

# 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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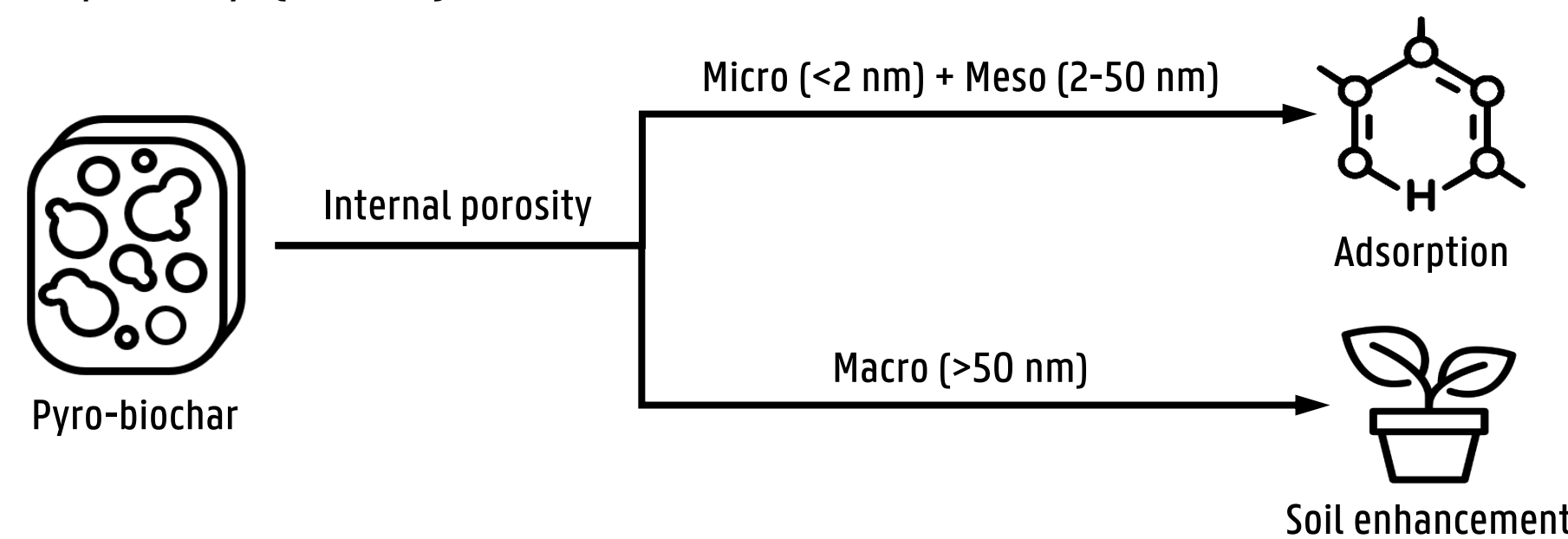
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## INTRODUCTION

Pyrolysis biochars are sustainable porous materials which find applications as pollutants adsorbents or catalyst supports. They also find applications as a soil amendment (water retention enhancement, bacterial habitat, heavy metals immobilisation). In terms of the adsorption and catalysis the micro-porosity (<2nm) and meso-porosity (2-50nm) play a major role and for water retention, the macro-porosity (>50nm).



## AIM AND METHODOLOGY

The study aimed at investigating the changes in the internal structure in relation to the pyrolysis conditions (300, 400, 500, 700 and 900 °C) in a single particle reactor, particle size (ø8x10 and ø8x16 mm) and leaching pre-treatment (0.5M citric acid, 24h). Ground and homogenised particles were degassed (24h, 105°C) and then analysed through N<sub>2</sub> and CO<sub>2</sub> adsorption (Qunatochrome NOVA 4200e). Specific surface area and pore size distribution from adsorption data were obtained through methods: Monte Carlo (CO<sub>2</sub>), BJH (N<sub>2</sub>) and BET (N<sub>2</sub>).

