Lignocellulosic waste valorization by hydrothermal carbonization and anaerobic digestion

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Background

2.2 \cdot 10^8 \text{ t MSW year}^{-1}

\approx 10\% \text{ lignocellulosic biomass}

47\% \text{ composting and recycling}

28\% \text{ energy valorization}

25\% \text{ landfill}
Background

Urban pruning waste

Energy resource

Industrial level

Home level
Urban pruning waste

Energy resource

Industrial level

Home level
Hydrothermal carbonization (HTC)

$T = 180 - 250 \, ^{\circ}C$
$t = 5 - 240 \, \text{min}$

Autogenerated pressure

Hydrochar

Energy production

Hydrochar

Biogas

$\text{CH}_4$

Process water

$\text{H}_2\text{O}$

$\text{CO}_2 + \text{CH}_4$

Struvite
Hydrothermal carbonization (HTC)

Biomass → Bio-solid → Hydrolysis → Lignin Monomers → Dehydration → Decarboxylation → CO₂, H₂O → Gas → Process water → Condensation, Aromatization, Polymerization → Maillard’s reactions → Hydrochar
Objective

HTC

$T = 180 - 210 - 230 \, ^\circ C$
$t = 60 \, \text{min}$

Electrical energy

HTC + AD

Thermal energy

Agro-industrial residues

Municipal pruning waste

Forest residues

Water

Hydrochar Process

Municipal pruning waste

HTC + AD
Characterization of urban pruning waste (UPW)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>UPW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)</td>
<td>4.8 ± 0.2</td>
</tr>
<tr>
<td>C (%)</td>
<td>46.9 ± 1.1</td>
</tr>
<tr>
<td>H (%)</td>
<td>6.1 ± 0.4</td>
</tr>
<tr>
<td>N (%)</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>S (%)</td>
<td>0.4 ± 0.2 X</td>
</tr>
<tr>
<td>O* (%)</td>
<td>40.6 ± 0.1</td>
</tr>
<tr>
<td>Volatile matter (d.b.%)</td>
<td>76.5 ± 0.1 X</td>
</tr>
<tr>
<td>Ash (d.b.%)</td>
<td>5.1 ± 0.1</td>
</tr>
<tr>
<td>Fixed carbon (d.b.%)</td>
<td>18.4 ± 0.1</td>
</tr>
<tr>
<td>HHV (MJ kg⁻¹)</td>
<td>19.7 ± 0.1</td>
</tr>
<tr>
<td>H/C</td>
<td>1.55</td>
</tr>
<tr>
<td>O/C</td>
<td>0.65</td>
</tr>
<tr>
<td>NPK</td>
<td>0.9/0.1/0.5</td>
</tr>
</tbody>
</table>
**Methods**

Urban Pruning Waste (UPW)

\[ T = 180 - 210 - 230 \, ^\circ C \]
\[ t = 60 \, \text{min} \]

\[ \text{UPW (20\% weight)} + \text{H}_2\text{O (80\% weight)} \]

Hydrochar (HC)

HC180, HC210, HC 230

Process water (PW)

PW180, PW210, PW 230
Results
8th International Conference on Sustainable Solid Waste Management

HHV > 17 MJ kg⁻¹
Nitrogen < 3%
Sulfur < 0.5%
Volatile matter < 75%
Nitrogen and Sulfur content

% N  % S
Limit %N  Limit %S

17  25

Graded thermally treated and densified biomass fuels

8th International Conference on Sustainable Solid Waste Management

Nitrogen and Sulfur content

HHV > 17 MJ kg⁻¹
Nitrogen < 2%
Sulfur < 0.3%
Volatile matter < 75%

UPW HC180 HC210 HC230

✓ ✓ ✓ ✓
Proximal analysis

- Fixed Carbon
- Volatile Matter
- Ash
- Limit VM (%)

Graph showing the proximal analysis of different biomass fuels:

- **UPW**
  - HHV > 17 MJ kg⁻¹
  - Nitrogen < 2%
  - Sulfur < 0.3%
  - Volatile matter > 75%

- **HC180**
  - HHV > 17 MJ kg⁻¹
  - Nitrogen < 2%
  - Sulfur < 0.3%
  - Volatile matter > 75%

- **HC210**
  - HHV > 17 MJ kg⁻¹
  - Nitrogen < 2%
  - Sulfur < 0.3%
  - Volatile matter > 75%

