]

- **Cracking**
  
  \[ IF: \text{Tar} \rightarrow \alpha_c \text{C} + \beta_c \text{CO} \text{CO} \beta_c \text{CO}_2 \text{CO}_2 + \beta_c \text{CH}_4 \text{CH}_4 + \beta_c \text{H}_2 \text{H}_2 + \beta_c \text{H}_2 \text{O} \text{H}_2 \text{O} \]

- **Drying**
  
  \[ GF: \text{Moisture (coal)} \rightarrow \text{H}_2 \text{O} \]

- **Water-gas shift reaction**
  
  \[ EF: \text{CO} + \text{H}_2 \text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \]

- **Gasification**
  
  \[ BF: \text{C} + \text{H}_2 \text{O} \leftrightarrow \text{CO} + \text{H}_2 \]
  \[ CF: \text{C} + \text{CO}_2 \leftrightarrow 2\text{CO} \]
  \[ DF: \frac{1}{2}\text{C} + \text{H}_2 \leftrightarrow \frac{1}{2}\text{CH}_4 \]

- **Combustion**
  
  \[ 0F: \text{H}_2 + 2\text{O}_2 \rightarrow \text{H}_2 \text{O} \]
  \[ 1F: \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2 \text{O} \]
  \[ 2F: \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \]
  \[ AF: 2\text{C} + \text{O}_2 \rightarrow 2\text{CO} \]
Coal gasification simulations

- We are conducting high resolution gasifier simulations with collaborators at NETL
  - 2 week run using 2048 processors for a 10M grid

- Earlier simulations led to design modifications
  - Lower riser gas and solids velocities
  - Down flow at the wall (clusters are present)
  - Improved mixing in the riser

- Coal gasifiers are integral part of current clean coal technologies
### PSDF reactor at Wilsonville: Validation

<table>
<thead>
<tr>
<th>MFIX/Experiment</th>
<th>PRB Oxygen Blown</th>
<th>PRB Air Blown</th>
<th>Hiawatha Air Blown</th>
<th>Hiawatha Oxygen Blown</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>12.7/11.7</td>
<td>14/11</td>
<td>3.4/3.5</td>
<td>8.5/6.4</td>
</tr>
<tr>
<td>CO2</td>
<td>11.2/14.1</td>
<td>5.1/7.4</td>
<td>11/9.3</td>
<td>13.8/12.6</td>
</tr>
<tr>
<td>CH4</td>
<td>2.2/2.8</td>
<td>1.9/1</td>
<td>2.6/1.3</td>
<td>3.5/2.3</td>
</tr>
<tr>
<td>H2</td>
<td>18/14.7</td>
<td>3/6.2</td>
<td>4.3/4.8</td>
<td>11/9.4</td>
</tr>
<tr>
<td>H2O</td>
<td>28/22.9</td>
<td>7/8.3</td>
<td>17/23</td>
<td>37/33.8</td>
</tr>
<tr>
<td>CO/CO2</td>
<td>1.1/.8</td>
<td>2.7/1.5</td>
<td>.3/.4</td>
<td>.62/.5</td>
</tr>
<tr>
<td>Exit Temp (F)</td>
<td>1668/1674</td>
<td>1749/1757</td>
<td>1763/1779</td>
<td>1783/1714</td>
</tr>
<tr>
<td>Percentage of Carbon Conversion</td>
<td>66%/87%</td>
<td>98%/98%</td>
<td>99%/97%</td>
<td>100%/96%</td>
</tr>
<tr>
<td>Syngas Rate in Lbs/hr</td>
<td>13400/16000</td>
<td>19800/21000</td>
<td>19400/21000</td>
<td>13200/14600</td>
</tr>
</tbody>
</table>

Courtesy: Chris Guenther @ NETL
MULTISCALE/MULTIPHYSICS COUPLING
MSMP modeling of heterogeneous chemically reacting flows

Goal: Develop a MSMP framework for accurate modeling of heterogeneous reacting flows over catalytic surfaces

Procedure: Perform upscaling and downscaling using CWM

Compound Wavelet Matrix (CWM)
Results from a prototype reaction diffusion problem

- Successfully applied CWM strategy for coupling reaction/diffusion system
- An unique way to bridge temporal and spatial scales for MSMP simulations

*Frantziskonis et al., International Journal for Multiscale Computational Engineering, 5-6, 755, 2006
Mishra et al., International Journal for Chemical Reactor Engineering, 6, A28, 2008
tpCWM (Time Parallel CWM)

Schematic of the TP and CWM methods. (a) The TP method. The fine method instantiates at several temporal “nodes” typically for a period $\delta t$ that covers time until the next node. (b) The temporal CWM. The fine method is employed for a fraction of the coarse method. (c) The CWM reconstruction updates the mean field. (d) The CWM reconstruction updates the temporal statistics.
tpCWM applied to Lotka-Volterra predator-prey equations

\[
\begin{align*}
X + Y_1 &\overset\alpha\rightarrow 2Y_1 \\
Y_1 + Y_2 &\overset\beta\rightarrow 2Y_2 \\
Y_2 &\overset\gamma\rightarrow Z
\end{align*}
\]

Lotka-Volterra System

\[
\begin{align*}
\frac{dY_1}{dt} &= \alpha XY_1 - \beta Y_1 Y_2 \\
\frac{dY_2}{dt} &= \beta Y_1 Y_2 - \gamma Y_2
\end{align*}
\]

Factor of computational savings, X as a function of the ratio \( r \) (number of processors/number of iterations) and the fraction \( f \) (fraction of KMC time used in each assigned time interval).

Three orders of magnitude savings can be achieved by \( r \) in the range of 20 and \( f \) in the order of 1/64.
Summary

- Integrated experiments and simulations at scale can revolutionize the design of energy devices
  - Include all relevant scales so that molecular scale interactions are included when designing device scale
  - Cut down the current 20-30 year design cycle
  - Break cultural barriers

- Develop computations based feedback control systems to run devices in most optimal fashion
  - Adjust for feedstock etc. online rather than offline adjustments with huge safety margins

- Simulation science can and has to play a catalytic and important role in bringing innovation to the energy market place
Collaborators

Oak Ridge National Laboratory
- Srdjan Simunovic
- Phani Nukala
- Badri Velamur
- Asokan
- Jay Boyalakuntla
- Ed D’Azevedo
- Bill Shelton
- Ramanan Sankaran

University of Arizona
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- Sudib Mishra
- Pierre Deymier
- Krishna Muralidharan

National Energy Technology Laboratory
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- Madhava Syamlal
- Chris Guenther
- Sofiane Benyahia
- Aytekin Gel
- Phil Nicoletti
- Mike Prinkey

Ames Laboratory
- Rodney Fox
- Zhaoseng Gao

[Logos of Oak Ridge National Laboratory, University of Arizona, National Energy Technology Laboratory, Iowa State University]