Co-pyrolysis of Coal and Biomass at Transport Gasifier Conditions

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NETL’s FY11 In-house Research: Advanced Gasification Program

- **Mission**: “Accelerate the development of advanced, affordable and efficient gasification-based technologies that promote coal-based fuel flexibility and reduce pollutants, trace elements, and the carbon footprint of existing and future coal fired applications.”

- **Tasks/Projects**:
  1. Biomass Processing
  2. Refractory Development
  3. Co-gasification Reactions and Kinetics
  4. Device/System Modeling
Advanced Gasification Team Approach

**Objective #1**
- Kinetic Data
- Product Properties

**Objective #2**
- Task 2: Gasifier Materials
- Task 4: Modeling

**Task 1**
- Prep/Feed

**Task 3**
- Transport Gasifiers
- Entrained Flow Gasifiers

**Blend**

**COAL**

**Raw / Treated Biomass**
NETL Modeling Approach

• NETL’s C3M program
  – Carbonaceous Chemistry for Computational Modeling
  – Interface between kinetics databases and high-fidelity computational models

• Kinetic databases need to be updated
  – Add biomass feedstocks
  – Account for coal/biomass co-feeding non-linearities
  – Pyrolysis, gasification, tar
  – Transport and entrained flow conditions
Project Objectives and Goals

• **Program Goal**: Successfully simulate the PSDF transport gasifier on co-fed coal/biomass

• **Project Goal**: Provide fundamental co-pyrolysis and co-gasification kinetic data for C3M platform
  – Determine root cause of nonlinear coal/biomass interactions, if present

• **C3M’s co-feed data needs:**
  – Devolatilization kinetics and product distributions
  – Gasification kinetics under CO$_2$, H$_2$, H$_2$O and O$_2$
  – Homogeneous & heterogeneous tar cracking kinetics
Transport Integrated Gasification (TRIG™)

- Non-slagging KBR gasifier at PSDF
- Operating conditions
  - 2 ton/hour combustor or gasifier
  - Air- or Oxygen-blown
  - Pressure: 11 – 17 atm
  - Temperature: 815 – 1040 °C
- Feedstocks
  - Coarse, dry feed
  - Works well on low rank, high moisture, high ash coals
    - PRB coal, Mississippi lignite
  - Biomass: 20% blend typical, up to 100%
- Basis for 582 MW plant in construction at Kemper, Mississippi
Test Matrix

- **8 test points:**
  - 600 & 800 °C at 1, 4 and 16 atm, 975 °C at 1 and 4 atm
- **4-5 dried fuel mixtures consistent with PSDF testing:**
  - Pure PRB coal, lignite & pine wood biomass
  - 80% PRB/20% wood mixture
  - 80% lignite/20% wood mixture (time permitting)
- **5 reaction environments:**
  - Inert argon for pyrolysis, CO₂, H₂, H₂O and O₂ for gasification
- **160-200 total data points**
- **Separate product distribution and kinetics tests**
- **Will also generate co-gasification model validation data with as-received feedstocks**
  - Must test the ability of C3M to capture nonlinear co-gasification behavior (coal-gas and coal-char interactions)
Sample Specifications

- **Feedstocks dried, ground, and sieved**
  - Powder River Basin (PRB) Sub-bituminous Coal
  - Mississippi Lignite (Red Hills)
  - Southern Yellow Pine Pellets
- **Products:**
  - 500 to 850 µm
- **Kinetics:**
  - 100 to 300 µm

