Biogas upgrading to biomethane with sewage sludge

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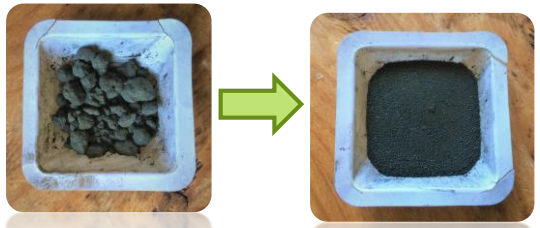
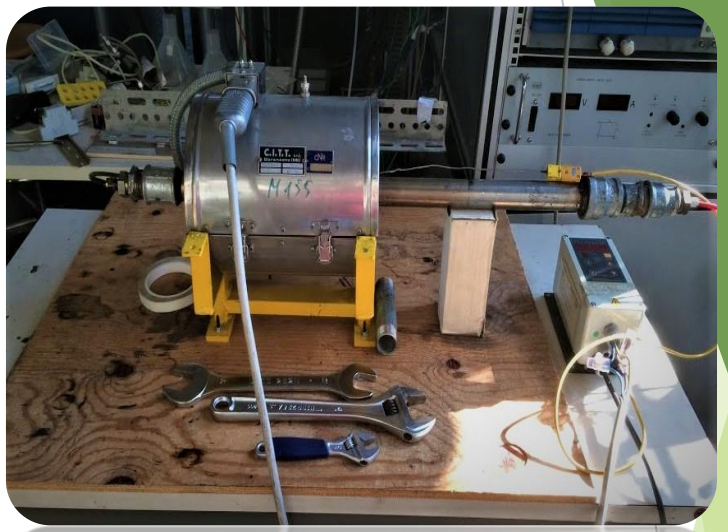
Experimental Summary