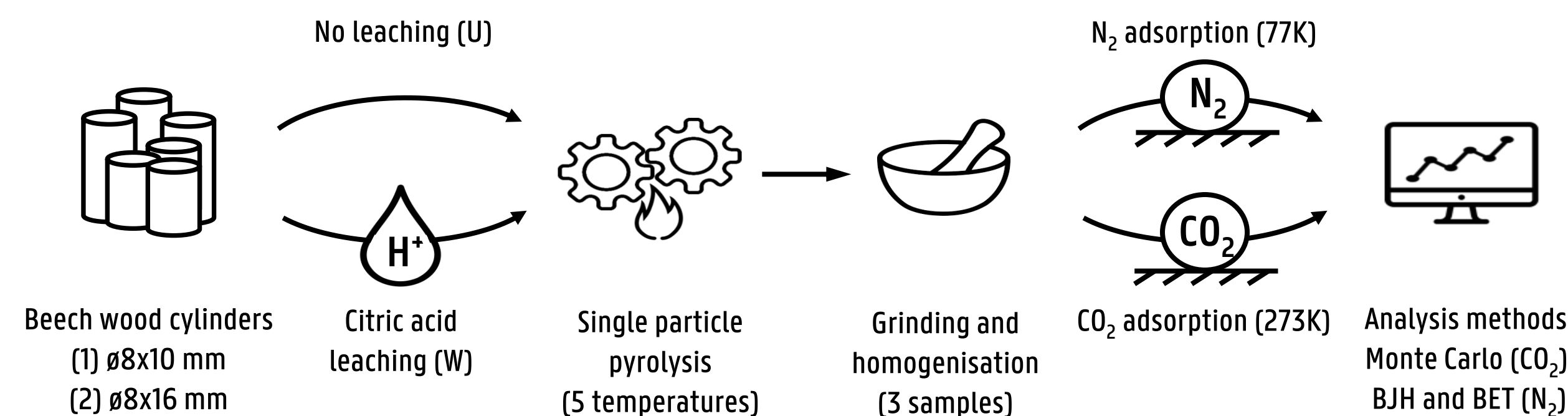


Fig. 1 Single particle reactor.

## RESULTS AND DISCUSSION

### Differential pore size distribution

- Pore size distribution was obtained by merging the data from CO<sub>2</sub> adsorption (Monte Carlo, 0.4-1.4 nm) and N<sub>2</sub> adsorption (BJH, 1.4 – 50 nm).
- For all samples, the micropores (<2 nm) accounts for most of the pore volume.
- The peak for 0.55 nm pore diameter, visible at 300 °C, disappears in higher temperatures. Simultaneously two peaks at 0.48 nm and 0.60 nm pore diameter start to appear above 300 °C.
- 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.

