Integration of hydrothermal processes for fuels and hydrogen production from digestates

Marco Baratieri
Introduction

In Europe, Directives 2016/2284/EU and 91/676/EEC regulate the distribution of digestate on agricultural land, limiting the intake of N to 170 kg ha\(^{-1}\) year\(^{-1}\).

- Water pollution: nitrate and nutrients leach into the groundwater causing eutrophication and hypoxia
- Air pollution: ammonia volatilization
- Very high water-content and residual biological activity management issues
- Negative economic and environmental impacts
Introduction

**Pre-treatment step to decrease the moisture content**

- Landfilling
- Composting
- Incineration

- Long times
- Bad odor
- GHGs emissions
- Land availability

**HTC**
Hydrothermal Carbonization - HTC

(Pre)treatment of biomass in hot (180-250 °C) compressed water at residence times varying from minutes to several hours. Ideal for biomass with high moisture content (> 60 %).
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Materials and Methods

Digestate

- 2.5 kg per experiment
- Previously kept in refrigerator at 4 °C
- No pre-treatment

<table>
<thead>
<tr>
<th>Digestate</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash content [%wt]</td>
<td>26.83</td>
<td></td>
</tr>
<tr>
<td>C [%wt]</td>
<td>39.11</td>
<td></td>
</tr>
<tr>
<td>H [%wt]</td>
<td>4.87</td>
<td></td>
</tr>
<tr>
<td>O [%wt]</td>
<td>26.56</td>
<td></td>
</tr>
<tr>
<td>N [%wt]</td>
<td>1.94</td>
<td></td>
</tr>
<tr>
<td>S [%wt]</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>HHV [MJ/kg]</td>
<td>14.31</td>
<td></td>
</tr>
<tr>
<td>LHV [MJ/kg]</td>
<td>13.24</td>
<td></td>
</tr>
</tbody>
</table>
Materials and Methods

Batch reactor – 4 L

Hydrochar – oven-dried at 105 °C for 24 h

Aqueous HTC Liquid

Scheme of the experimental lay-out

1. Electric furnace
2. HTC reactor
3. Temperature controller
4. HTC controller
5. Pressure transducer
6. Cold trap
7. Safety valve
8. Manometer

Operating condition

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Experimental range</th>
</tr>
</thead>
<tbody>
<tr>
<td>digestate</td>
<td>180 220 250</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>endogenous</td>
</tr>
<tr>
<td>Pressure</td>
<td>3</td>
</tr>
<tr>
<td>Residence time [h]</td>
<td>3</td>
</tr>
<tr>
<td>Repetitions</td>
<td>3</td>
</tr>
</tbody>
</table>
Hydrothermal Carbonization - HTC

(Pre)treatment of biomass in hot (180-250 °C) compressed water at residence times varying from minutes to several hours. Ideal for biomass with high moisture content (> 60 %).
# HC characterization results

<table>
<thead>
<tr>
<th></th>
<th>Digestate</th>
<th>HC180</th>
<th>HC220</th>
<th>HC250</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volatile matter</strong></td>
<td>%wt$_{\text{dry}}$</td>
<td>55 ± 1</td>
<td>55 ± 1</td>
<td>53 ± 1</td>
</tr>
<tr>
<td><strong>Fixed carbon</strong></td>
<td>%wt$_{\text{dry}}$</td>
<td>18 ± 1</td>
<td>17.9 ± 0.3</td>
<td>18.5 ± 0.4</td>
</tr>
<tr>
<td><strong>Ash</strong></td>
<td>%wt$_{\text{dry}}$</td>
<td>26.6 ± 0.5</td>
<td>27.2 ± 0.8</td>
<td>28.8 ± 0.8</td>
</tr>
<tr>
<td><strong>Fuel ratio</strong></td>
<td>-</td>
<td>0.33</td>
<td>0.33</td>
<td>0.34</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>%wt$_{\text{dry}}$</td>
<td>39.1 ± 0.5</td>
<td>40.1 ± 1.6</td>
<td>42.5 ± 0.8</td>
</tr>
<tr>
<td><strong>H</strong></td>
<td>%wt$_{\text{dry}}$</td>
<td>4.87 ± 0.05</td>
<td>5.01 ± 0.11</td>
<td>4.92 ± 0.15</td>
</tr>
<tr>
<td><strong>N</strong></td>
<td>%wt$_{\text{dry}}$</td>
<td>1.94 ± 0.09</td>
<td>2.03 ± 0.06</td>
<td>2.16 ± 0.03</td>
</tr>
<tr>
<td><strong>S</strong></td>
<td>%wt$_{\text{dry}}$</td>
<td>0.68 ± 0.03</td>
<td>0.71 ± 0.05</td>
<td>0.62 ± 0.01</td>
</tr>
<tr>
<td><em><em>O</em>%</em>*</td>
<td>%wt$_{\text{dry}}$</td>
<td>26.56</td>
<td>24.09</td>
<td>19.71</td>
</tr>
<tr>
<td><strong>HHV</strong></td>
<td>MJ/kg</td>
<td>14.3 ± 0.5</td>
<td>15.9 ± 0.1</td>
<td>16.9 ± 0.2</td>
</tr>
</tbody>
</table>