SMAT WWTP



Sieving and Grinding

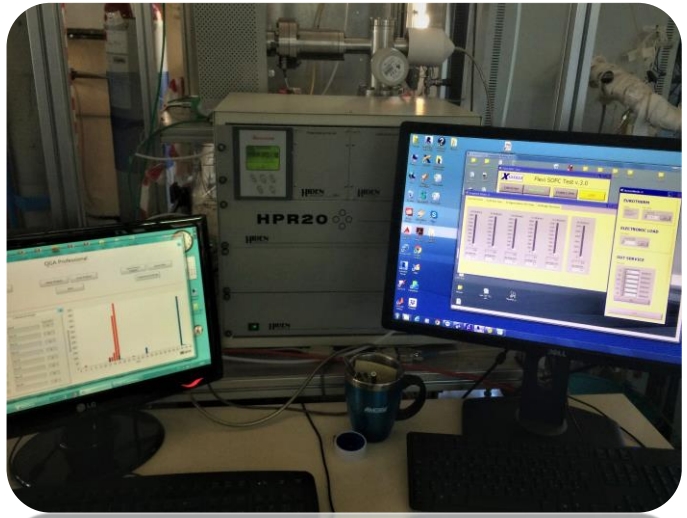


Physical activation

Char

Gas

Bio-oil



Adsorption test

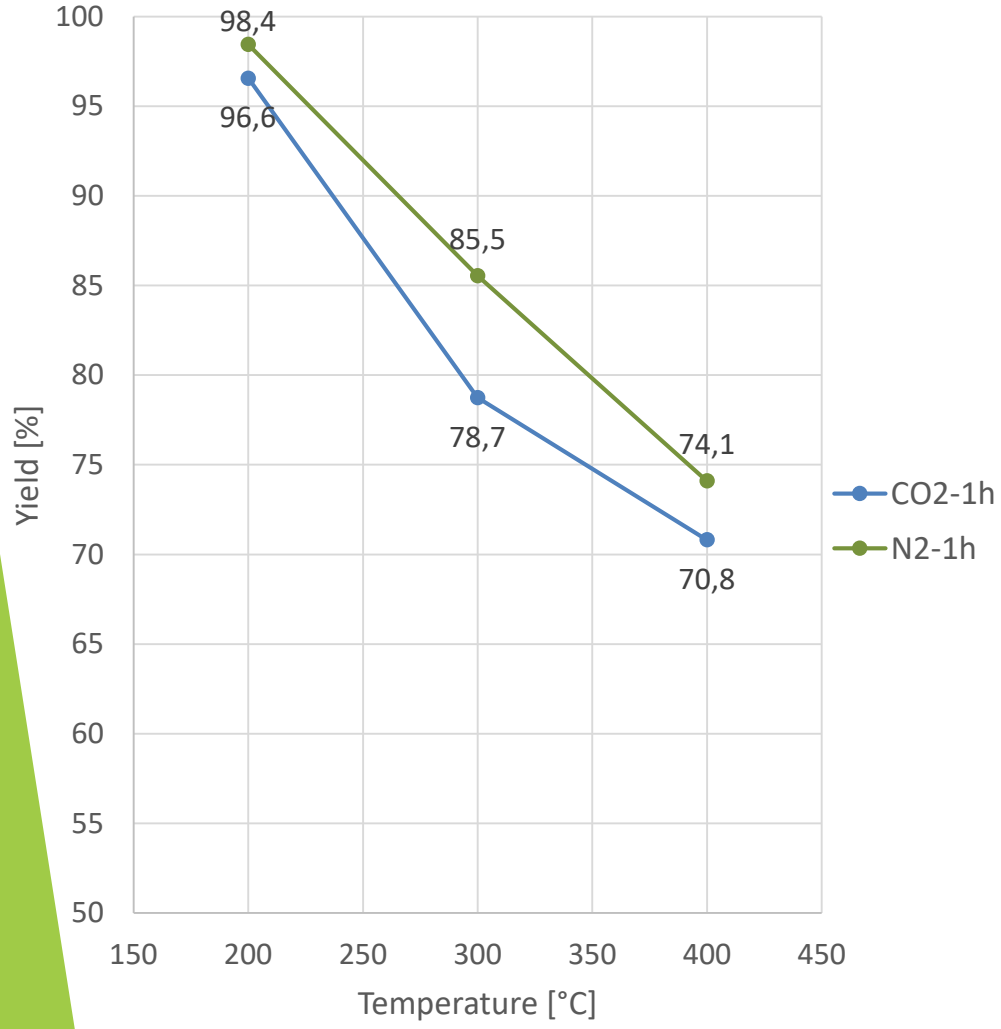
Physical Activations

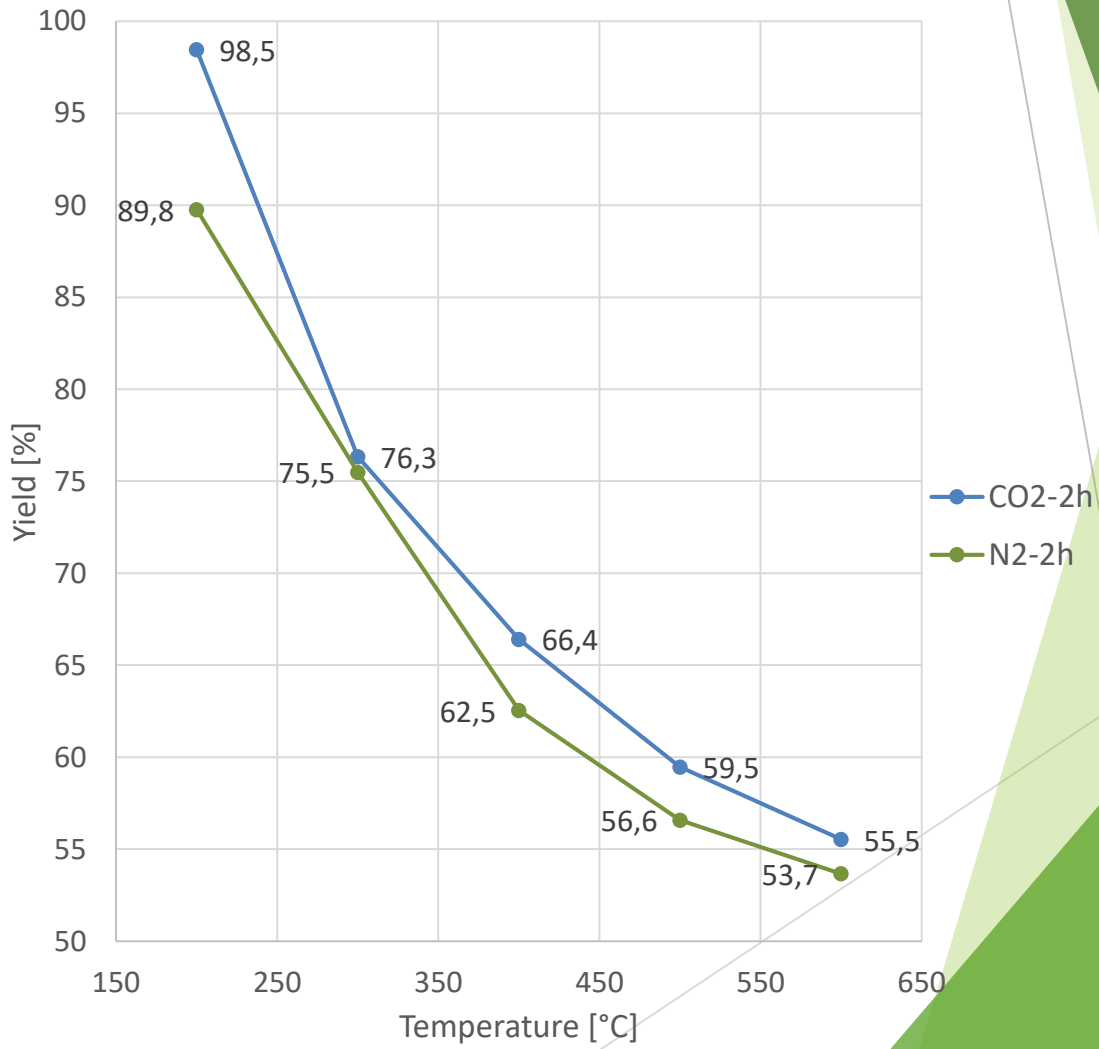
- **Considered variables:**

- **Dwell time** → 1 h, 2 h;