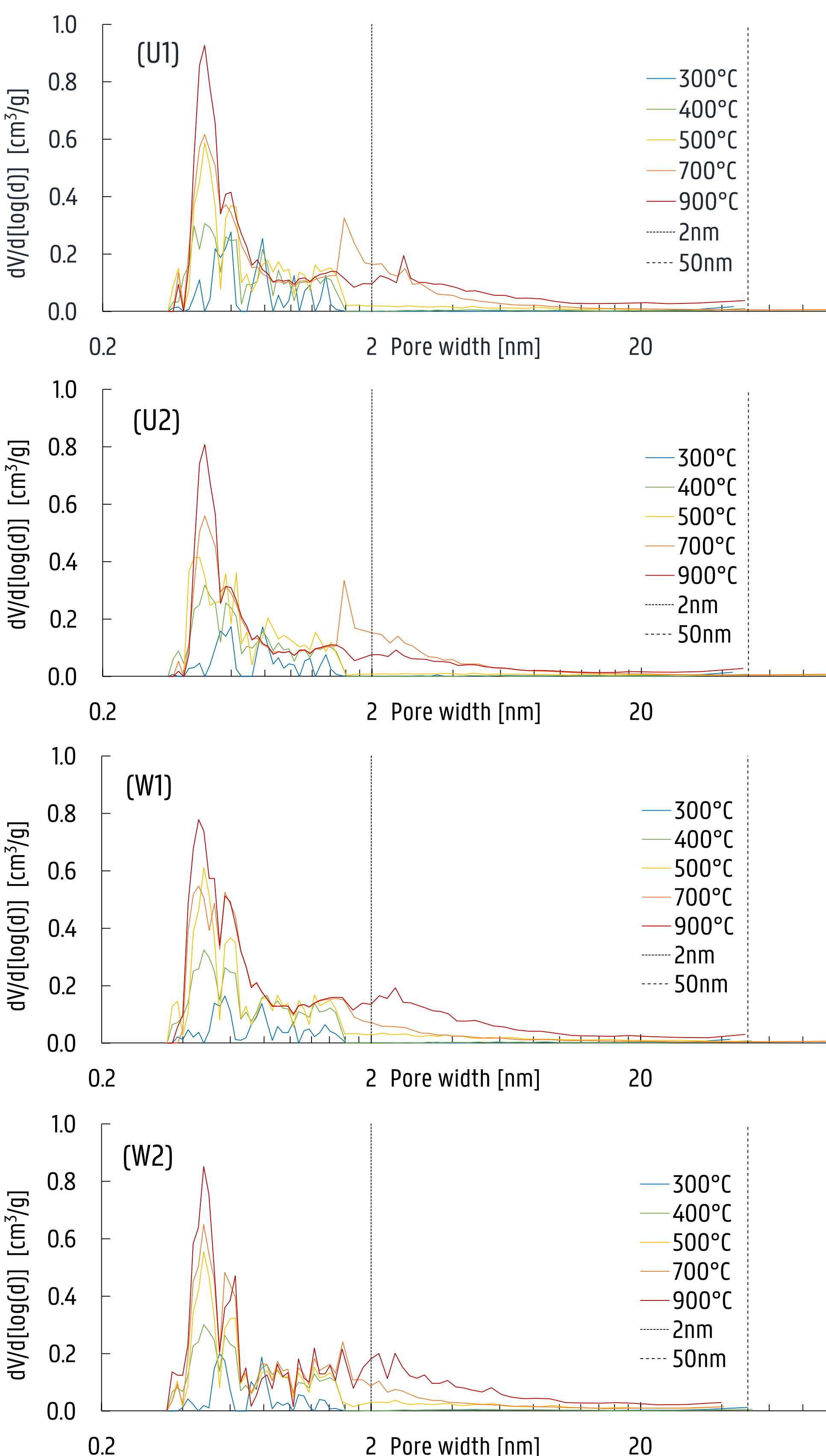


Fig. 2 Pore size distribution in relation to temperature for all samples (U- not leached, W – leached, 1 – ø8x10mm, 2 – ø8x16mm)

### Carbon and hydrogen content in relation to investigated parameters

- The initial higher content of the carbon for the leached samples (W) was levelled at a temperature of 400 °C. The opposite relationship was noticed in 500 °C, and for 700 °C the difference again was not visible.
- Between 300 °C and 500 °C, the hydrogen content is slightly higher for larger samples (2). At 700 °C, the difference between leached (W) and not leached (U) samples appear, and it disappears at 900 °C.

