Corn cobs’ biochar as a host support of salt hydrates for heat storage applications

ZBAIR Mohamed
NGUYEN Minh Hoang
DUTOURNIE Patrick
LIMOUSY Lionel
BENNICI Simona
Problem of intermittence

Increasing demand for energy consumption

Transition

Renewable energies

Depletion of fossil fuels reserves

Thermal Energy Storage

- Sensible Heat
  - Solid
  - Liquid
- Latent Heat
  - Solid-liquid
  - Liquid-Gas
- Thermochemical storage
  - Sorption storage
  - Chemical storage

How it works
**Salt hydrates**: high theory heat storage density and non-toxic

Low Charging temperature (150 °C)  

Suitable for domestic applications

- High cost
- Toxic and corrosive
- Deliquescence
- Slow kinetic
- Limited mass transfer

MgSO₄ = best candidate

- Low-cost (3.8 €/kg)
- Non-corrosive nor toxic
- High DRH : 90 % at 30 °C
- High theory ESD : 2.8 GJ/m³
- Low charging temperature

Dispersion of MgSO₄ onto a porous support

**Composites MgSO_4/biochar CC**

- Pore size
- High surface area and High thermal conductivity

Corncob collected-pyrolyzed in Alsace region

2.5 – 4 mm

**Synthesis**

- Impregnation
- MgSO_4(aq)
- Drying

**Composite xMgCC**

x : wt.% of MgSO_4

- Valorization of agriculture co-product
- Answer to circular economy issues
Characterization

• **X-Ray Fluorescence**: determine the chemical composition of the sample

• **X-Ray Diffraction**: analysis of the present crystalline phases

• **SEM coupling with EDX**: analysis sample morphology and perform elemental composition mapping

• **CO₂ isotherm adsorption**: analysis of the porosity, pore size distribution and surface area

• **Hg intrusion porosimetry**: analysis of the macroporosity

• **Water adsorption experiments**

A Sensys TG-DSC apparatus, equipped with a Wetsys flow humidity generator
CO₂ adsorption isotherm and PSD of the CC

$S_{\text{BET}} = 175 \text{ m}^2/\text{g}$

Hg intrusion analysis of CC
Total porosity = 70.4 %
$V_p = 1.89 \text{ cm}^3/\text{g}$

Total porosity ↓
70.4 % to 54.8 %
$V_p \downarrow$
1.89 to 0.81 cm$^3$/g
The heat released increases with the salt content

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat released (J/g\text{\textsubscript{comp}})</th>
<th>Water adsorption (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC</td>
<td>183</td>
<td>0.070</td>
</tr>
<tr>
<td>5MgCC</td>
<td>360</td>
<td>0.126</td>
</tr>
<tr>
<td>10MgCC</td>
<td>426</td>
<td>0.157</td>
</tr>
<tr>
<td>15MgCC</td>
<td>574</td>
<td>0.207</td>
</tr>
<tr>
<td>20MgCC</td>
<td>635</td>
<td>0.235</td>
</tr>
</tbody>
</table>
Composites MgSO$_4$/biochar CC – Heat released

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat released ($\text{J/g}_{\text{comp}}$)</th>
<th>Heat released ($\text{J/g}_{\text{H}_2\text{O}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC</td>
<td>183</td>
<td>2607</td>
</tr>
<tr>
<td>5MgCC</td>
<td>360</td>
<td>2854</td>
</tr>
<tr>
<td>10MgCC</td>
<td>426</td>
<td>2940</td>
</tr>
<tr>
<td>15MgCC</td>
<td>574</td>
<td>3031</td>
</tr>
<tr>
<td>20MgCC</td>
<td>635</td>
<td>3100</td>
</tr>
</tbody>
</table>

**Case of biochar CC**

Heat released of the support biochar: $Q_{\text{sup}} = 2607 \text{ J/g}_{\text{H}_2\text{O}}$

Latent heat of water at 30 °C: $L_v = 2406 \text{ J/g}_{\text{H}_2\text{O}}$

$Q_{\text{sup}} \approx L_v$

$\text{MgSO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

$\text{MgSO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
The hydration behavior is similar for all composites

\[ w_e = 0.762 \times \omega_{MgSO_4} + 0.077 \, \frac{g_{H_2O}}{g_{comp}} \]
Composites MgSO$_4$/biochar CC – Kinetic

Intra-particle diffusion model (Weber-Morris)

$$q_t = k_i \ast t^{0.5} + C$$

with $k_i$ intra-particle diffusion rate constant (g·g$^{-1}$·h$^{-0.5}$)

$C$ represents the material transfer resistance (g/g)

0.09 ≤ $k_i$ ≤ 0.11
Discussion

**Composites MgSO$_4$/biochar CC-cyclability**

Composite 20MgCC after 6 cycles
dehydration/hydration

SEM/EDX after 6 cycles
• Corn-cobs biochar is a promising host for salt hydrates for TES materials.
• Calorimetry coupled with TG is fundamental for the study of heat storage materials.
• Salt composites have a good stability over multiple hydration/dehydration cycles.
THANK YOU