- **Temperature** → 200 °C, 300 °C, 400 °C, 500 °C, 600 °C;
- **Atmosphere** → Nitrogen, Carbon Dioxide, Air;
- **Activation method** → Pyrolysis, Direct Activation, Pyrolysis+Activation (1 stage)[1];
- **Heating rate** → 10 °C min^{-1}, 20 °C min^{-1};
- **Flow rate** → 300 Nml min^{-1}, 400 Nml min^{-1}, 500 Nml min^{-1}.

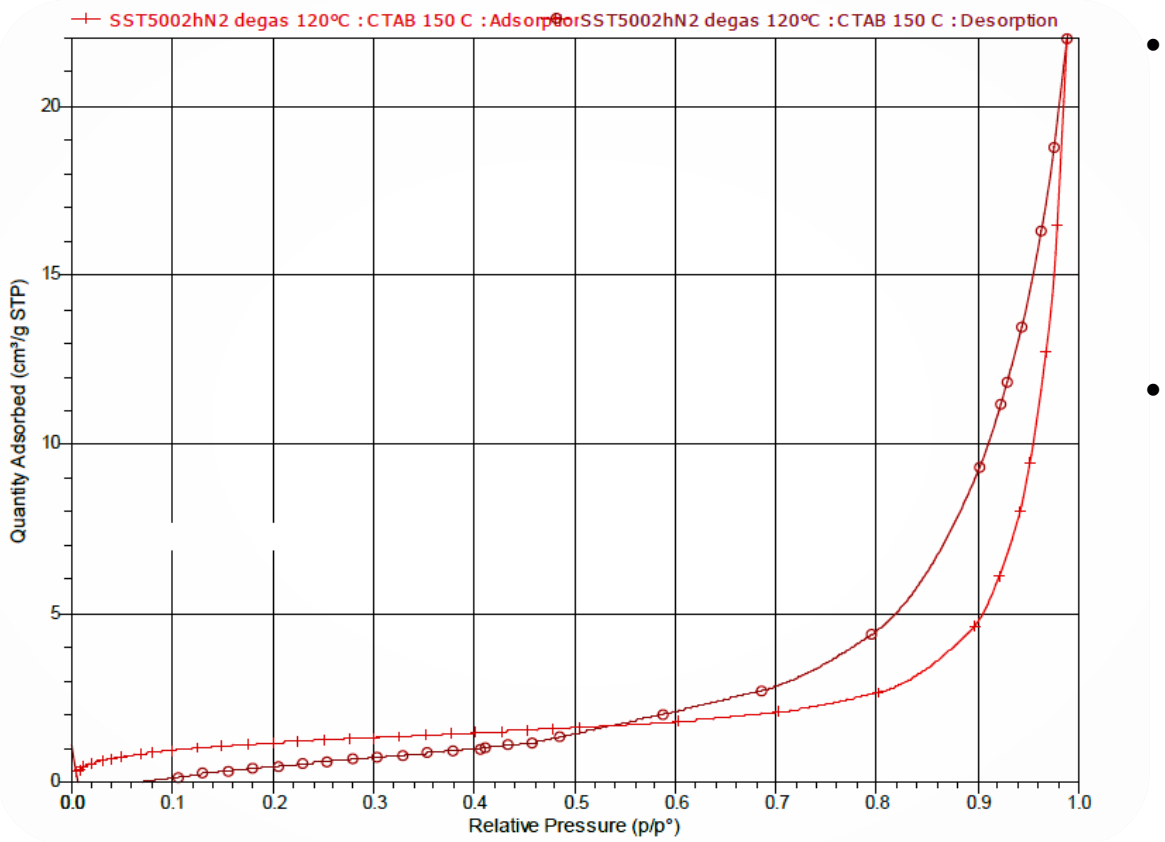
[1] **Pyrolysis**: whole process with inert atmosphere (N_2 flow rate);
Pyrolysis+Activation: until the activation temperature inert atmosphere (N_2 flow rate), then activating agent (CO_2) for 2h.

