Biomass Torrefaction – A Promising Pretreatment Method for Thermo-Chemical Conversion Technologies

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Introduction

- **Issues with biomass feedstock**
  
  - Wide range of moisture content (60-15% wb)
  - Low bulk density (4 – 8 lbs/ft³)
  - Low energy density (4,500-7,500 Btu/lb)
  - Uneven particle sizes (no flow)
  - Difficult to handle, store and transport
  - High transport and storage cost
  - Self heating and emission of off gases during storage
Introduction

- Issues with thermo-chemical conversion technologies
  - **Combustion:**
    - Difficult to co-fire with coal
    - Low energy density
    - High energy demand for grinding biomass
  - **Gasification**
    - Tar formation
    - Low C/H ratio for liquid fuel production
  - **Pyrolysis:**
    - Bio-oil instability & coke formation
  - **Densification:**
    - Low energy density & self heating
Biomass Pyrolysis to Liquid Fuels

Critical Problems

- Long-term storage and stability of biomass
- High energy input for grinding to defined particle size
- Formation of high molecular weight compounds
- Bio-oil is unstable
  - Viscosity increases with time and temperature
  - Low pH, corrosive
- Catalytic upgrading difficult
  - High oxygen content
  - Catalytic deactivation due to coke formation
What is Torrefaction?

- **Solid-state thermal hydrolysis** of biomass in an inert atmosphere (e.g., N₂)
- Temperature range – 180 to 300°C
- **Hemicellulose is hydrolyzed** via release of acetic acid and subsequent hydrolysis reaction
- Moisture reduction, oxygen content reduced
- Some extractives volatilized, but 70-80% solids recovered
- Most familiar example – roasting coffee
Torrefaction History

- 1930’s – heat treatment of wood for high durability, structural stability & fungal resistance (wood roasting), provides aesthetic value
- 1939 – US Patent (Bergstrom et al) on thermal heating of wood >220°C
- 1976 – Pyrochar process for solid biomass into fuels
- 1980’s – heat treatment of wood logs (180-220°C), retifaction/torrefaction process (Yvan, 1985, Bourgeois et al, 1988), Torrefaction process development & reactor design (four patents)
- 2000 – Significant research & development on biomass torrefaction process
Mass & Energy Balance

Non-condensable: 
H₂, CO, CO₂, CH₄, Toluene, benzene

Condensable: 
Water
Organic acids, alcohols
Furans, ketones
Terpenes, phenols
Waxes, tannins, lipids

Volatile off gases

Torrefaction Process

External heat supply
Temp: 180-280°C
Heating rate: <50°C/min
Residence time: > mins

Biomass

Torrefied biomass

0.3 m ~0.2 E 0.7 m 0.9 E

1 m 1 E ~0.1 E
Research Objectives

- **Biomass Torrefaction kinetics**
  - Does it improve biomass storability and transportability?
  - Does it improve biomass grindability and reduce energy input?
  - **Effect of torrefaction on,**
    - bio-oil stability
    - Eliminate or reduce coke forming precursors and improve catalytic upgrading of bio-oil to fuels
    - Syngas quality and tar concentration during gasification
    - Pellet quality
    - Combustion behavior
Mass loss with time for a range of torrefaction conditions – TG-MS

The graph shows the percentage of mass remaining over time for different torrefaction conditions. The x-axis represents time in seconds, ranging from 0 to 8000. The y-axis represents the percentage of mass remaining, ranging from 0 to 100. Several curves are plotted, each corresponding to a different torrefaction temperature, labeled as 200, 215, 230, 245, 260, 275, and pyr. @ 700.
Proposed Torrefaction Kinetics Model

- Model equations:

For components a, b and c:

\[
a'(t) = -(k_1 + k_{v1})a(t), \quad a(0) = 1 \quad \text{(normalized vs. starting mass)}
\]

\[
b'(t) = k_1a(t) - (k_2 + k_{v2})b(t), \quad b(0) = 0
\]

\[
c'(t) = k_2b(t), \quad c(0) = 0
\]
Torrefaction Experiment

Torrefaction Reactor

Condensed liquids

Non-condensable gases

Torrefied biomass

Experiment 1.3.2 - Torrefaction - Pine Chips
30 minutes - 280°C - 30% Moisture

Forest Residue chips

Temperature (°C)

Time (minutes)

Experiment 1.3.2 - Torrefaction - Pine Chips
30 minutes - 280°C - 30% Moisture

0 0 5 1 0 5 1 2 0

0 5 0 5 2 5 0 2 5 5 0 2 5 0

0 5 0 5 2 5 0 2 5 5 0 2 5 0

0 5 0 5 2 5 0 2 5 5 0 2 5 0
Torrefied Auger Reactor - UGA

- Continuous Reactor
- Capacity – 5 to 10 kg/h
- Capability to collect condensable
- Non-condensables gases can be recalculated in the auger
Rotary drum reactor – UGA
(indirect heating)
Capacity = 400 lbs/run
Results – Torrefied biomass yield

Pine Chips 30 Minute run

Torrefied biomass yield (%)

- Red: 10% M.C.
- Green: 30% M.C.
- Blue: 50% M.C.

