Process Intensification of a Fluidized Bed Pyrolyzer via Autothermal Operation

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Heat transfer is the bottleneck to fast pyrolysis
Conventional systems use hot gases or hot solid heat carriers to convey heat into the pyrolyzer.

**Indirect Heat Transfer**
- Biomass
- Hot gas in
- Biochar & Bio-Oil
- Hot gas out

**Direct Heat Transfer**
- Hot solids in
- Biomass
- Biochar & Bio-Oil
- Hot solids out

*These conventional approaches to heat management can be complicated to construct and operate, but still limit throughput.*
Heat transfer bottleneck is exacerbated as the reactor is scaled up

Heat transfer only scales as *square of reactor diameter* while the energy demand for pyrolysis scales as the *cube of reactor diameter*

- Heat transfer from reactor perimeter: $\dot{Q} \sim 2\pi DL$
- Heat transfer from tube array: $\dot{Q} \sim (SA/tube)(tubes/XS) \pi D^2$
- Heat transfer from granular heat carrier: $\dot{Q} \sim (m_p C_p \Delta T) j_p \pi D^2$
Autothermal Pyrolysis

Part of the biomass and/or pyrolysis products are oxidized to provide energy for endothermic pyrolysis reactions

- **Advantages**
  - Heat transfer no longer bottleneck
  - Throughput scales as diameter cubed
- **Challenge**
  - Preserve organic yields of bio-oil under partial oxidative conditions

\[
\phi = \frac{\text{Air}}{\text{Air}_{\text{Stoich}}}
\]

- **Autothermal Pyrolysis**
  \(0.04 \leq \phi \leq 0.06\)
- **Gasification**
  \(0.15 \leq \phi \leq 0.35\)
- **Combustion**
  \(\phi > 1.0\)

Part of the biomass and/or pyrolysis products are oxidized to provide energy for endothermic pyrolysis reactions

Autothermal Pyrolyzer (adiabatic)

Pyrolysis \(\phi = 0.00\)

Combustion \(\phi > 1.0\)
ISU’s Pyrolysis PDU adapted to perform autothermal pyrolysis tests

- Fluidized bed provides good mixing of biomass and N$_2$/air mixtures when operated in a turbulent fluidization regime
  - Important for avoiding “hot spots” during partial oxidation

- High ventilation rate rapidly transports products to the bio-oil recovery system
  - Prevents secondary reactions that can degrade bio-oil

- Automated guard heaters counteract parasitic heat losses from this relatively small reactor (15 cm dia.)
  - Simulates adiabatic reactor, which allows operation at very low equivalence ratios
Bio-oil is recovered with series of condensers and electrostatic precipitators.
Electric guard heaters simulate adiabatic conditions and allow autothermal operation

- Baseline parasitic heat losses determined for N$_2$ flow before biomass feed
- Change in power requirement to maintain reactor temperature upon feeding biomass gives the enthalpy for pyrolysis
- Air addition brings power back to baseline heat loss and indicates the equivalence ratio for autothermal pyrolysis in adiabatic reactor

$H_P = 1.14 \pm 0.05 \text{ kJ/kg}$

Biomass feed
Conventional Pyrolysis Steady State
Autothermal Pyrolysis Steady State

Elapsed Time (Hours)
Process Intensification

4 Fundamental Principles by Van Gerven & Stankiewicz (2009)

I. Maximize the effectiveness of intra- and intermolecular events

II. Give each molecule the same processing experience

III. Optimize the driving forces at every scale and maximize the specific surface area to which these forces apply

IV. Maximize the synergistic effects from partial processes

In the Context of Autothermal Pyrolysis

I. Quickly pyrolyze biomass and cool bio-oil products

II. Well-mixed fluidized bed with no “hot spots”

III. Utilize partial oxidation to remove heat transfer bottleneck

IV. Exploit increased throughput to operate as “air blown” reactor
Process intensification achieved when the fluidizing gas becomes entirely air

### Experimental Conditions

<table>
<thead>
<tr>
<th>Pyrolysis Atmosphere</th>
<th>Biomass Feed Rate (kg/hr)</th>
<th>Equivalence Ratio $\phi$</th>
<th>Fluidizing Air %</th>
<th>Product Yields (wt. % biomass basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\frac{m_{\text{Air}}}{m_{\text{Air Stoich}}}$</td>
<td>$\frac{V_{\text{Air}}}{V_{\text{Total}}}$</td>
<td>Total Bio-Oil</td>
</tr>
<tr>
<td>Nitrogen ($N_2$)</td>
<td>5</td>
<td>0.000</td>
<td>0.0</td>
<td>61.62</td>
</tr>
<tr>
<td>Autothermal (AT)</td>
<td>5</td>
<td>0.045</td>
<td>15.3</td>
<td>59.55</td>
</tr>
<tr>
<td>Autothermal Process Intensification (AT-PI)</td>
<td>24</td>
<td>0.061</td>
<td>100.0*</td>
<td>68.48</td>
</tr>
</tbody>
</table>

*Represents “air-blown” pyrolysis*
Oil yields were not compromised by autothermal operation of the pyrolyzer

N2 – nitrogen blown (conventional) pyrolysis (5 kg/h)
AT – autothermal pyrolysis (5 kg/h)
AT-PI – autothermal pyrolysis-process intensified (24 kg/h)
AT pyrolysis improves carbon balance

**Pyrolysis Conditions**

- **N2**
  - Unaccounted: 17.3 g
  - NCG's: 17.8 g
  - Light Ends: 12.1 g
  - Intermediates: 5.1 g
  - Heavy Ends: 33.5 g
  - Biochar: 14.2 g

