Changes in carbon structure distribution and nanostructure of functionalized biochars

Elsa Weiss-Hortala  
*Mines Albi, RAPSODEE UMR CNRS 5302, France*

Marion Ducousso  
*Mines Albi, RAPSODEE UMR CNRS 5302, France*

Maxime Hervy  
*Mines Albi, RAPSODEE UMR CNRS 5302, France*

Sarah Berhanu  
*Mines ParisTech, MAT-Centre des matériaux UMR CNRS 7633, France*

Doan Pham Minh  
*Mines Albi, RAPSODEE UMR CNRS 5302, France*

*See next page for additional authors*

Follow this and additional works at: [http://dc.engconfintl.org/biochar](http://dc.engconfintl.org/biochar)

Recommended Citation  
[http://dc.engconfintl.org/biochar/60](http://dc.engconfintl.org/biochar/60)
Authors
Elsa Weiss-Hortala, Marion Ducousso, Maxime Hervy, Sarah Berhanu, Doan Pham Minh, Anthony Chesnault, Alain Thorel, and Ange Nzihou
ENGINEERED BIOCHARS: CARBON STRUCTURES

Marion Ducousso
Maxime Hervy
Doan Pham Minh
Elsa Weiss-Hortala
Ange Nzihou

Sarah Berhanu
Anthony Chesnaud
Alain Thorel

Marco J. Castaldi
Context

Pyrolysis vs. Gasification

CO/H₂ + CH₄ → syngas

H₂

SOx + PAH + CO₂

Catalytic cracking

Electricity or solar

Biomass wastes

Light hydrocarbons

Catalytic cracking

Syngas should be cleaned for further uses.

**Syngas compounds**

<table>
<thead>
<tr>
<th>Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>CO, H₂, CO₂, CH₄</td>
</tr>
<tr>
<td>Pollutants</td>
<td>tar, sulfur, nitrogen, chlorine, particles</td>
</tr>
</tbody>
</table>
Carbonaceous matrix

Metals, minerals (ashes)

Oxygenated groups

Porosity / specific surface area

Structure of chars vs temperatures towards graphitic structures

H. Marsh, Introduction to Carbon Science, 1989, 52
A. Nzihou et al., Energy, 2013, 58
BIOCHAR USES
From by-product to added value material

- Soil amendment / Fertilizer
- Additive in building sector
- Sorption / activated carbons
- Supercapacitors / electrodes
- Catalyst / supported catalyst
BIOCHAR PROPERTIES
Characterization techniques

**Chemical properties**
- Carbon matrix
  - Raman spectroscopy
    → Carbon structure distribution
  - Transmission Electron Microscopy (TEM)
    → Nanostructure
- O- groups
  - Fourier transformed infrared (FTIR)
    → Nature of O-containing groups
  - Temperature Programmed Desorption (TPD)
    → Quantification
- Minerals
  - X-ray fluorescence (XRF)
    → Elemental analysis
  - X-ray diffraction (XRD)
    → Structure
  - ESEM analysis
    → Distribution

**Physical properties**
- Textural properties
  - BET analysis
    → Specific surface area
    → Porosity
  - DVS analysis
    → Active surface area
Surface properties of sorbents and catalysts

- Chemical properties
  - carbon matrix
  - O- groups
  - minerals

- Physical properties
  - textural properties

Understanding of properties to increase and adapt the reactivity to the usage
ENGINEERED BIOCHARS
Functions modified

Impact on carbon structures and reactivity?

- Oxygenation at the surface
- Mineral and metals impregnation
- Activation to increase porosity

biochar
Reactivity towards CH$_4$ cracking

Muradov N. / Catal Commun (2001)
Side effects on carbon matrix

amorphous

fullerene

graphite (ABA stacking)

turbostratic

graphene sheet

I. Suelves et al., Int J of Hydrogen Ener 32 (2007), 3320-3326,
CARBON-BASED MATERIALS
Carbon structures and defects

Non-sp² Carbon Defects

Folding

Bond Rotations

STW-type Defects

graphene oxide

C. Cong et al. SCIENTIFIC REPORTS, 2013, 3.

OXYGENATED BIOCHARS
Efficiency of the oxygenation (TPD analysis)


M. Ducousso et al., Fuel, 2015, 159.
Carbon structure modification (Raman spectroscopy)

Very short ordered carbons (turbostratic)
D band

Ordered carbons (graphene sheets, graphite)
G band

Amorphous carbon

λ=532 nm

Ordered carbons:
- Graphene sheets
- Graphite

Very short ordered carbons:
- Turbostratic

Higher D band
Lower valley
Carbon structure modification (TEM and HRTEM)

- Raw charcoal (raw_char)
- Oxidized at 280°C (Ox2h_280C)
- Oxidized at 400°C (Ox2h_400C)

- No organization
- Graphene sheets stacking
- Nanocrystallites Onion-like structures
Impact on carbon nanostructure

spherical pores with diameter ranging from ~5 to 10 nm

Larger pores from ~10 to 25 nm

interconnected pores

~ 20 nm spheroidal shape homogeneous shape and size unconnected
### Carbon structure modification after activation

<table>
<thead>
<tr>
<th></th>
<th>c.WUP700</th>
<th>a.c.WUP700</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Graphene sheets</strong> (I_G / I_tot)</td>
<td>0.174</td>
<td>0.179</td>
</tr>
<tr>
<td><strong>Disordered graphitic lattice</strong> (I_D / I_tot)</td>
<td>0.408</td>
<td>0.427</td>
</tr>
<tr>
<td><strong>Total graphitic and disordered graphitic structures</strong></td>
<td>0.826</td>
<td>0.842</td>
</tr>
<tr>
<td><strong>Amorphous carbon</strong> I_D'' / I_tot</td>
<td>0.173</td>
<td>0.158</td>
</tr>
</tbody>
</table>

λ=532 nm

---

**SBET (N₂)**

- c.WUP700: 50.6 ± 47.3 m²/g
- a.c.WUP700: 625.4 ± 48.4 m²/g
Presence of onion-like structures
## CONCLUSIONS

Realation between physico-chemical properties and activity

<table>
<thead>
<tr>
<th>Properties</th>
<th>Tar cracking</th>
<th>H$_2$S adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ashes</td>
<td>Catalytic effect</td>
<td>Removal enhanced by Ca and Fe</td>
</tr>
<tr>
<td></td>
<td>Reactivity of hydroxyapatite</td>
<td></td>
</tr>
<tr>
<td>Specific surface area, porosity</td>
<td>High Sp</td>
<td>High Sp</td>
</tr>
<tr>
<td></td>
<td>Mesoporosity limits deactivation</td>
<td>Mesoporosity enhances removal</td>
</tr>
<tr>
<td>O-groups</td>
<td>Activation of cracking</td>
<td>Basic groups favor removal</td>
</tr>
<tr>
<td>Carbon matrix</td>
<td>Reactivity of turbostratic structure</td>
<td>Reactivity of turbostratic structure</td>
</tr>
</tbody>
</table>