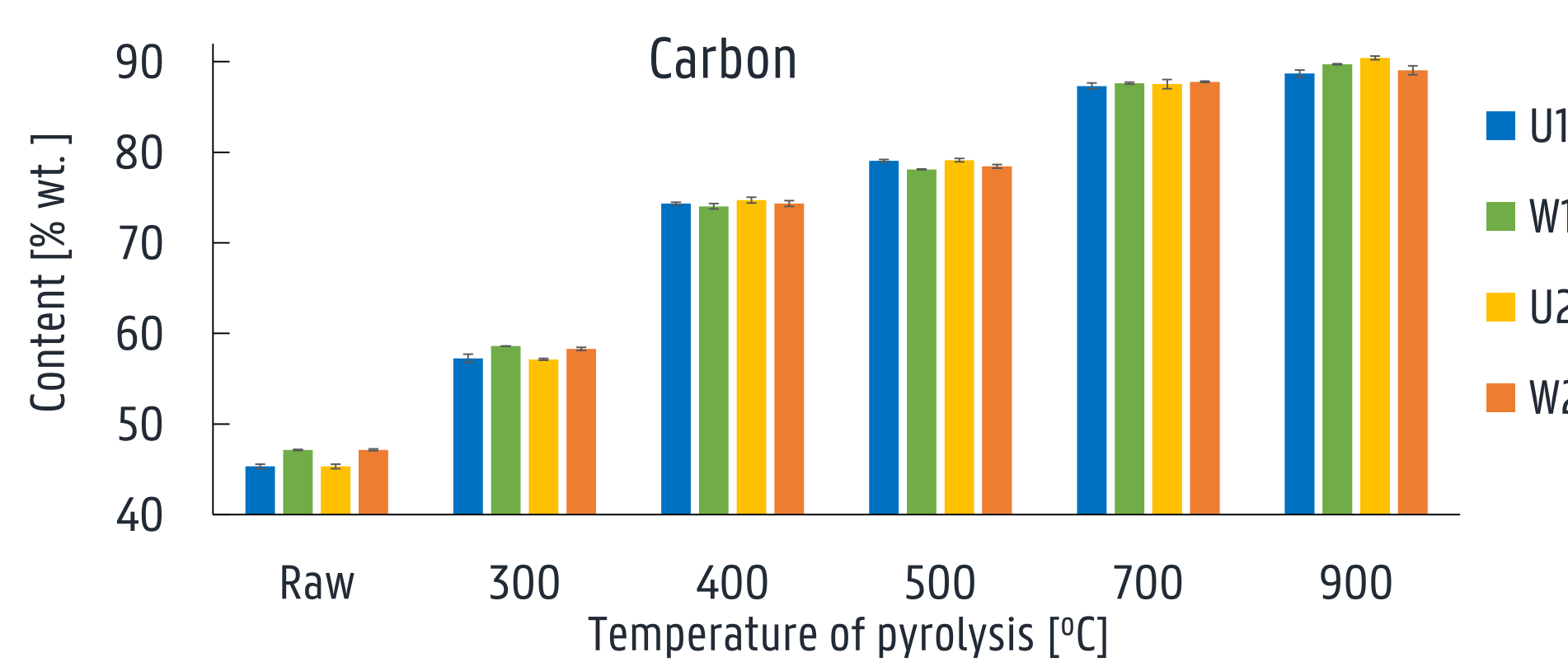


Fig. 3 Carbon content (% wt.) of investigated samples on dry basis.