Benedetti et al., Combustion kinetics of hydrochar from cow-manure digestate via thermogravimetric analysis and peak deconvolution, Bioresource Technology 353 (2022) 127142
HC characterization results

Van Krevelen Diagram

*decarboxylation and dehydration* reactions occur during the HTC process
HC characterization

Thermogravimetric analysis

- T: 40 - 900 °C
- Ramp rate (β): 5, 10, 20, 40 °C min⁻¹
- Purge gas: air, 20 mL min⁻¹
- Protective gas: N₂, 20 mL min⁻¹
- Replicates: 3

Combustion kinetics

Kissenger-Akahira-Sunose (KAS) method

\[
\ln \left( \frac{\beta}{T_{\alpha}^2} \right) = \ln \left( \frac{A E_\alpha}{R g(\alpha)} \right) - \frac{E_\alpha}{R T_{\alpha}}
\]

\[
\alpha = \frac{m_i - m_t}{m_i - m_f}
\]

Benedetti et al., Combustion kinetics of hydrochar from cow-manure digestate via thermogravimetric analysis and peak deconvolution, Bioresource Technology 353 (2022) 127142
TG – DTG curves

Four main peaks:

1. 290°C - Devolatilization
2. 370°C - Combustion
3. 450°C - Char combustion
4. 630°C - Secondary degradation reactions

Residual mass higher for HC obtained at higher T

Benedetti et al., Combustion kinetics of hydrochar from cow-manure digestate via thermogravimetric analysis and peak deconvolution, Bioresource Technology 353 (2022) 127142
Isoconversional curves – KAS method

Results

<table>
<thead>
<tr>
<th>R²</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC 180°C</td>
<td>0.9979</td>
<td>0.9990</td>
<td>0.9960</td>
<td>0.9877</td>
<td>0.9533</td>
<td>0.8989</td>
<td>0.8262</td>
<td>0.7985</td>
<td>0.5708</td>
</tr>
<tr>
<td>HC 220°C</td>
<td>0.9989</td>
<td>0.9985</td>
<td>0.9991</td>
<td>0.9874</td>
<td>0.9723</td>
<td>0.9439</td>
<td>0.9149</td>
<td>0.8620</td>
<td>0.7564</td>
</tr>
<tr>
<td>HC 250°C</td>
<td>0.9577</td>
<td>0.9968</td>
<td>0.9874</td>
<td>0.9684</td>
<td>0.9379</td>
<td>0.9052</td>
<td>0.8709</td>
<td>0.8196</td>
<td>0.7453</td>
</tr>
</tbody>
</table>

Benedetti et al., Combustion kinetics of hydrochar from cow-manure digestate via thermogravimetric analysis and peak deconvolution, Bioresource Technology 353 (2022) 127142
Activation energy

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_a$ average [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC 180°C</td>
<td>100</td>
</tr>
<tr>
<td>HC 220°C</td>
<td>88</td>
</tr>
<tr>
<td>HC 250°C</td>
<td>67</td>
</tr>
</tbody>
</table>

Benedetti et al., Combustion kinetics of hydrochar from cow-manure digestate via thermogravimetric analysis and peak deconvolution, Bioresource Technology 353 (2022) 127142
Hydrothermal Carbonization - HTC

(Pre)treatment of biomass in hot (180-250 °C) compressed water at residence times varying from minutes to several hours. Ideal for biomass with high moisture content (> 60 %).
AHL characterization

Characterization

AHL

Valorization
AHL characterization

TOC analysis

Semi-continuous analysis
Spillages every 30 min during operation

HPLC analysis
- Glucose
- Lactic, Formic, Acetic, Fumaric Acid
- Hydroxymethylfurfural (HMF), Furfural

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHL 180 °C</td>
<td>[g/L] 7.07</td>
</tr>
<tr>
<td>AHL 220 °C</td>
<td>[g/L] 7.43</td>
</tr>
<tr>
<td>AHL 250 °C</td>
<td>[g/L] 7.89</td>
</tr>
</tbody>
</table>
• Increased rate of hydrolysis, decarboxylation and dehydration that become the governing reactions of the process.
• Sugars, HMF and furfurals are less stable at high temperature and residence time.
• Polymerization and formation of secondary char.
AHL valorization

