Improvement of the physicochemical and combustion properties of hydrochars from hydrothermal carbonization of swine manure

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In the last 10 years the swine population increase ≈ 3% 150·10^6 heads in 2020

Spain, France, Germany, Denmark and Netherlands account for up to 60% of the total swine population.
Swine crisis: Swine manure management key to tackling climate change

18·10^6 t swine manure (SM) d.b.

In the last 10 years the swine population increase ≈ 3%

146·10^6 heads in 2019

Greenhouse gases emission in EU

25·10^6 t CO_2equiv.

≈ 7% of the total CO_2 generated by agriculture in EU

3.3·10^9 t CO_2equiv. was generated in EU
Useful methods, insufficient for large-scale farms

Aerobic compost
- Stabilization of manure
- Reduce the volume of waste
- Compost rich in organic matter and nutrients

90%

Anaerobic digestion
- Stabilization of manure
- Reduce the volume of waste
- Biogas rich in methane

6%
Useful methods, insufficient for large-scale farms

Aerobic compost
- Runoff of nutrients
- Greenhouse gases emissions
- Long period of time

Anaerobic digestion
- Poor substrate biodegradability
- Low methane production
- Inhibition of the process

30% Composted

High investment

30% Composted
Hydrothermal carbonization (HTC)

Thermochemical process:
- $T = 180 - 250 \, ^\circ C$
- $t = 5 - 240 \, \text{min}$
- Autogenous pressure
- $> 40\%$ moisture content

Inputs:
- Animal manure
- Sewage sludge
- Food waste

Outputs:
- Hydrochar (HC)
- Process water (PW)
- Gas
- $\text{CO}_2$
- $\text{CO}$
- $\text{H}_2\text{O}$
- Organic compounds
- Nutrients (N, P)
Energy production

Hydrochar (HC)

- Microalgae
- Animal manure
- Sewage sludge

NOx

SO2

N

S

Ash

Fouling & Slagging

ISO 17225-8
Solid biofuels specifications

×
Swine manure (SM)

Objective

N < 3%
S < 0.5%
HHV > 17 MJ kg\(^{-1}\)
VM < 75%
Ash < 20%

ISO 17225-8
Solid biofuels specifications
Experimental procedure

Swine manure (SM)

HTC

T = 180, 210 and 230 °C
t = 60 min

HC-Wa

HCl [5 M]

HC-Wb

Acetone [20, 50 and 75% v:v]

ISO 17225-6: Solid biofuels specifications
Experimental procedure

Swine manure (SM) → HTC assisted with acid HTC-A → HC-A

T = 180, 210 and 230 °C
t = 60 min
[\text{HCl}] = 0.1, 0.25, 0.5 and 1.0 M
## Swine manure origin and characteristics

<table>
<thead>
<tr>
<th>Swine manure (SM)</th>
<th>La Serrota by Kerbest</th>
</tr>
</thead>
</table>

### Swine manure (SM)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value (± Standard Deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (%)</td>
<td>35.3 ± 0.6</td>
</tr>
<tr>
<td>N (%)</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>S (%)</td>
<td>0.7 ± 0.0</td>
</tr>
<tr>
<td>HHV (MJ kg(^{-1}))</td>
<td>14.1 ± 0.3</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>60.0 ± 1.2</td>
</tr>
<tr>
<td>Fixed carbon (%)</td>
<td>15.7 ± 0.5</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>24.3 ± 0.4</td>
</tr>
</tbody>
</table>

### Metals Composition (g kg\(^{-1}\))

<table>
<thead>
<tr>
<th>Element</th>
<th>Value (± Standard Deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>31.2 ± 0.2</td>
</tr>
<tr>
<td>Mg</td>
<td>13.5 ± 0.3</td>
</tr>
<tr>
<td>K</td>
<td>35.4 ± 0.2</td>
</tr>
<tr>
<td>Na</td>
<td>10.2 ± 0.1</td>
</tr>
</tbody>
</table>
Hydrochar characteristics; Mass yield