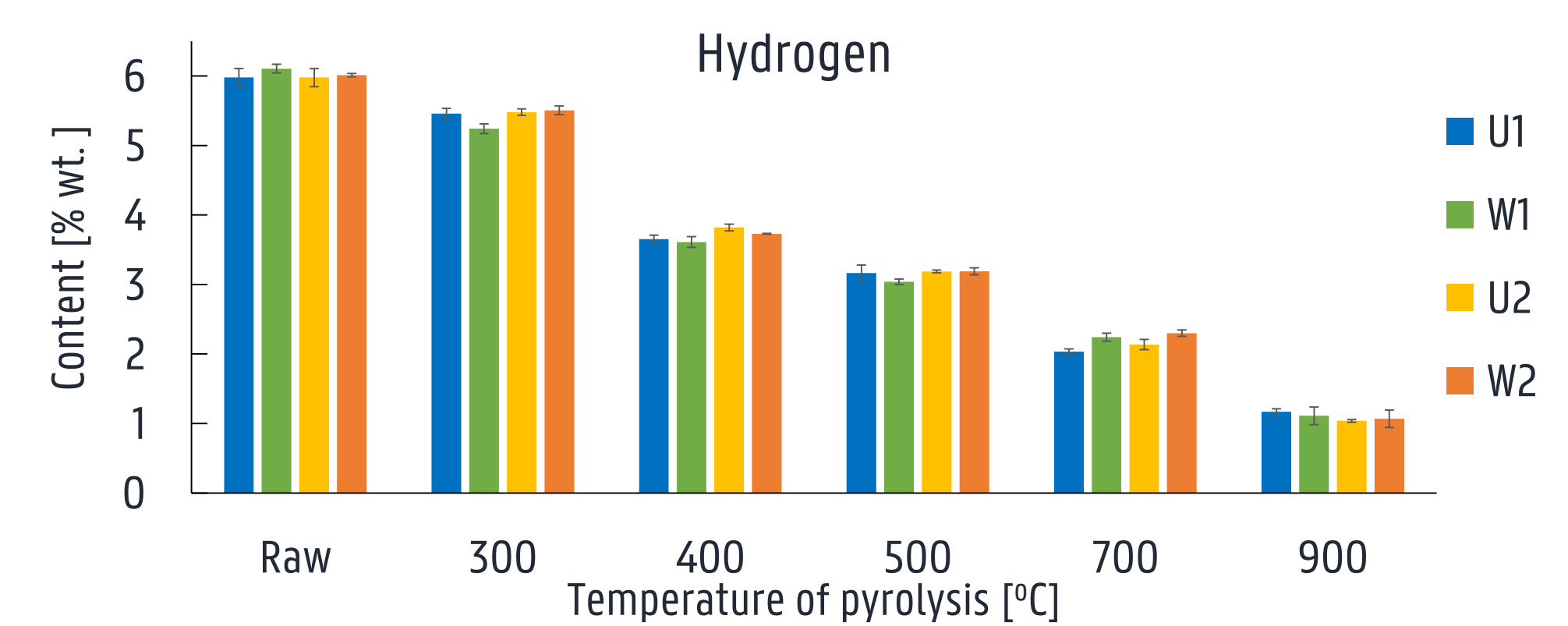


Fig. 4 Hydrogen content (% wt.) of investigated samples on dry basis.

### Comparison of different methods for specific surface area (SSA) evaluation from N<sub>2</sub> adsorption

- The BET method uses different range of P/P<sub>0</sub> (to comply with the positive C value requirement). The BJH method uses stiff P/P<sub>0</sub> range 0.09-0.99, corresponding to 1.5-50 nm pore width. Both methods calculated only on the adsorption isotherm due to significant hysteresis of desorption curve.
- The BET results show a typical drop above 700 °C for all samples. The drop is visible on results from the BJH but only for not leached samples (U).
- The values for the BET method are significantly higher than from the BJH method, due to differences in the pore size width that they take in count.

