On the Effect of Pressure on Black Liquor Pyrolysis and Gasification

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US Forest Biomass Availability

Source: Billion ton biomass report
Black Liquor

- By-product from kraft pulping of wood
- Contains dissolved organics from wood and inorganic cooking chemicals (NaOH, Na$_2$S)
- A liquid with 15-30% water content
- Currently burnt to recover cooking chemicals and produce steam/electricity

### Typical Black Liquor Composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>37%</td>
</tr>
<tr>
<td>H</td>
<td>4%</td>
</tr>
<tr>
<td>Na</td>
<td>20%</td>
</tr>
<tr>
<td>S</td>
<td>4%</td>
</tr>
<tr>
<td>K</td>
<td>0.5%</td>
</tr>
<tr>
<td>Cl</td>
<td>0.5%</td>
</tr>
<tr>
<td>O</td>
<td>34%</td>
</tr>
</tbody>
</table>
Black Liquor Gasification

• Being developed to improve efficiency
  – Higher electricity generation
  – Production of fuels or chemicals from syngas
  – More efficient pulping
    • Separation of sulfur and sodium during gasification enables liquor recovery for several high-yield pulping processes
Black Liquor Gasification Technologies

• Low-temperature gasification
  – Below inorganic melting temperature (~600°C)
  – Fluidized bed technology
  – Atmospheric

• High-temperature gasification
  – Above inorganic melting temperature (900-1000°C)
  – Entrained-flow reactors
  – Atmospheric and pressurized
Objectives of Current Work

- To evaluate the impact of pressure on
  - black liquor char characteristics
  - the rate of carbon conversion
  - the fate of sulfur in black

at conditions relevant to high-temperature
black liquor pyrolysis and gasification
  - high heating rate
  - temperature ~900-1000C
Experimental

- Dried black liquor particles pyrolyzed or gasified in a pressurized entrained-flow reactor (PEFR)
- Carbon gasification rate and distribution of sulfur between gas and condensed phase measured
- Char properties evaluated by
  - SEM, optical microscopy for morphology
  - Mercury porosimetry for pore size distribution and porosity
  - $\text{N}_2$ absorption for surface area measurements
  - Light scattering for particle size distribution measurements
# Experimental Conditions

<table>
<thead>
<tr>
<th>Process</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis</td>
<td>10, 15 bar, 900°C, 100% N₂, 0.9 - 3.5 s</td>
</tr>
<tr>
<td>Constant Partial Pressure</td>
<td>5, 10, 15 bar, 900°C, 0.25 bar H₂O, 0.5 bar CO₂ in N₂, 0.6 - 3.5 s</td>
</tr>
<tr>
<td>Gasification</td>
<td></td>
</tr>
<tr>
<td>Constant Mole Fraction Gasification</td>
<td>10, 15 bar, 900°C, 10% CO₂, 2% H₂O, 1.7% CO, 0.3% H₂ in N₂, 0.9 - 3.5 s</td>
</tr>
</tbody>
</table>
Particle Size of Short Residence Time Pyrolysis Chars

% Volume Distribution

Diameter (micron)

5 Bar
10 Bar
15 Bar
Physical Characteristics of Short Residence Time Pyrolysis Chars

- Skeletal Density (100 kg/m^3):
  - 5 Bar: 1400
  - 10 Bar: 1600
  - 15 Bar: 1100

- Solid Fraction (%):
  - 2%
  - 3%
  - 6%

- Bulk Density (10 kg/m^3):
  - 5 Bar: 30
  - 10 Bar: 55
  - 15 Bar: 66
Physical Characteristics of Short Residence Time Pyrolysis Chars

- Total S.A. (m^2/g)
  - 5 Bar: 19.0
  - 10 Bar: 10.4
  - 15 Bar: 4.3

- External S.A. (m^2/g)
  - 5 Bar: 13.1
  - 10 Bar: 5.1
  - 15 Bar: 3.7

- Total/External S.A.
  - 5 Bar: 1.4
  - 10 Bar: 2.0
  - 15 Bar: 1.2
Pore Sizes of Short Residence Time Pyrolysis Chars

Incremental Hg Intrusion (mL/g)

Pore Diameter (micron)
Pore Sizes of Short Residence Time Pyrolysis Chars

Incremental Hg Intrusion (mL/g)

Pore Diameter (micron)

Incremental Hg Intrusion (mL/g)

15 Bar

Pore Volume Distribution by Hg porosimetry for Short Residence Time Pyrolysis Char
Specific Surface Area of BL Gasification Chars as a Function of Carbon Conversion

Pyrolysis Chars

Carbon Conversion (%)
Conclusions

• Cenospheric chars (hollow spheres)

• Char from pyrolysis
  • Increasing pressure decreases porosity
  • Increasing pressure increases agglomeration of particles

• Char from gasification
  • Surface area as function of carbon conversion goes through maximum
  • Surface area not dependent on pressure at carbon conversions $>40\%$
  • Gasification rate not proportional to surface area
Black Liquor Carbon Gasification:
Langmuir-Hinshelwood Kinetics:

\[-r = \frac{kP_{CO_2}}{1 + aP_{CO} + bP_{CO_2}}\]

\[-r = \frac{k'}{1 + \frac{P_{H_2}}{a'P_{H_2O}} + b'P_{CO}}\]
Release of Carbon during Pyrolysis at 10 and 15 bar

pyrolysis, 900°C

Fixed C in Char, % of Liquor C

Time, s

0%  20%  40%  60%  80%  100%

01234

10 bar

15 bar
Constant Partial Pressure Gasification: Impact of Pressure

900°C, 0.5 bar CO₂, 0.25 bar H₂O
Constant Mole Fraction Gasification: Impact of Pressure

Fixed C in Char, % of Liquor C

Time, s

10% CO2, 2% H2O, 1.7% CO, 0.3% H₂
Fate of Sulfur during Pyrolysis

![Graph showing the fate of sulfur during pyrolysis at 900°C. The graph indicates the percentage of sulfur in char as a function of time at pressures of 10 bar and 15 bar.]
Fate of Sulfur during Gasification

Equilibrium range

Time, s

900°C, 0.5 bar CO$_2$, 0.25 bar H$_2$O
Conclusions (I)

• Pressure did not impact carbon release carbon during pyrolysis
• During pyrolysis, sulfur was initially released, then recaptured in the char
  – Organic sulfur
  – Sulfide
• During gasification, S reaches constant distribution between gas/condensed phase fast
Conclusions (II)

• Gasification rates fairly constant in fixed carbon conversion range of 20-80%

• Constant mole fraction gasification
  – No impact of pressure on carbon gasification rate at gas concentrations studied
  – Experiments at higher CO/H₂ partial pressures ongoing

• Constant partial pressure gasification
  – Increasing pressure slightly decreased rate