- **AT**
  - Unaccounted: 12.9 g
  - NCG's: 23.2 g
  - Light Ends: 11.0 g
  - Intermediates: 5.2 g
  - Heavy Ends: 30.1 g
  - Biochar: 17.5 g

- **AT-PI**
  - Unaccounted: 5.5 g
  - NCG's: 20.1 g
  - Light Ends: 10.8 g
  - Intermediates: 6.8 g
  - Heavy Ends: 39.3 g
  - Biochar: 17.6 g
Better carbon balances associated with less fouling of condensers at high gas flow rates
AT-PI increased pyrolytic sugar yields

Hydrolyzed Sugar Content in Bio-Oil

- Sorbitol
- Xylose
- Glucose

<table>
<thead>
<tr>
<th>Stage Fraction &amp; Pyrolysis Conditions</th>
<th>N2</th>
<th>AT</th>
<th>AT-PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF1</td>
<td>14.75</td>
<td>15.54</td>
<td>6.67</td>
</tr>
<tr>
<td>SF2</td>
<td>2.55</td>
<td>2.35</td>
<td>2.57</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th>Hydrolyzed Sugar Content in Bio-Oil</th>
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<tbody>
<tr>
<td>Concentration (g / 100g bio-oil)</td>
</tr>
<tr>
<td>Sorbitol</td>
</tr>
<tr>
<td>Xylose</td>
</tr>
<tr>
<td>Glucose</td>
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</table>

Total Sugar Yields from Biomass

- SF1
- SF2

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<thead>
<tr>
<th>Pyrolysis Conditions</th>
<th>N2</th>
<th>AT</th>
<th>AT-PI</th>
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<tbody>
<tr>
<td>SF1</td>
<td>4.38</td>
<td>4.10</td>
<td>8.72</td>
</tr>
<tr>
<td>SF2</td>
<td>2.99</td>
<td>2.65</td>
<td>5.24</td>
</tr>
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<tr>
<th>Total Sugar Yields from Biomass</th>
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<tr>
<td>Yield (g / 100g biomass)</td>
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IOWA STATE UNIVERSITY
Bioeconomy Institute
AT-PI produced more phenolic monomers

Suggests that oxygen helps crack lignin and stabilize phenolic monomers

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<thead>
<tr>
<th>Concentration (g / 100g PO)</th>
<th>N2</th>
<th>AT-PI</th>
<th>N2</th>
<th>AT-PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF1</td>
<td>89.47</td>
<td>43.76</td>
<td>86.98</td>
<td>82.90</td>
</tr>
<tr>
<td>SF2</td>
<td>10.53</td>
<td>13.02</td>
<td>17.10</td>
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Bio-Oil
Heavy Ends

1:1 Water Wash

Pyrolytic Sugars
Phenolic Oil

1:1 Toluene Wash

Monomers
Oligomers

Stage Fraction & Pyrolysis Conditions
Light, flammable pyrolysis gases provided about half of the enthalpy for pyrolysis.

\[
\text{Relative Percent Change} = \frac{\text{Yield}_{\text{GasSpecies}} - \text{Yield}_{\text{N2Baseline}}}{\text{Yield}_{\text{N2Baseline}}}
\]

- **Carbon Dioxide**
- **Carbon Monoxide**
- **Ethylene**
- **Ethane**
- **Methane**
AT Pyrolysis has better process scalability

- Enthalpy of pyrolysis provided internally, eliminating the need for bed internals or granular heat carrier

- Scale-up is improved compared to heat transfer limited operation

- Potential for air-blown operation removes the need for inert or recycle gas and maximizes biomass throughput
  - Less equipment for integrated system
  - Could be utilized for modular pyrolysis systems

- How does this affect estimated cost projections?
  - Performed preliminary techno-economic analysis (TEA)
Investigated the effects of AT-PI using a preliminary techno-economic analysis (TEA) on bio-oil fractionation

• 2000 MT/Day biomass throughput
• Integrated commercial plant
  – Biomass pretreatment (drying & milling)
  – Autothermal pyrolysis reactor with process intensification
  – Bio-oil fractionating recovery system
  – On-site power generation
  – AT-PI operation reduced pyrolysis and power generation equipment sizes
AT-PI helps reduce estimated costs

- Capital costs reduced for pyrolysis reactor and co-generation equipment
  - Decreased by 25.6% overall

- Lower fixed capital costs translated into decreased production costs for bio-oil via AT-PI operation
  - Decreased by 16.5% overall

Comparison of bio-oil production cost

<table>
<thead>
<tr>
<th>Minimum Selling Price ($/gal)</th>
<th>Conventional</th>
<th>Autothermal</th>
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<tbody>
<tr>
<td>0.91</td>
<td>0.76</td>
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Comparison of capital costs:

- Conventional:
  - Balance of Plant: $49.27
  - Power generation: $24.93
  - Fractionation: $11.07
  - Pyrolysis: $22.16
  - Pretreatment: $22.16

- Autothermal:
  - Balance of Plant: $84.06
  - Power generation: $30.68
  - Fractionation: $11.07
  - Pyrolysis: $22.16
  - Pretreatment: $22.16

25.6% decrease in capital costs overall.
Conclusions

• Autothermal pyrolysis overcomes heat transfer bottleneck of traditional pyrolyzers

• Process intensification manifested as four to five fold increase in biomass throughput

• Bio-oil yields increased under autothermal pyrolysis with process intensification

• Simplified reactor decreases capital costs and improves scaling law
Take a virtual tour of ISU’s Pyrolysis Process Development Unit

Stop by the Bioeconomy Institute Booth at TCS 2016
Acknowledgements

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