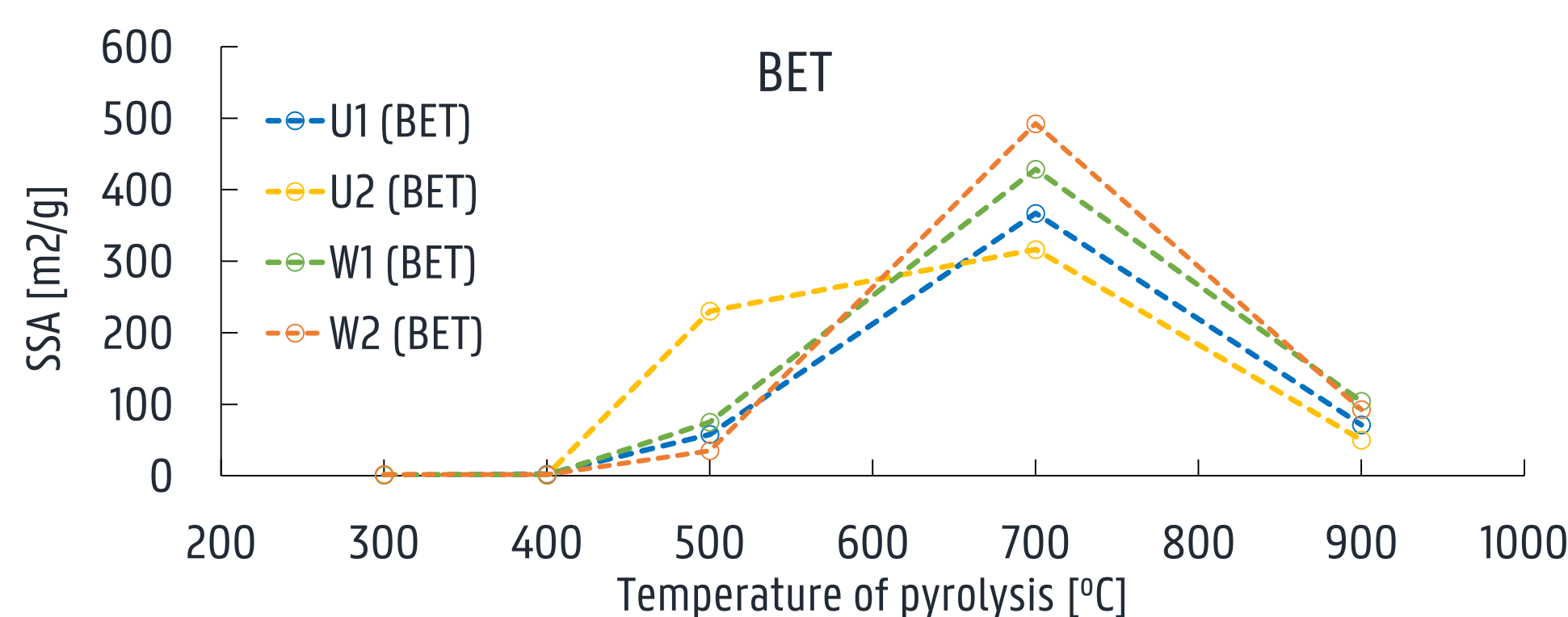


Fig. 5 Results of SSA from the BET calculation method (unknown pore size).

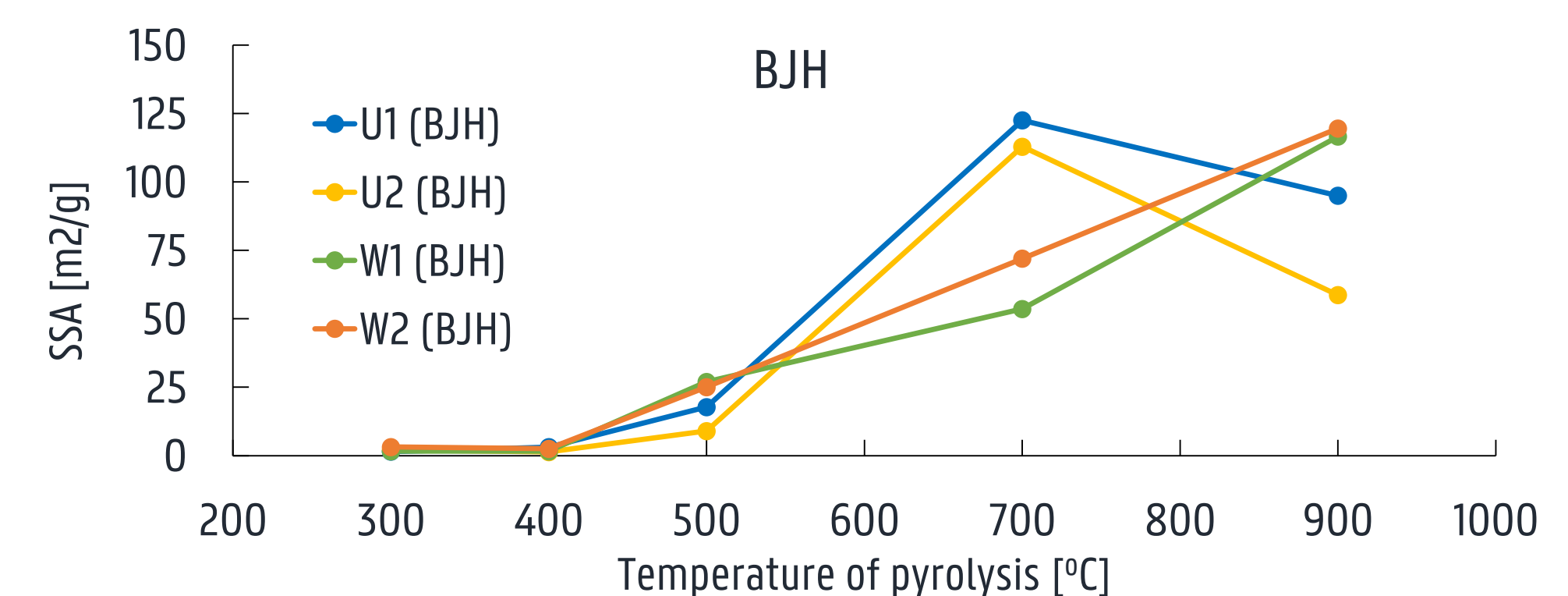


Fig. 6 Results of SSA from the BJH calculation method (pore size 1.5-50 nm).