- **HC230**
  - HHV > 17 MJ kg⁻¹
  - Nitrogen < 2%
  - Sulfur < 0.3%
  - Volatile matter > 75%
Proximal analysis

Ash content
- 5 – 35%
  - SI < 0.3 Low
  - FI < 4 Medium
  - AI < 0.2 Low

<table>
<thead>
<tr>
<th></th>
<th>UPW</th>
<th>HC180</th>
<th>HC210</th>
<th>HC230</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_b/a</td>
<td>1.3</td>
<td>1.0</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>SI</td>
<td>0.53</td>
<td>0.16</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>FI</td>
<td>7.47</td>
<td>3.08</td>
<td>2.56</td>
<td>2.08</td>
</tr>
<tr>
<td>AI (kg GJ⁻¹)</td>
<td>0.30</td>
<td>0.09</td>
<td>0.07</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Proximal analysis

- Fixed Carbon
- Volatile Matter
- Ash
- Limit VM (%)

Graph showing proximal analysis for UPW, HC180, HC210, and HC230.
Thermogravimetric and differential TG profiles

**Loss of moisture and light volatile compounds**

- **< 100 °C**

**Devolatization of VM, cellulose and hemicellulose**

- **240 – 320 °C**

**Combustion of high molecular weight compounds, lignin and FC**

- **420 – 440 °C**

**Inorganic matter decomposition like carbonates**

- **760 – 780 °C**
Thermogravimetric and differential TG profiles

<table>
<thead>
<tr>
<th></th>
<th>UPW</th>
<th>HC180</th>
<th>HC210</th>
<th>HC230</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_i$ ($^\circ$C)</td>
<td>239</td>
<td>242</td>
<td>251</td>
<td>254</td>
</tr>
<tr>
<td>$T_m$ ($^\circ$C)</td>
<td>326</td>
<td>325</td>
<td>318</td>
<td>313</td>
</tr>
<tr>
<td>$T_h$ ($^\circ$C)</td>
<td>533</td>
<td>528</td>
<td>528</td>
<td>536</td>
</tr>
<tr>
<td>$CCI \cdot 10^{-7}$ ($\text{min}^{-2} \cdot ^\circ\text{C}^{-3}$)</td>
<td>7.8</td>
<td>8.0</td>
<td>8.4</td>
<td>9.6</td>
</tr>
<tr>
<td>$Z_i$ ($% \text{ min}^3$)</td>
<td>8.6</td>
<td>10.6</td>
<td>11.4</td>
<td>11.6</td>
</tr>
<tr>
<td>$H_i$ ($% \text{ min}^4$)</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>
## Process water characterization

### Process water characteristics

<table>
<thead>
<tr>
<th></th>
<th>PW180</th>
<th>PW210</th>
<th>PW230</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH</strong></td>
<td>3.5 ± 0.1</td>
<td>3.4 ± 0.1</td>
<td>3.5 ± 0.1</td>
</tr>
<tr>
<td><strong>COD (g L⁻¹)</strong></td>
<td>51.1 ± 1.3</td>
<td>39.3 ± 0.5</td>
<td>44.9 ± 2.4</td>
</tr>
<tr>
<td><strong>TOC (g L⁻¹)</strong></td>
<td>21.1 ± 0.1</td>
<td>17.0 ± 0.1</td>
<td>18.4 ± 0.1</td>
</tr>
<tr>
<td><strong>TVFA (g L⁻¹)</strong></td>
<td>1.5 ± 0.0</td>
<td>0.9 ± 0.0</td>
<td>0.2 ± 0.0</td>
</tr>
<tr>
<td><strong>TS (g L⁻¹)</strong></td>
<td>30.7 ± 0.3</td>
<td>19.3 ± 0.3</td>
<td>21.6 ± 0.4</td>
</tr>
<tr>
<td><strong>VS (g L⁻¹)</strong></td>
<td>27.0 ± 0.4</td>
<td>16.1 ± 0.2</td>
<td>18.5 ± 0.3</td>
</tr>
</tbody>
</table>

### Biochemical methane potential

- ISR = 2
- 15 g VS L⁻¹ granular anaerobic sludge
- 7.5 g VS L⁻¹ substrate

![Biogas analysis](image1)

- Vials to be sacrificed
- Positive controls
- Blanks

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Biochemical methane potential

