Hydrothermal Carbonization: A Thermochemical Pathway to Convert Wastes to Conversion-ready Feedstocks

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BETO Workshop
Advancing the Bioeconomy: From Waste to Conversion-Ready Feedstocks
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"Organic waste" is:
- food waste
- green waste
- pruning waste
- wood waste
- food-soiled paper waste mixed in with food waste

Heterogeneity of MSW Example: California

- Organic: 48.6%
- Inerts and others: 11.2%
- HHW: 0.3%
- Special Waste: 1.5%
- Mixed Residue: 2.5%
- Paper: 19.6%
- Glass: 2.4%
- Metal: 4.0%
- Plastics: 9.20%
- Electronics: 0.70%

Problems associated with MSW

1. Heterogeneous
2. High water content
3. Poor mechanical dewaterability
4. High ash content
5. Low bulk density
6. Low friability
7. Contaminated with organic and inorganic contaminants

Preprocessing of diverse biomass concept proposed by INL
Sorting/Metal Recovery
Materials Recovery

• More than 300 facilities in the US
• Operated by Waste Management, Republican Services, and Waste connections
• Primarily designed for recycle metals and glass
• Organic fraction of waste is still a liability
Feedstock (unsorted MSW) preparation

Size separated autoclave products

Biogenic fraction
MSW pulp (<3/8”)

Non-biogenic fraction
(1”+)
Comparison of Various Pretreatment Processes

- Energy Input (KWh t\(^{-1}\))
- Autoclave/thermal hydrolysis, grinding/mechanical, and microwave
- Grinding or physical homogenization takes lower energy for further enhancement
- Microwave is the most energy extensive route

Fan, Y.V.; et.al. J of Env Manag. 2018, 223, 888-897
Anaerobic Digestion
USDA pilot AD system

1500 gal high solids anaerobic digester
(20 % solids)

(MSW pulp) < 3/8”

Receiving slope

Reaction zone

Attached growth zone

Weir

back

front
VS content increases, NVS content decreases
Mass and H₂O balance

4689 lb wet pulp
- 1630 lb TS
- 1214 lb VS
- 473 lb cellulose
- 176 lb hemicellulose
- 406 lb sCOD
- 145 lb acid insoluble mat’l (i.e., lignin)
- 416 lb NVS
- 3059 lb H₂O (367 gal)

87 dry lb TS
- 63 lb VS
- 24 lb NVS
- 2440 lb H₂O (293 gal)

157,800 L CH₄

3144 lb wet digestate
- 825 lb TS
- 520 lb VS
- 77 lb cellulose
- 54 lb hemicellulose
- 80 lb dissolved solids
- 240 lb lignin
- 69 lb est. biomass/others
- 306 lb NVS
- 2319 lb H₂O (367 gal)

511 gal H₂O (4262 lbs)

817 gal H₂O (6814 lbs)

Anaerobic Digestion

Hydrothermal Carbonization
Hydrothermal Carbonization

- Hot compressed water (180 – 260 °C)
- Short contact time (< 20 min)
- High Pressure: vapor pressure of liquid water (1-5 MPa)

Biomass → Water $\xrightarrow{180-260\, ^\circ C}$ Gases → HTC process liquid → Hydrochar

Advantages of HTC

1. Wet process
2. Enhance homogenization
3. Decontaminate wastes
4. Non-catalytic process
5. Straightforward process
6. Hydrophobic hydrochar resulting in ease of filtering
7. Soil amendment, and production of NPK fertilizer

Hydrochars

(a) Raw dry MSW digestate
(b) HTC 250 °C 30 min MSW digestate hydrochar
(c) HTC 250 °C 2 h MSW digestate hydrochar
(d) HTC 300 °C 30 min MSW digestate hydrochar

(a) Raw dry MSW pulp
(b) HTC 250 °C 30 min MSW pulp hydrochar
(c) HTC 250 °C 2 h MSW pulp hydrochar
(d) HTC 300 °C 30 min MSW pulp hydrochar
Van-Krevelen Diagram

Reza, M.T. et al. ACS Sus Chem Engr, 2016, 4 (7), 3649-3658
Grindability

- Specific case for fibrous biomass
- HTC could improve grindability several times even when biomass is treated at 200 °C
Combustion Characteristics

Combustion mass loss curves and DTG curves for untreated and HTC treated samples at 230 ℃

Reza, M.T. et al. Waste and Biomass Valorization, under-review
Inorganics Leached From Biomass

Leaching of specific inorganic elements during MHP at different temperatures for corn stover (left) and switch grass (right). Note that inorganic elements present in raw biomass is considered as 100%.
Degradation of Organic Contaminants

Estradiol

Oxytetracycline

Saha, N. et al. SN Applied Science, under-review
Dewaterability and Hydrophobicity