### Trends in changes of specific surface area related to micropores and mesopores

- For calculation of the micro-SSA data, was used from ads.: CO<sub>2</sub> (0.4-1.4 nm, MC) and N<sub>2</sub> (1.4-2.0 nm, BJH). For meso-SSA data was used from ads.: N<sub>2</sub> (2-50 nm, BJH).
- The microporous SSA for all samples rises monotonically with the temperature. Its value is visibly lower for the larger samples (2).
- The mesoporous specific surface area rises with temperature for all samples beside U2. Not leached (U) samples show the most rapid rise is SSA in temp. range 500-700 °C and leached (W) in temp. range 700-900 °C. The influence of the sample size is inconclusive.

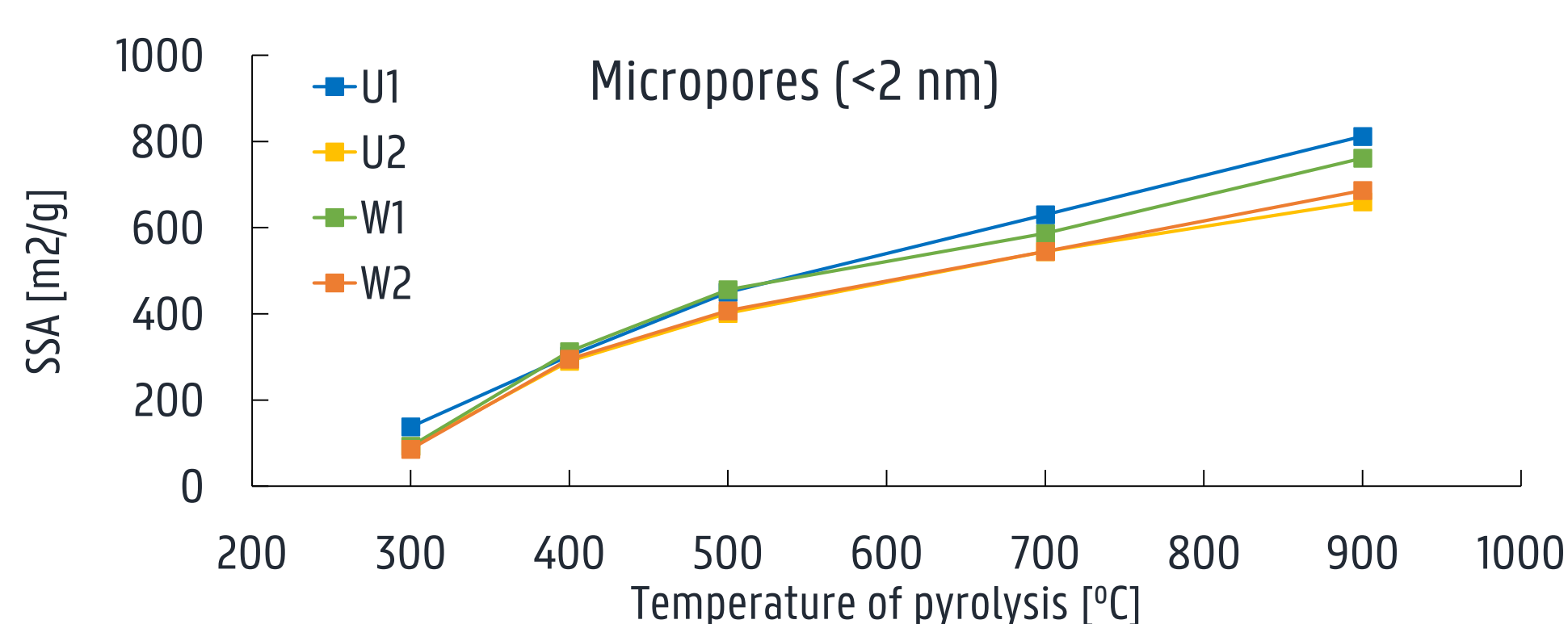


Fig. 6 Microporous SSA for all samples as function of temperature.