Physical Activations – Influence of the Temperature on the char Yield





Textural characteristics



- The adsorption/desorption isotherms curves for nitrogen are distinctive of macroporous or nonporous adsorbents (II Type);
- The porosity developement is witnessed by the increment of the specific surface areas and pores volumes, despite they are much smaller than the ones typical of the commercial activated carbons.

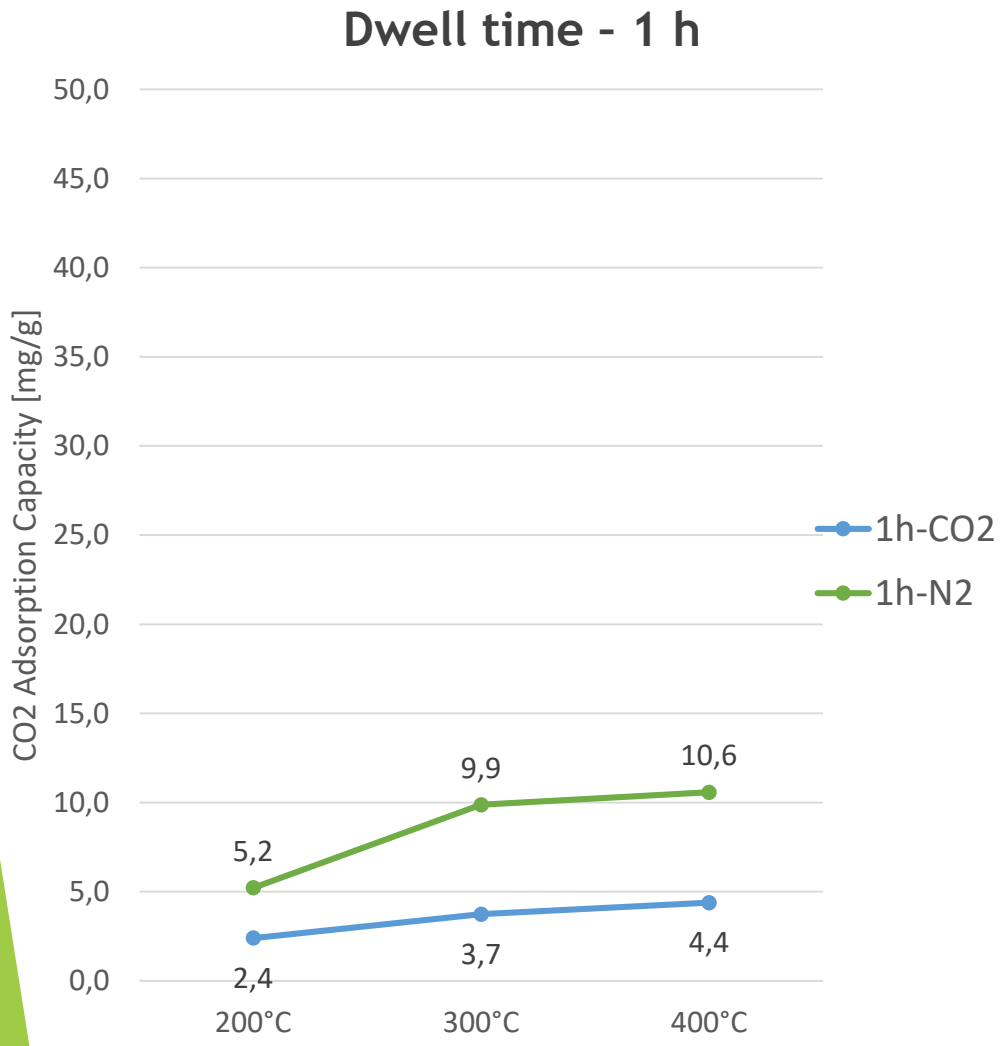
Parameter	S0	SST4001hCO2	SST4002hCO2	SST4002hN2	SST5002hN2
BET Surface Area [m^2/g]	0,323	2,6551	3,2895	2,324	4,3246
t-Plot external surface area [m^2/g]	0,377	3,2701	3,8221	2,7468	4,7013
Volume in Pores (< 1,308 nm) [cm^3/g]	0,00002	0,00038	0,00024	0,00015	0,00074
Total Volume in Pores (≤ 44,883 nm) [cm^3/g]	0,00122	0,01386	0,01913	0,01457	0,02263
Total Area in Pores (≥ 1,308 nm) [m^2/g]	0,111	2,064	3,485	2,399	3,409

