Process Analysis of Multistage Heat Recovery and Integration in Pyrolysis Systems

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Biomass pyrolysis

• Pyrolysis is endothermic thermal decomposition of a carbonaceous material in absence of oxygen.

• Fast pyrolysis requires rapid heating followed by rapid quenching of pyrolysis vapours.
Vapour quench in fast pyrolysis

- Fast pyrolysis requires rapid heating followed by rapid quenching of pyrolysis vapours.
- Nearly all of the commercial pyrolysis processes involve single stage quench with recycling cooled oil as a direct contact quench fluid.
Single stage vapour quench

• Single stage rapid quenching leads to:
  – Low pH liquid mixture having 100s of oxygenated compounds with wide range of physical and chemical attributes.
  – Thermodynamically unstable products causing polymerization and phase separation over time.
  – Loss of high quality heat which otherwise could be recovered and reintegrated with upstream heat demand.
Objective

• Staged thermal quenching of pyrolysis vapours facilitating
  – early isolation of sugars from acids.
  – recovery and recycle of high quality heat.
Re-design of condensation

- Thermal quench with selective heat recovery
- Early isolation of fractions to stabilize the product streams.

Hot pyrolysis vapours $\sim 500 \, ^\circ C$

Heat integration

Product fraction 1

Product fraction 2

Product fraction 3

Off gas
Modelling challenges

- Biomass pyrolysis is very complex and different compared to combustion and gasification.
- Biomass and char are non-conventional solids.
- No commercial thermodynamic methods exist to adequately represent biomass pyrolysis and bio-oils containing more than 300 oxygenated compounds.
Model development

• Process model was developed using Aspen Plus v10.
• This model uses 14 compounds from Aspen Plus library representing major functional groups in bio-oil (acids, high and low molecular weight sugars and lignin).
• Pinewood was used as biomass feedstock at a rate of 100 kg/hr (wet basis)
• For staged condensation, pyrolysis reactor temperature was kept at 500 °C.
• Pyrolysis model was validated with results from NREL/PNNL 2013 studies on Fluid-bed reactor.

Pinewood (w % et basis)

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<tbody>
<tr>
<td>C</td>
<td>35.6</td>
</tr>
<tr>
<td>H</td>
<td>4.22</td>
</tr>
<tr>
<td>N</td>
<td>0.12</td>
</tr>
<tr>
<td>S</td>
<td>0.02</td>
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<tr>
<td>Ash</td>
<td>0.64</td>
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<tr>
<td>Water</td>
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Model development

Continued…

• Two different kinds of pyrolysis systems were considered
  – Fluid bed systems with biomass to recycle fluidization off gas ratio of 1:3 (w/w basis)
  – Ablative based system with biomass to recycle off gas ratio of 10:1 (w/w basis).
Model development  Continued…

• For high temperature heat recovery from stage 1 and 2, CALFLO AF was used as the thermal fluid of choice and high temperature limits were set at manufacturer recommended temperature at 316°C (600°F).

• For low temperature recycle from 3rd stage condensation, an Organic Rankine Cycle (ORC) was integrated using R123 as working fluid and process conditions were adapted in line with commercially available portable ORCs.
Aspen Plus process model

Staged condensation and heat recovery

Biomass drying and feeding

Pyrolyser

Char combustor

Thermal fluid circuit

ORC for power
Staged condensation

500°C → 270°C → 150°C → 40°C

- **Ablative**
  - Bio-Oil flow rates [kg/hr]
  - Stage 1: 25 kg/hr, Stage 2: 15 kg/hr, Stage 3: 10 kg/hr

500°C → 250°C → 140°C → 40°C

- **Fluidized bed**
  - Bio-Oil flow rates [kg/hr]
  - Stage 1: 25 kg/hr, Stage 2: 15 kg/hr, Stage 3: 10 kg/hr

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Heat available for recovery

<table>
<thead>
<tr>
<th></th>
<th>Fluid bed</th>
<th>Ablative</th>
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<tbody>
<tr>
<td>Stage 1</td>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>Stage 2</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>Stage 3</td>
<td>75</td>
<td>30</td>
</tr>
</tbody>
</table>

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Product recovery

- Each stage offers a different product quality.
- Equipment sizing varies significantly from stage 1 to stage 3.
Energy Distribution

Ablative

- Biomass in: 1371 MJ/hr
- Condensate 1: 460 MJ/hr (33%)
- Condensate 2: 253 MJ/hr (18%)
- Condensate 3: 135 MJ/hr (10%)
- Bio-char: 254 MJ/hr (18%)
- Additional power required: 2.25 kWₑ

Fluid bed

- Biomass in: 1371 MJ/hr
- Condensate 1: 340 MJ/hr (25%)
- Condensate 2: 313 MJ/hr (23%)
- Condensate 3: 196 MJ/hr (14%)
- Bio-char: 109 MJ/hr (8%)
- Additional power required: 0.23 kWₑ

HHV basis
Process efficiency

\[ \eta_{th} = \left( \frac{Q_{\text{condensate}} + Q_{\text{char}}}{Q_{\text{feedstock}} + 2.86P} \right) \]

where \( Q \) is energies in the feedstock and products on HHV basis and \( P \) is the power input. Power input was converted to fuel equivalent assuming an efficiency of 35%.
A fast pyrolysis model representing major functional groups in bio-oil was developed and validated.

Each stage offers a distinct product quality. For ablative as well for fluid bed systems, model predicts separation of sugars and lignin in early stages with lignin captured in stage 1 and stage 2 condensates.

The 3rd stage heat recycle offers additional process efficiency gain by nearly 1% and 2.5% for ablative and for fluid bed respectively.
Summary and ongoing research

- Integration of commercially available portable ORC enhances prospects of small and mobile pyrolysis units for remote and small communities.
- Ongoing work involves experimental evaluation of condenser configurations in pilot scale ablative and fluid bed pyrolysis systems, detailed sensitivity and techno-economic analysis of staged condensation.
Acknowledgement

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Questions?

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