<table>
<thead>
<tr>
<th></th>
<th>PRB Coal as rec'd dry basis</th>
<th>Miss. Lignite as rec'd dry basis</th>
<th>Wood Pellets as rec'd dry basis</th>
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<tbody>
<tr>
<td><strong>Proximate Analysis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Moisture</td>
<td>20.43</td>
<td>19.06</td>
<td>4.00</td>
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<tr>
<td>% Ash</td>
<td>7.03</td>
<td>15.43</td>
<td>19.06</td>
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<tr>
<td>% Volatile</td>
<td>32.49</td>
<td>29.60</td>
<td>81.78</td>
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<tr>
<td>% Fixed Carbon</td>
<td>40.06</td>
<td>35.91</td>
<td>12.86</td>
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<tr>
<td><strong>Ultimate Analysis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Carbon</td>
<td>53.50</td>
<td>45.62</td>
<td>51.07</td>
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<tr>
<td>% Hydrogen</td>
<td>3.37</td>
<td>3.42</td>
<td>5.99</td>
</tr>
<tr>
<td>% Nitrogen</td>
<td>1.22</td>
<td>0.86</td>
<td>0.12</td>
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<tr>
<td>% Sulfur</td>
<td>0.30</td>
<td>0.47</td>
<td>0.02</td>
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<tr>
<td>% Oxygen(diff)</td>
<td>14.16</td>
<td>15.14</td>
<td>37.44</td>
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<tr>
<td><strong>Energy Analysis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Btu/lb</td>
<td>9102</td>
<td>7786</td>
<td>8485</td>
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<tr>
<td>MAF BTU/lb</td>
<td>11439</td>
<td>9619</td>
<td>8839</td>
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<tr>
<td></td>
<td>12547</td>
<td>11884</td>
<td>8966</td>
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Product Distribution Tests

• HPTR Tests at NETL Pittsburgh
  – Isothermal pyrolysis of a ~1 gram sample, dropped onto a heated quartz frit
  – Semi-batch operation (1 test/day)
• Ex-situ tar and water trapping
• Quantitative gas sampling by mass spec:
  – CO$_2$, CO, CH$_4$, C$_2$H$_4$, H$_2$S, H$_2$, H$_2$O
• Tests with mass closures between 95 and 105% retained for product distribution analysis
Primary Products vs. Biomass Blend

- Linear primary pyrolysis product distributions with respect to wt. % biomass
- Distribution nonlinearities seen in literature at lower temperature not observed in these experiments
Primary Products vs. Temperature

- Primary pyrolysis product distributions slightly nonlinear wrt temperature, as expected
- In general, condensable fractions and char converted to gas at high temperatures
Gaseous Products vs. Biomass Blend

- Linear gaseous pyrolysis product distributions with respect to biomass wt. %
- Higher CO and lower CO2 release with biomass wt. % and temperature
  - Consistent with literature
Gaseous Products vs. Biomass Blend

- **More H\textsubscript{2} generated by coal than biomass on volume basis**
  - Biomass gas ~2x PRB gas
  - Biomass has 50% more H, released as hydrocarbons
- **H\textsubscript{2}/CO ratio decreases as biomass wt.% increases**
  - H\textsubscript{2}/CO ~ 2 for PRB, 0.1 for WB
Gaseous Products vs. Temperature

- Increases in total gas production with temperature mostly due to CO and hydrocarbons
  - ~40% of biomass weight converted to CO at 975 °C
GC-MS Gas Analysis

- Qualitative analysis of gas bag samples taken during pyrolysis at 800 °C
  - Trace sulfur species appear in PRB tests
  - Acetylene, acetaldehyde, toluene more prevalent with biomass
Current H PTR-1 Kinetics

- H PTR gas production data previously unsuitable for kinetics
- Procedure modifications yield more accurate and consistent kinetic data

<table>
<thead>
<tr>
<th>Test Type</th>
<th>Product Distribution</th>
<th>Kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample quantity</td>
<td>1.0 g</td>
<td>0.1 g</td>
</tr>
<tr>
<td>Sample size</td>
<td>300-1000 μm</td>
<td>100-300 μm</td>
</tr>
<tr>
<td>Sweep gas flow rate</td>
<td>2.0 slm Ar</td>
<td>4.5 slm Ar</td>
</tr>
<tr>
<td>Reaction location</td>
<td>9” from bottom</td>
<td>4” from bottom</td>
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<tr>
<td>Residence time</td>
<td>4.4 s</td>
<td>0.13 s</td>
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</table>
Reactor Setup for Isothermal Kinetics

Temperature [°C]