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial dry matter (DM %)</th>
<th>After Centrifugation (DM%)</th>
<th>After Mechanical Pressing (DM %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sewage Sludge 1</td>
<td>30</td>
<td></td>
<td>37±0.5</td>
</tr>
<tr>
<td>Hydrochar_1_205_7</td>
<td>20</td>
<td>26</td>
<td>52±5.5</td>
</tr>
<tr>
<td>Sewage Sludge 2</td>
<td>10</td>
<td>21</td>
<td>30±1.4</td>
</tr>
<tr>
<td>Hydrochar_2_205_7</td>
<td>11</td>
<td>28</td>
<td>70±8.0</td>
</tr>
</tbody>
</table>

# Mass and Energy Densification

## Component Density Range (kg/m³) Typical value (kg/m³)

<table>
<thead>
<tr>
<th>Component</th>
<th>Density Range (kg/m³)</th>
<th>Typical value (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food waste</td>
<td>120-480</td>
<td>290</td>
</tr>
<tr>
<td>Paper</td>
<td>30-130</td>
<td>85</td>
</tr>
<tr>
<td>Glass</td>
<td>160-480</td>
<td>195</td>
</tr>
<tr>
<td>Metal</td>
<td>120-1200</td>
<td>320</td>
</tr>
<tr>
<td>Uncompact MSW</td>
<td>90-180</td>
<td>130</td>
</tr>
<tr>
<td>Truck Compact</td>
<td>180-450</td>
<td>300</td>
</tr>
<tr>
<td>Well Compact MSW</td>
<td>600-750</td>
<td>600</td>
</tr>
</tbody>
</table>

\[ \text{MD} = \frac{\text{weight of the pellet}}{\text{volume of the pellet}} \]

\[ \text{EY} = \text{MD of the pellet} \times \text{HHV of the pellet} \]

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https://slideplayer.com/slide/10213265/
Carbon Quantum Dots from HTC process liquid

A) CQDs under daylight; B) CQDs under UV light

• Graphene CQDs are $400-600 per liter with ~0.1% concentration (w/v)
• Global medical imaging market is $34.1 B in 2017
• Catalyst Market Size Expected To Reach $34.3 Billion By 2024
• The global optronics market will attain revenues of $5.05bn in 2015
Ongoing Research

NSF-INFEWS

Title: INFEWS/T2: Organic Waste Lifecycles at the Interface of Food, Energy and Water Systems (OWL-FEWs)

Collaborator and Lead: Ohio University
Ongoing Research

USDA-NIFA-AFRRI
Award no: 2019-67019-29288

Title: Development and Optimization of Mild Hydrothermal Preprocessing for High Ash Biomass into Pelletized Biorefinery Feedstocks

Collaborator: INL
Future Research

**EERE/BETO**

Title: Decontaminated Pelletized Biorefinery Feedstocks Processing from Non-recyclable Municipal Solid Waste

Collaborator: Universities, National Labs, and Industries
Conclusions

• MSW is heterogeneous, contains high moisture, inorganic and organic contaminants, and have low density

• Sorting/materials recovery/preprocessing will be required to separate recyclables from MSW

• Organic-rich fraction could be benefitted by hydrothermal carbonization as it will
  • Increase hydrophobicity
  • Enhance friability
  • Increase density
  • Reduce inorganic content on the solid phase
  • Decontaminate from emerging organic pollutants

• Future research will require to integrate HTC with other technologies (e.g., AD, air classification, pelletization) to produce a homogeneous and decontaminated feedstock for conversion processes
Acknowledgements

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Thank you.

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Initial Carbon:Ash Ratio should be greater than 10:1 for treatment to have a positive effect.
Mass% Carbon

Treatment Temperature (°C)

Hydrochar Carbon/Ash Ratio

Positive Effect

Negative Effect

Initial Carbon should be greater than 40 for treatment to have a positive effect.
HTC Process Liquid

- Dark in color
- OFMSW derived ones are acidic
- Digestate derived ones are slightly basic
- Have high TOC
- Strong odor
Reza Research Group

Core Research
- Deep Eutectic Solvents (DES)
- Hydrothermal Carbonization (HTC)

Personnel
- Graduate Students: 5
- Undergraduate students: 10

Funding agencies
- USDA-AFRI-Agricultural Wastes
- NSF-INFEWS- Food Waste
- ACS-PRF – Refinery waste

Diagram:
- Hydrothermal carbonization (HTC)
  - CO₂ gasification of biochar
- Hydrothermal upgrading of coal waste-biomass
- Carbon quantum dots synthesis from Ohio coal
- SO₂-CO₂ co-capture by deep eutectic solvents
- Produced water treatment by deep eutectic solvents
- FGD wastewater quality monitoring by ion selective electrodes
- Enhanced shale porosity by hydrothermal degradation
- Adsorption of BTX from aliphatics by deep eutectic solvents