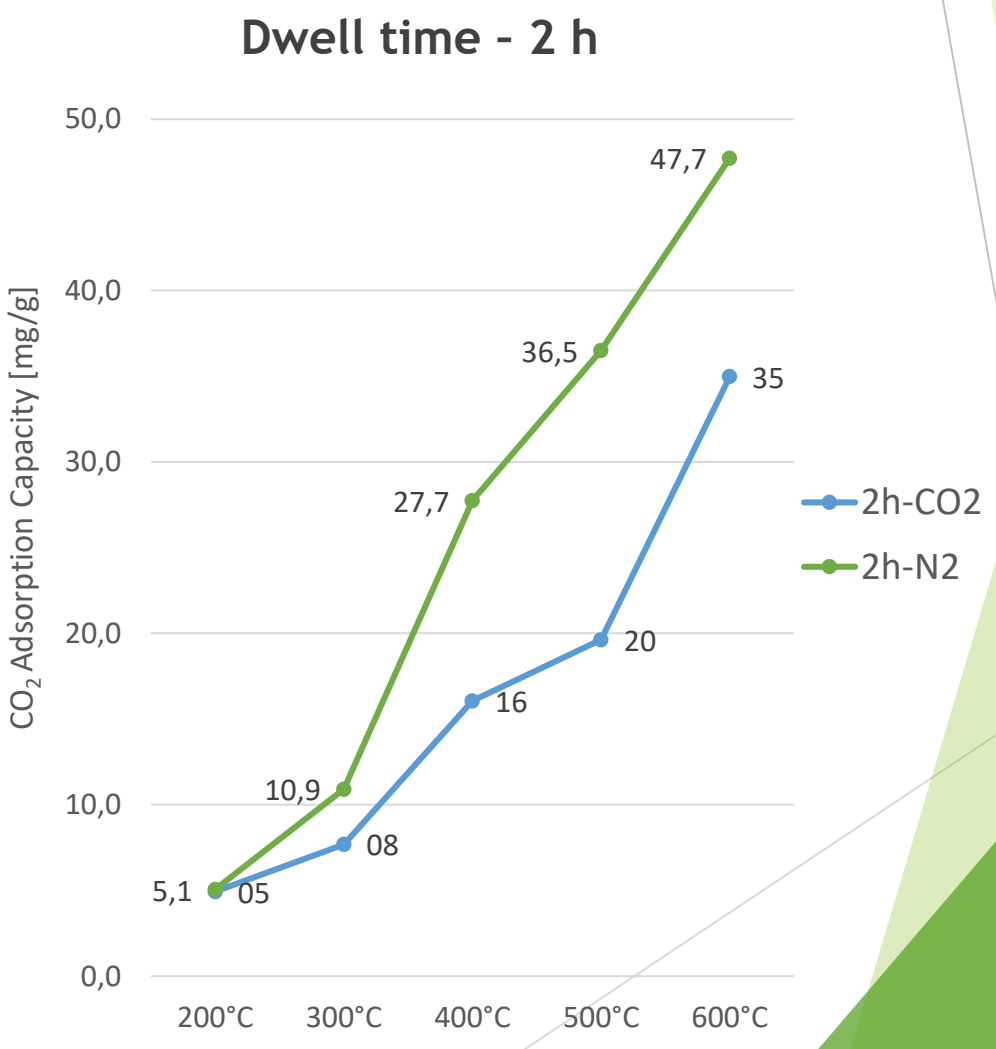
Adsorption tests – Data

- Biogas simplified mixture (35% CO_2 – 65% CH_4):
- **Flow rate**: 153,8 Nml/min;
- **GHSV:** 131 h^{-1};
- **L/d:** 3,33;
- **CO_2 breakthrough limit:** 2,5%[1].

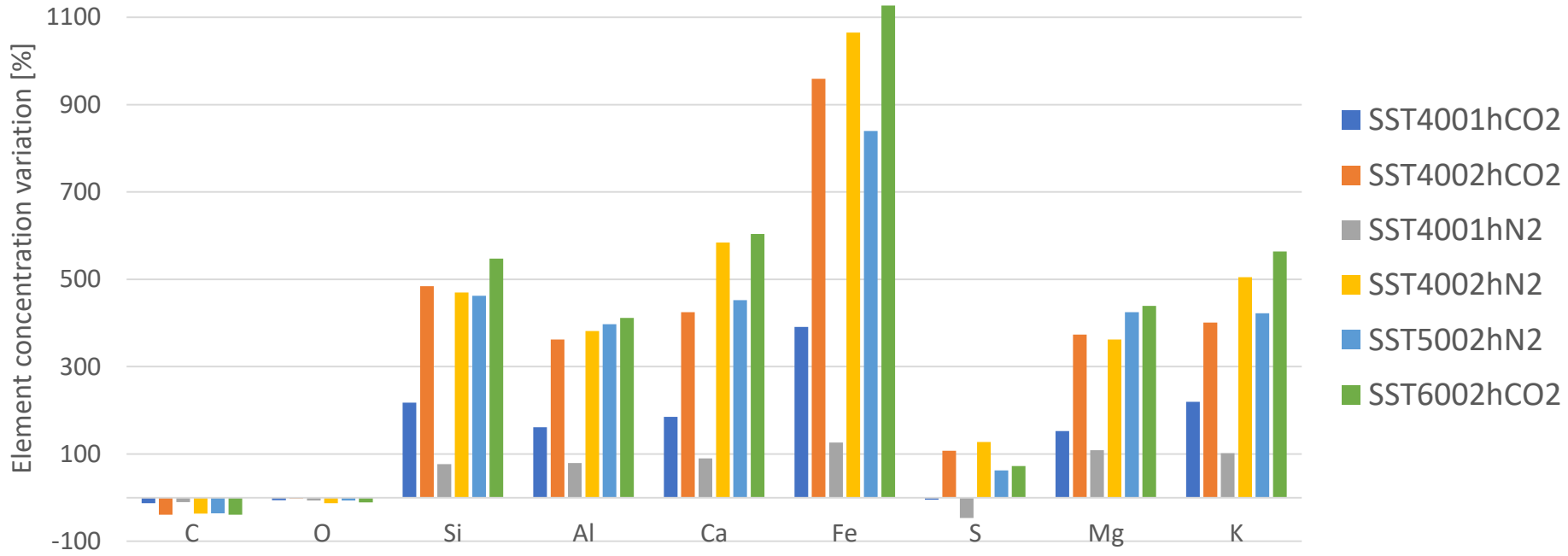
[1] Limit imposed by the CEN EN 16723-1 (“**Specifications for biomethane for injection in the natural gas network**”) and CEN EN 16723-2 (“**Automotive fuels specification**”).