Temperature

220 250 280
Torrefaction of Pine Chips

Torrefaction Process
Torrefaction Results

- **GC/MS of Non-condensables (gas phase)**
  - Acetaldehyde, $\alpha$-pinene, $\beta$-pinene, camphene, phellandrene observed at low temperatures (220°C)
  - Acetaldehyde evolution increased with time
  - Pinenes decreased with holding time
  - As temperature increased, acetic acid, methylester and furans appeared (220 to 250°C and above)
    - Furan, 2-methylfuran, 250°C
    - 2,3-dihydrofuran and 2,5-dimethylfuran, 280°C
Results – Non-condensable at 280°C

Non-Condensables vs. Time; Torrefaction at 280°C

- Methane
- Carbon dioxide
- Methyl acetylene
- Propylene
- n-Butane
- Ethylene
- Ethane

Time (min)
Results – Condensable at 280°C

Condensables vs. Time; Torrefaction - 280°C

- α-pinene
- camphene
- β-pinene
- β-phellandrene

Relative Abundance vs. Time (min)
### Results – Compositional changes

<table>
<thead>
<tr>
<th>Forest residue chips</th>
<th>Cellulose (% wt)</th>
<th>Hemi-cellulose (% wt)</th>
<th>Lignin (% wt)</th>
<th>Heating value (Btu/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-torrefied (10% m.c.)</td>
<td>43.1</td>
<td>18.4</td>
<td>20.9</td>
<td>7,774</td>
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<tr>
<td>Torrefied at 220°C</td>
<td>40.7</td>
<td>12.0</td>
<td>25.1</td>
<td>8,474</td>
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<td>Torrefied at 250°C</td>
<td>37.3</td>
<td>5.0</td>
<td>31.8</td>
<td>9,376</td>
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<td>Torrefied at 280°C</td>
<td>20.6</td>
<td>2.9</td>
<td>47.3</td>
<td>10,167</td>
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</table>

<table>
<thead>
<tr>
<th>Forest residue chips</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>Ash (% wt)</th>
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<tbody>
<tr>
<td>Non-torrefied (10% m.c.)</td>
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<td>5.9</td>
<td>48.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.6</td>
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<td>Torrefied at 220°C</td>
<td>49.4</td>
<td>5.5</td>
<td>44.1</td>
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<td>0.0</td>
<td>1.1</td>
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<td>50.5</td>
<td>5.4</td>
<td>41.8</td>
<td>0.4</td>
<td>0.0</td>
<td>1.2</td>
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<tr>
<td>Torrefied at 280°C</td>
<td>56.4</td>
<td>5.4</td>
<td>36.1</td>
<td>0.9</td>
<td>0.1</td>
<td>1.4</td>
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</table>
### Results – Compositional changes

<table>
<thead>
<tr>
<th>Forest residue chips</th>
<th>Moisture (%)</th>
<th>Volatile C (% wt)</th>
<th>Fixed C (% wt)</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-torrefied (10% m.c.)</td>
<td>10</td>
<td>75.3</td>
<td>16.3</td>
<td>0.4</td>
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<td>Torrefied at 220°C</td>
<td>3.2</td>
<td>76.8</td>
<td>19.1</td>
<td>1.1</td>
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<td>Torrefied at 250°C</td>
<td>2.3</td>
<td>74.9</td>
<td>20.6</td>
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<td>Torrefied at 280°C</td>
<td>2.1</td>
<td>70.8</td>
<td>25.6</td>
<td>1.4</td>
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</table>
Change in bulk density during Torrefaction

Bulk density, kg/m^3

Torrefaction temperature °C

220 250 280

179.51 160.43 152.13

Forest biomass chips – 18% change
Improved Pelletizing Process

Raw material → Drying process → Torrefaction → Pelletization → High quality Pellets

Grinding → Pelletization
Effect of Torrefaction on Pellet Density

![Graph showing the effect of torrefaction on pellet density. The x-axis represents applied forces in Newtons (N) ranging from 0 to 8000, and the y-axis represents pellet density in kg/m³ ranging from 600 to 1200. Four lines represent different conditions: Control, 220, 250, and 280. Each line shows an increase in pellet density with increasing applied forces.](image-url)
Torrefaction - Pellet Production Cost

- **Packing cost**
  - $40

- **Land use & building**
  - $27
  - $24

- **Personnel cost**
  - $30

- **Miscellaneous equipment**
  - $6.45

- **Pellet cooler**
  - $0

- **Pellet mill**
  - $0

- **Hammer mill**
  - $0

- **Screening**
  - $0

- **Torrefaction**
  - $0

- **Drying operation**
  - $0
Torrefaction - Pyrolysis
TG/MS Analysis of Torrefied Biomass