Position from Top of Heater (inches)
Drop-Tube (Isothermal) Pyrolysis Kinetics

- **Total devolatilization**
  - Measure CO, CO\(_2\), CH\(_4\), C\(_2\)H\(_4\), H\(_2\) and H\(_2\)O via QMS
  - Total gas evolution: \(m_{\text{total}} = \sum(m_{\text{gas}})\)
  - Solid mass loss: \(m_{\text{solid}}(t) = m_{\text{feed}} - m_{\text{gas}}(t) - m_{\text{tar}}(t)\)
  - Assuming that the rate of \(m_{\text{tar}}(t)\) is proportional to \(m_{\text{gas}}(t)\):
    \[
    X = \frac{m_{\text{feed}} - m_{\text{solid}}(t)}{m_{\text{feed}} - m_{\text{solid}}(\infty)} = \frac{m_{\text{gas}}(t)}{m_{\text{gas}}(\infty)}
    \]

- **General Rate Equation:**
  \[
  \frac{dX}{dt} = k \bigtriangleup - X^n
  \]
  \[
  k = A * \exp \bigtriangleup \frac{E_A}{R * T} \]

- **Integrate for** \(n = 1\):
  \[
  \ln(1 - X) = k t
  \]
Preliminary Pyrolysis Kinetics Results

- Mass spec sample rate
  - ~0.7 s/sample
- Reaction progress, $X$, characterized by dimensionless gas release
- Reaction rate, $k$, fit to initial slope of $\ln(1-X)$
  - Best fit covers first 75-90% of reaction
- Multiple slopes may better fit a DAEM model
Preliminary Pyrolysis Kinetics Results

- **Fit of reaction rates on an Arrhenius plot**
  - Considerable scatter in the reaction rate data

- **Potential coal/biomass reaction rate synergy**
  - Lower mixture activation energy and pre-exponential
  - Similar to literature results:

- **Requires further study and refinement**

<table>
<thead>
<tr>
<th></th>
<th>PRB</th>
<th>20% WB</th>
<th>WB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_A$ (kJ/mol)</td>
<td>30.9</td>
<td>24.2</td>
<td>32.9</td>
</tr>
<tr>
<td>$A$ (1/s)</td>
<td>16.3</td>
<td>6.5</td>
<td>24.6</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.934</td>
<td>0.967</td>
<td>0.912</td>
</tr>
</tbody>
</table>
Summary

• Pyrolysis product distributions
  – Linear primary and gaseous product distributions with respect to biomass weight %
  – Elemental H in PRB coal more likely to evolve as $\text{H}_2$
  – Elemental H in wood evolves as hydrocarbons, with more $\text{H}_2$ at high temperature
  – Pyrolysis $\text{H}_2$/CO ratio decreases significantly with increasing biomass wt. %

• Preliminary pyrolysis kinetics
  – Potential nonlinear kinetic coal/biomass synergy
  – Preliminary results suggest 2-stage process
Future Work

• Refine pyrolysis kinetic analysis
• Modify reactor to increase testing rate
• Study pressurized pyrolysis product distributions and kinetics
• Gasification rate data for CO2, H2O, O2 and H2
• Generate C3M model validation data on as-received feedstocks in simulated syngas
• New lab being constructed for studying tar cracking kinetics
  – High speed TGA (100 °C/s), tube furnace, mass spec
  – Study tar generation rate, homogeneous and heterogeneous tar cracking kinetics
Tar Cracking Kinetics

**TGA**
Generate fresh vapor tar

**Parameters**
**Temperature:** 300-500°C

**Poplar volatile generating rate (1/s)**

![Graph showing Poplar volatile generating rate](image)

**Coal volatile generating rate (1/s)**

![Graph showing Coal volatile generating rate](image)

**Coal/biomass**

**Tar cracking kinetics:**
- Homogeneous without char
- Heterogeneous with char

**Coal**

**Poplar**

**Lignite coal volatile generating rate (1/s)**

![Graph showing Lignite coal volatile generating rate](image)

**Tubular reactor**
Tar cracking kinetics: homogeneous without char heterogeneous with char

**Parameters**
**Temperature:** 600-1200°C
**Residence time:** 2-6 s

**On-line MS**
Gas analysis
- \( H_2 \), \( CO \), \( CO_2 \),
- \( H_2O \), \( CH_4 \)

**Off-line GC-MS**
Tar compositions

**Off-line BET**
Char surface area
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