Adsorption tests – Influence of the Temperature on the Adsorption Capacity



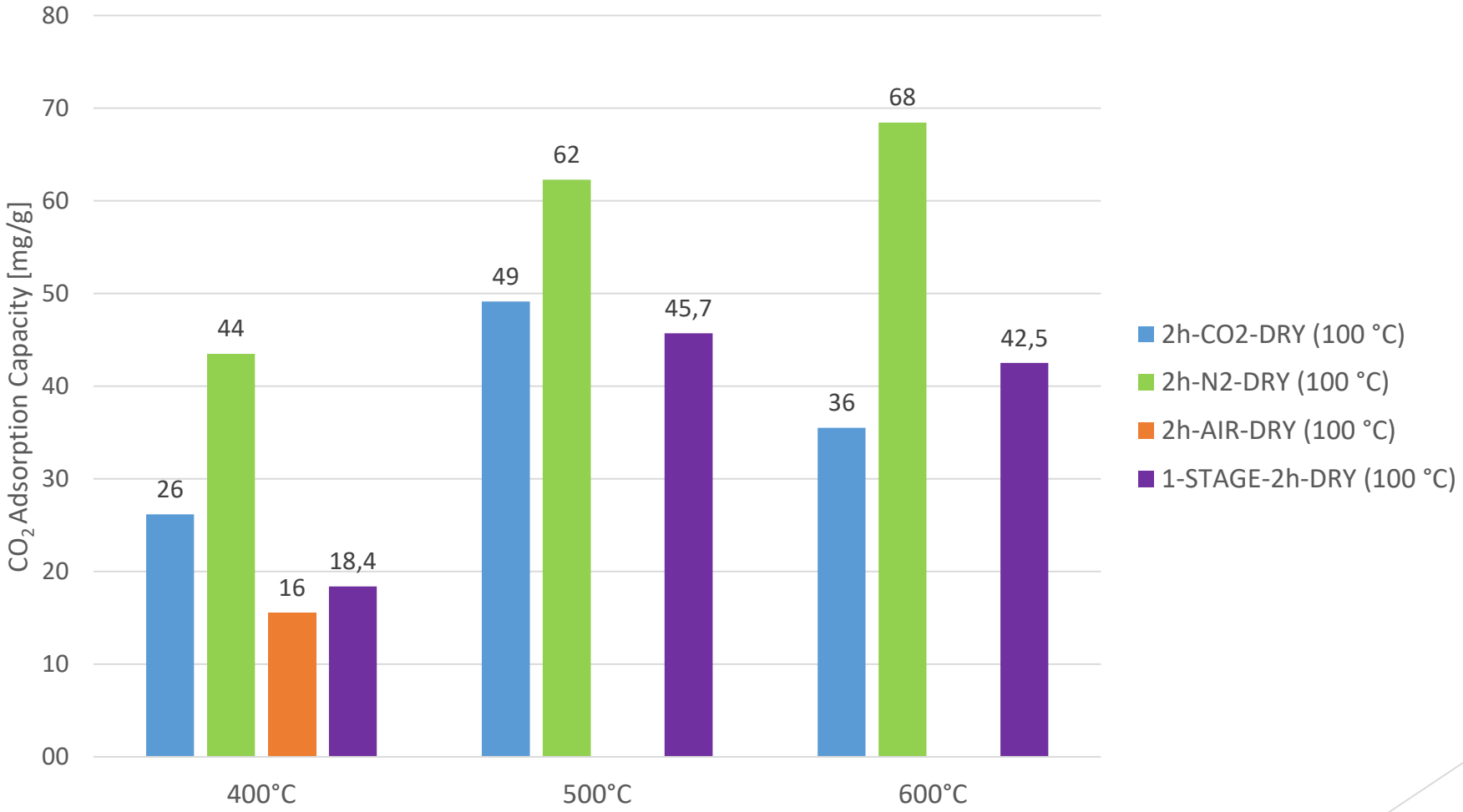


EDS (energy dispersive x-ray spectroscopy) Analysis



- The EDS analysis highligthed that, increasing the activation temperature, an increment of the ash/mineral concentration and a decrease of the most volatile elements occurred;
- The main consequence is the production of neutral/basic biochar samples, enhancing the base sites concentration, where the CO_2 may react like a Lewis acid.