- **Plain HTC**
  \[ Y_{HC} = 51 - 56\% \]

- **Acid washed**
  \[ Y_{HC} = 28 - 39\% \]

- **Acetone washed**
  \[ Y_{HC} \approx 44\% \]

- **Acid-HTC**
  \[ Y_{HC} = 26 - 43\% \]
Results

Hydrochar characteristics; Plain Hydrochar

- T = 180, 210, 230 °C
- C = 6 – 10%
- HHV = 9 – 13%
- N = 1.8 – 2.1%
- VM ≈ 55%
- HHV = 15 – 16 MJ kg\(^{-1}\)
- S = 0.5 – 0.7
- Ash ≈ 32%
Results

Hydrochar characteristics; Washed hydrochars

Acid washed

HC-Wa

Ash \approx 39%

HHV = 22 – 25 MJ kg\(^{-1}\)

N < 3%

Ash < 10%

VM < 75%

HC-W

S = 0.5 – 0.7%

Acetone washed

HC-Wb

HHV \approx 19 MJ kg\(^{-1}\)

N < 2%

Ash < 12%

VM < 75%

S < 0.2%

ISO 17225-8 Solid biofuels specifications
Results

Hydrochar characteristics; Acid-Hydrochars

\[ \text{T} = 180, 210, 230 \, ^\circ\text{C} \]

\[ \text{C} = 10 - 60\% \]
\[ \text{HHV} = 20 - 70\% \]

\[ \text{HHV} = 17 - 24 \, \text{MJ kg}^{-1} \]
\[ \text{Ash} = 8 - 15\% \]
\[ \text{VM} \approx 70\% \]
\[ \text{S} \approx 0.7\% \]
\[ \text{N} = 2.8 - 4.0\% \]

ISO 17225-8
Solid biofuels specifications

Nitrogen content
Results

Ash agglomeration; Slagging and fouling indexes

Not recommended for combustion

Swine manure (SM)

- FI = > 2000
- SI = > 26
- AI = > 4

Extremely high

Plain HTC

- FI = ≈ 800
- SI = ≈ 14
- AI = 1.2 – 1.8

High

Ash deposits forming during the combustion
Results

Ash agglomeration; Slagging and fouling indexes

Suitable for combustion

- **FI** = 1.4 – 2.3
- **SI** = 0.9 – 1.8
- **AI** = 0.2

**Acid washed**

**Acetone washed**

- **FI** = 2.5 – 5.5
- **SI** = 0.1 – 0.3
- **AI** = 0.1

**HTC-Acid**

- **FI** = 31 – 45
- **SI** = 2.5 – 5.0
- **AI** = 0.5 – 0.8

Low

Low

Low-medium
Results

Thermogravimetric analysis; Kinetic and combustion properties

Low molecular compounds

Higher molecular compounds

SM

HC180

HC180-Wa

HC180-Wb-20

HC180-0.5
Thermogravimetric analysis; Kinetic and combustion properties

**Results**

**Plain HTC**

- Ea = 55 – 68
- $CCl \cdot 10^7 = 5.6 – 6.2$

**Acid washed HTC**

- Higher content of fixed carbon: 104 – 184
- Higher content of volatile matter: 44 – 49

**Acetone washed HTC-Acid**

- Higher content of fixed carbon: 110 – 118
- Similar to Acid washed HTC

Higher and properly combustion stability
In summary

- Plain HTC slight improved the hydrochar energy characteristics
- Hydrochar washing using hydrochloric acid

Energy densification and Combustion performance

$S > 0.5\%$
In summary

- Hydrochar washing using acetone
- Acid concentration and temperature
- Acid-assisted HTC
In summary

• Blending is necessary
Improvement of the physicochemical and combustion properties of hydrochars from hydrothermal carbonization of swine manure

Acknowledgements

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