AIM
- Obtain valuable gaseous product rich in $H_2$
- Minimize the waste, gasifying organic matter
Supercritical water gasification: SCWG

Hydrothermal process

• Alternative to conventional gasification and anaerobic digestion
• No need for pre-drying
• High temperature and pressure, low residence time
• Water in supercritical conditions becomes a very aggressive medium (and reactant)

Source: Yakaboylu et al., Supercritical water gasification of biomass

Drop in density
Decrease of dielectric constant
Decrease in viscosity
Materials and methods

Feedstock | Temperature | Pressure | Residence time | Flow rate
---| ---| ---| ---| ---
AHL 180 °C | 500 | 550 | 25 | 8.0
| | 600 | 25 | 30 | 7.0
| | | 550 | 7.0 | 6.3
AHL 220 °C | 500 | 550 | 25 | 8.0
| | 600 | 25 | 30 | 7.0
| | | 550 | 6.3 | 6.3
AHL 250 °C | 500 | 550 | 25 | 8.0
| | 600 | 25 | 30 | 7.0
| | | 550 | 6.3 | 6.3

1. Water
2. Pump
3. Feeding system
4. Pre-heater
5. Temperature controller
6. Furnace
7. Heat exchanger
8. Cooling system
9. Filter
10. Ball valve
11. Back pressure regulator
12. Sampling port

SCWG

- CHAR
- TAR
- LIQUID
- GAS
Effect of Temperature

Gas composition

- No differences among AHLs
- Gas generation rate increases with T
- $H_2$ % increases with T
  (other main gases: $CO_2$, $CH_4$)

Taufeer et al., Coupling hydrothermal carbonization of digestate and supercritical water gasification of liquid products, Renewable Energy 173 (2021) 934-941
Effect of Temperature

Carbon balance

- SCWG 500: most of the carbon is in the liquid phase
- SCWG 600: most of the carbon is in the gas phase
- Amount of organic matter gasified increases with temperature

Tauf er et al., Coupling hydrothermal carbonization of digestate and supercritical water gasification of liquid products, Renewable Energy 173 (2021) 934-941
Effect of Residence Time

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Residence time</th>
<th>Flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHL 220 °C</td>
<td>600 MPa</td>
<td>25 s</td>
<td>15 s</td>
<td>12.5 mL/min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30 s</td>
<td>6.3 mL/min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60 s</td>
<td>3.1 mL/min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>90 s</td>
<td>2.1 mL/min</td>
</tr>
</tbody>
</table>

- Minor effect of residence time
- $\text{H}_2$ % max at 30 s
- C yield % in the gas phase max at 15 s

Tauler et al., Coupling hydrothermal carbonization of digestate and supercritical water gasification of liquid products, Renewable Energy 173 (2021) 934-941
Effect of Feedstock Concentration

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Residence time</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHL 180 °C</td>
<td>600 [°C]</td>
<td>25 [MPa]</td>
<td>30 [s]</td>
<td>6.7 [%]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.6 [%]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.0 [%]</td>
</tr>
</tbody>
</table>

• CO₂ % and CH₄ % increases
• H₂ % decreases (from 80 to 60%)
• Carbon yield not affected

Taufer et al., Coupling hydrothermal carbonization of digestate and supercritical water gasification of liquid products, Renewable Energy 173 (2021) 934-941
Carbon Balance

Results

[ HTC @ 180 °C / 3 h ] + [ SCWG @ 600 °C / 30 s ]

- HC: most of C retained (72%)  
- AHL: 50% of C is gasified / 30% in liquid phase

Taufer et al., Coupling hydrothermal carbonization of digestate and supercritical water gasification of liquid products, Renewable Energy 173 (2021) 934-941
- Hydrothermal carbonization (HTC) effectively treated digestate to produce hydrochar

- An HTC temperature of 250 °C converts the low-temperature volatiles to more stable compounds, producing a better fuel compared to 180 and 220 °C. This is supported by the high apparent activation energy at low conversions for HC250, but a lower apparent activation energy afterwards.

- Semi-continuous analysis of HTC liquids showed the presence of bio-inhibiting compounds

- Coupling with super-critical water gasification (SCWG) was possible, yielding a gas rich in $H_2$

- SCWG showed optimal results for operation at 600 °C and 30 s residence time

- Up to 50% of the carbon in the HTC liquids was valorised
People

- Vittoria BENEDETTI
- Francesco PATUZZI
- Matteo PECCHI
- Noah Luciano TAUFER

Prof. Yukihiro MATSUMURA

Eng. Daniele BASSO

https://www.hbigroup.it/hb-ponics/
Thank you for your attention

Integration of hydrothermal processes for fuels and hydrogen production from digestates

E-mail: marco.baratieri@unibz.it
Website: https://bnb.groups.unibz.it/