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Changes in pore size distribution with pyrolysis temperature, particle aspect ratio and pre-treatment by leaching of large beech wood particles

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What are the problems with the production of the biochar for novel applications? Lack of knowledge.
This study focuses on the investigation of the pore size related to the adsorptive properties of biochar.

**Diagram:**
- **N$_2$ adsorption curve**
  - P$_0$: 760 Torr
  - Applied P/P$_0$ range (N$_2$): 0.005 - 0.99
  - Pore width: 1-100 nm

- **CO$_2$ adsorption**
  - P$_0$: 26140 Torr
  - Applied P/P$_0$ range (CO$_2$): 0.00014 - 0.03
  - Pore width: 0.4-1.4 nm

**Calculation methods:**
- **Pore size distribution:**
  - DFT - Density Functional Theory
  - BJH - Barrett-Joyner-Halend

- **Specific surface area:**
  - BET - Brunauer-Emmet-Teller

**Legend:**
- Fungal hyphae
- Plant cells
- Bacteria
- Plant available water
- Chemical sorption
- He pycnometry
- Hg porosimetry
- N$_2$ sorption
- CO$_2$ sorption
- Macropores: (<50 nm)
- Mesopores: (50-2 nm)
- Micropores: (50-2 nm)
Procedures and methodology applied in this study:

Initial research matrix

- Beech wood cylinders
- ø8x10 mm (1)
- ø8x16 mm (2)

No leaching (U)

Leaching (W):
- 0.5M, 24h, citric acid

4 sample types:
- U1 – not leached, size 1
- U2 – not leached, size 2
- W1 – leached, size 1
- W2 – leached, size 2
Procedures and methodology applied in this study:

**Pyrolysis method and its conditions**

No leaching (U)

Leaching (W): 0.5M, 24h, citric acid

Pyrolysis of each single particle

5 Temperatures:
- 300°C
- 400°C
- 500°C
- 700°C
- 900°C

Beech wood cylinders
Single particle reactor at BIOENERGY2020+ used for pyrolysis each sample separately at 5 temperatures (6 repetitions).
Procedures and methodology applied in this study: **Final sample selection and preparation**

- Beech wood cylinders
- No leaching (U)
- Leaching (W): 0.5M, 24h, citric acid
- Pyrolysis of each single particle
- Grinding and homogenisation

3 samples of each (out of 6 repetitions)
Procedures and methodology applied in this study:
**Gas adsorption procedure**

- Beech wood cylinders
- No leaching (U)
- Leaching (W): 0.5M, 24h, citric acid
- Pyrolysis of each single particle
- Grinding and homogenisation
- N₂ adsorption (77K)
- CO₂ adsorption (273K)
- Samples degassed 24h in 150°C
Procedures and methodology applied in this study: Evaluation method of adsorption results

No leaching (U)

Leaching (W): 0.5M, 24h, citric acid

Pyrolysis of each single particle

Grinding and homogenisation

N₂ adsorption (77K)

CO₂ adsorption (273K)

Calculation methods:

N₂ adsorption
Brunauer-Emmet-Teller (BET)
Barrett-Joyner-Halenda (BJH)

CO₂ adsorption
Monte Carlo (MC)
Pore size distribution and its change in relation to: pyrolysis temperature, aspect ratio and leaching

Differences in specific surface area values between BET and BJH calculation method

Changes of the microporous and mesoporous specific surface area (SSA) in relation to: pyrolysis temperature, aspect ratio and leaching
Pore size range for adsorption in CO₂ and N₂ does not meet the ranges for pore size types and has to be adjusted.

Micropores (<2 nm)
Mesopores (2-50 nm)
Macropores (>50nm)

CO₂ adsorption (MC: 0.4-1.4 nm)
N₂ adsorption (BHJ: 1.4-100 nm)

Cumulative pore volume [cm³/g]

Treatments:
- 900°C
- 700°C
- 500°C
- 400°C
- 300°C

Pore width [nm]
With the increase of the temperature volume of certain pores (0.48nm, 0.60nm and 2.5nm) increases for all samples.

Peak at 0.55 nm above 300°C, changes into two peaks at 0.48 nm and 0.60 nm.

From 500°C, the volume of the pores larger than 1.4 nm starts to increase.

From 700°C, peak around 2.5 nm starts to appear.
• Pore size distribution and its change in relation to: pyrolysis temperature, aspect ratio and leaching

• Differences in specific surface area (SSA) values between BET and BJH calculation method

• Changes of the microporous and mesoporous specific surface area (SSA) in relation to: pyrolysis temperature, aspect ratio and leaching
The *calculation method* of results from the $N_2$ adsorption affects the value of SSA and can mislead with trends.

Results of SSA from the BET method are significantly higher than from the BJH method.

Results from the BET show strong drop in SSA above 700 °C for all the samples.

Results from the BJH show that only not leached samples show drop in SSA above 700 °C.
Selected P/P0 range for calculation method strongly affects taken in count pore size range, so also the SSA value.

BJH method was calculated on the stiff P/P0 range (0.09-0.99), which corresponds to 1.4-100 nm pore width.

To obtain positive BET’s C-constant value, the P/P0 range have to be adjusted accordingly to determination graph.

For samples produced in different temperature correct P/P0 range varies, and for some samples only microporous range was taken in count for BET calculation.
• Pore size distribution and its change in relation to: pyrolysis temperature, aspect ratio and leaching

• Differences in specific surface area (SSA) values between BET and BJH calculation method

• Changes of the microporous and mesoporous specific surface area (SSA) in relation to: pyrolysis temperature, aspect ratio and leaching
Microporous SSA shows **steady rise** with temperature, but for mesoporous SSA influence of temperature is **inconclusive**.

The microporous SSA is significantly **higher** than mesoporous and it accounts for most of the internal surface.

The microporous SSA **rise monotonically** with temperature. For smaller samples slightly higher.

The mesoporous SSA show a **different trend** with temperature for samples with different aspect ratio and pre-treatment.
Summary

- Investigated parameters have a significant impact on pore size distribution, which has a direct link with the values of specific surface area.

- Strong caution has to be taken during the SSA calculation due to significant differences in the results in case of application different P/P0 range and method.

- Rising pyrolysis temperature clearly lead to increase the microporous SSA, but for mesoporous SSA the influence is inconclusive because possible impact of other parameters.
Conclusions

• Is strongly suspected that leaching combined with high pyrolysis temperature can have a positive influence on the SSA, so also on biochars adsorptive properties.

• Results obtained in this study can lay the foundation for a mathematical description of the SSA or/and pore size distribution changes.

• In future it may lead to the development of a model which will ease the future predictions of internal changes during pyrolysis of the biomass.
This study is a **small step**, hopefully in a good direction, but there is still a long and winding road to achieve the **goal**
Acknowledgments
I would like to invite you! to the PYRO2020 Conference!

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