- TGA/MS (Mettler Toledo)
- Performed under pyrolytic conditions – N₂ or Ar carrier gas
- 10mg sample, 50 ml/min, 30-900°C at 10°C/min
- Monitored Off Gas in Selective Ion Mode (SIM)

• Non-condensables, CO-28, CO₂-44, H₂-2, H₂O-18
• Potential tar compounds,
  - Benzene – 78
  - Guaiacol – 124
  - Naphthalene – 128
  - Phenol – 94
• Potential hemicellulose breakdown products
  - Acetaldehyde – 29
  - Acetic acid – 60
  - Acetol – 45
Effect of Torrefaction on Pyrolysis Kinetics (TGA Analysis)

- $X$, fractional biomass conversion
- Higher temperature torrefaction (> 300°C) appears to reduce biomass thermal decomposition and alter pyrolysis kinetics
- More research needed to confirm effect
## Torrefaction-Pyrolysis-Solids Properties

- Oxygen content reduced
- Fixed carbon increased

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>PP BM</th>
<th>PP T250</th>
<th>PP T300</th>
<th>PP T350</th>
<th>PP P500</th>
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<td>Volatiles</td>
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<td>Ash</td>
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<td>2.8</td>
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<td>Fixed Carbon</td>
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<td>25.8</td>
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<td>64.9</td>
<td>69.1</td>
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<td>HHV (MJ/kg)</td>
<td>20.6</td>
<td>20.9</td>
<td>28.8</td>
<td>29.7</td>
<td>31.0</td>
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<td>Bio-Oil Characteristics</td>
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<tr>
<td></td>
<td>Pa^a</td>
<td>PU^b</td>
<td>TP^c</td>
<td>TPU^d</td>
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<td>Ultimate analysis (wt % dry)</td>
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<td>C</td>
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<td>0.19</td>
<td>0.17</td>
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<td>S</td>
<td>0.05</td>
<td>0.0</td>
<td>0.01</td>
<td>0.02</td>
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<td>Oe</td>
<td>22.0</td>
<td>18.4</td>
<td>20.5</td>
<td>18.0</td>
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<tr>
<td>HHV (MJ/kg, wet basis)</td>
<td>29.1</td>
<td>30.9</td>
<td>28.6</td>
<td>30.7</td>
<td></td>
</tr>
<tr>
<td>H2O (wt. %)</td>
<td>2.4</td>
<td>4.0</td>
<td>9.3</td>
<td>6.7</td>
<td></td>
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<tr>
<td>pH</td>
<td>3.1</td>
<td>3.2</td>
<td>3.7</td>
<td>3.5</td>
<td></td>
</tr>
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</table>

^aP: Pyrolysis (catalytic upgrading feedstock, no torrefaction)

^bPU: Pyrolysis + catalytic Upgrading (no torrefaction)

^cTP: Torrefaction + Pyrolysis (catalytic upgrading feedstock)

^dTPU: Torrefaction + Pyrolysis + catalytic Upgrading
Torrefaction - Combustion
Torrefaction reactor integrated with power plant

- Air
  - Cryogenic air separation system
  - Nitrogen gas supply
  - Oxygen supply to the combustion system

- Biomass
  - Volatiles
  - Exhaust gas from the boiler
  - Minimal fly ash
  - Grinder

- Power boiler with combustor
  - Ash used as a fertilizer

- Torrefied biomass
  - Steam turbine and power generation
Comparison of combustion of torrefied biomass, untreated biomass and coal
Conclusions

- Condensable compounds are mainly released from extractives in the biomass as α, β-pinene, camphene etc. These compounds can be redirected to supply heat energy during torrefaction.

- During torrefaction, hemi-cellulose is almost removed and results in higher energy density product with a heating value of 10,000 Btu/lb. Torrefaction temperature plays a major role in defining the energy density of biomass and can be optimized for any specific applications.

- Torrefaction followed by pelleting costs about $30/t of pellets. Torrefaction process alone costs about $6.5/t.
Conclusions

- Biomass torrefaction process can produce high energy density and consistent feedstock for thermal conversion technologies (gasification, co-firing & pyrolysis)
- Pelleting of Torrefaction of biomass may be difficult due to hydrophobic nature of the material and require additional binders to increase the bulk density
- Future research at UGA is focused on optimizing the best reactor configuration for a torrefaction process and promote its application to co-firing, gasification and pyrolysis processes
Acknowledgement

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  - University of Georgia Research Foundation
  - State of Georgia – Traditional Industries Program
  - Georgia Power – Southern Company
Thank you

Densification
Direct combustion
Gasification
Co-firing with coal

Biocoal

Biomass Torrefaction Technology