- pH (7.5 – 7.8)
- Alkalinity (> 2.5 g CaCO₃ L⁻¹)
- Total ammonia nitrogen (1700 mg L⁻¹ < inhibition values)

Adequate for the AD process

Soluble chemical oxygen demand (SCOD)

Volatile fatty acids (VFA)

SCOD (g O₂ L⁻¹)

Time (d)

TVFA (mg acetic acid L⁻¹)

Time (d)

Removal 64%

Removal 73%

Removal 25%
Biochemical methane potential

- **Propionic inhibition > 900 mg**

- **a) PW180**
- **b) PW210**
- **c) PW230**
Biochemical methane potential

Cumulative methane yield

Cumulative methane yield
(mL CH\textsubscript{4} STP g\textsuperscript{-1} COD\textsubscript{added})

Time (d)

- PW180-Firts order eq.
- PW210-M. Gompertz eq.
- PW230-M. Gompertz eq.
- UPW

326 mL CH\textsubscript{4} g\textsuperscript{-1} VS
269 mL CH\textsubscript{4} g\textsuperscript{-1} VS
253 mL CH\textsubscript{4} g\textsuperscript{-1} VS
76 mL CH\textsubscript{4} g\textsuperscript{-1} VS
Biochemical methane potential

a) PW180

- Alkyl chain
- Non-Aromatic
- Aromatics
- N-Aromatics
- Pyridines
- Pyrazines

Normalized Composition (% Peak area)

b) PW210

- Alkyl chain
- Non-Aromatic
- Aromatics
- N-Aromatics
- Pyridines
- Pyrazines

Normalized Composition (% Peak area)

c) PW230

- Alkyl chain
- Non-Aromatic
- Aromatics
- N-Aromatics
- Pyridines
- Pyrazines

Normalized Composition (% Peak area)
Energy synergy

Energy recovery

HC + CH₄

Energy Produced (MJ kg⁻¹ Feedstock)

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy Produced (MJ kg⁻¹ Feedstock)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>14</td>
</tr>
<tr>
<td>(HC+PW)180</td>
<td>94</td>
</tr>
<tr>
<td>(HC+PW)210</td>
<td>91</td>
</tr>
<tr>
<td>(HC+PW)230</td>
<td>94</td>
</tr>
</tbody>
</table>

Energy recovery (%)

- HC Combustion
- AD
- Energy recovery
HTC + AD process

- UPW + Water (20:80 w:w)
- Hydrothermal carbonization
- Filter press
- Shurry
- Wet Hydrochar
- Biogas
- Compressor
- Biogas tank
- Anaerobic digestion
- Digestate
- Process water
- Pump
- Bioas gas chamber
- Air
- Condenser
- LST
- HST
- Energy
- Boiler HC
- Ash
# Energy balance

<table>
<thead>
<tr>
<th>HTC reactor</th>
<th>Dewatering</th>
<th>Thermal dry</th>
<th>Pelletizer</th>
<th>Pump</th>
<th>Total input</th>
<th>Energy HC</th>
<th>Energy CH₄</th>
<th>Total output</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTC180</td>
<td>364</td>
<td>8</td>
<td>82</td>
<td>9</td>
<td>7</td>
<td>469</td>
<td>1008</td>
<td>97</td>
<td>1086</td>
</tr>
<tr>
<td>HTC210</td>
<td>505</td>
<td>9</td>
<td>65</td>
<td>7</td>
<td>13</td>
<td>599</td>
<td>921</td>
<td>128</td>
<td>1048</td>
</tr>
<tr>
<td>HTC230</td>
<td>462</td>
<td>9</td>
<td>63</td>
<td>7</td>
<td>14</td>
<td>555</td>
<td>930</td>
<td>152</td>
<td>1082</td>
</tr>
</tbody>
</table>
Conclusions

- Hydrochar
  - Higher energy densification
  - Better physical and chemical properties
  - Higher combustion reactivity and behavior
  - Fulfill the requirements for energy production at industrial level

- Process water
  - Higher organic carbon content
  - Higher methane potential yield
  - Higher organic removal in PW at lower temperatures

- Anaerobic digestion
Conclusions

According to the circular economy approach, strong synergy is achieved between the productive sector, raw material, and transformation processes. Hydrothermal carbonization leads to energy self-sustainability and the creation of new products, aligning with the principles of a bioeconomy and biorefinery within a circular economy.
Acknowledgements

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“Nothing is impossible for the person who fights”

R. P. Ipiales