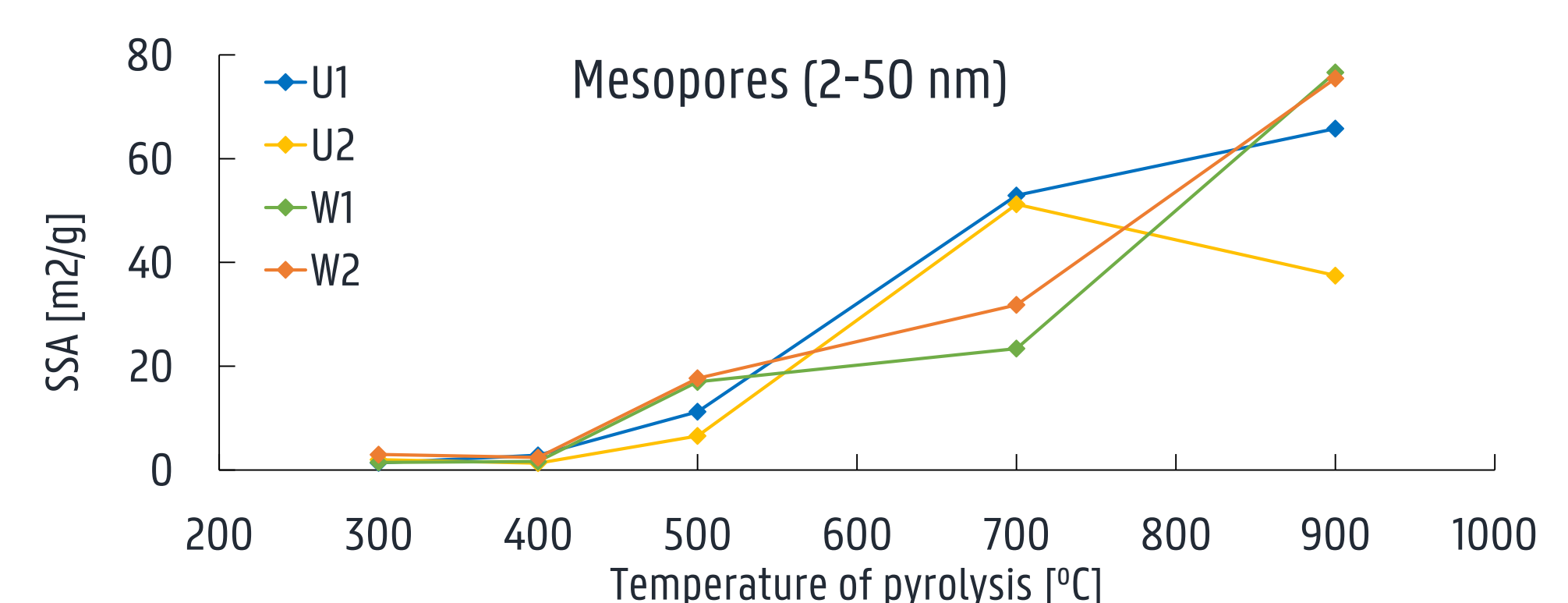


Fig. 7 Mesoporous SSA for all samples as function of temperature.

## CONCLUSIONS

Studies show that the influence of investigated parameters is significant on pore size distribution, which has a direct impact on the specific surface area. Strong caution has to be taken in choice of the SSA calculation, due to significant differences in the result in terms of application of different P/P<sub>0</sub> range and method. Change in the structure related to rising in pyrolysis temperature clearly increase the microporous SSA, but for mesoporous SSA the influence is inconclusive. Results obtained in this study can lay the foundation for a mathematical description of the SSA or/and pore size distribution changes, and in future lead to the development of a model which will ease the future predictions of internal changes during pyrolysis of the biomass.

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## Research partners