Adsorption tests – Comparison with different Activation Methods (Dry conditions)



Adsorption tests – Optimization – Dry at 170 - 180°C

Adsorption tests – Comments

- The experimental activity has shown that:
- The **increase** of the activation **temperature** (with fixed dwell time) and **dwell time** (with fixed temperature) has always brought advantages in terms of adsorption performances;
- The **water content** reduction has allowed to reach higher adsorption performances regard with the respective not-dried samples;
- The **best biochar sample SST6002hN_2_Dry_180** (**102,5 mg_{CO2} g^{-1}_{sorb}**) has been produced with the following **conditions**:

→ Temperature: 600 °C;

→ Dwell time: 2 hours;

→ Atmosphere: Nitrogen;

→ Drying temperature: 170 – 180 °C;

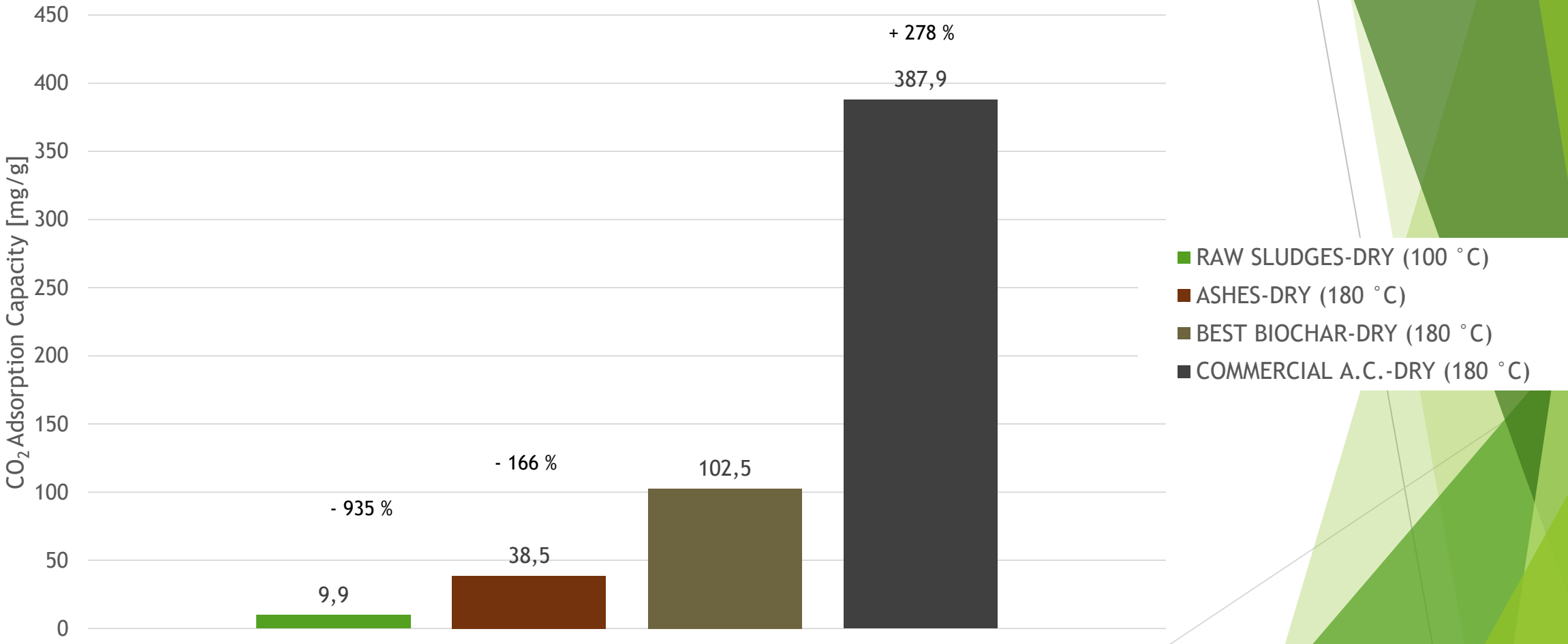
→ Flow rate: 300 Nml min^{-1};

→ Heating rate: 10 °C min^{-1}.

Adsorption tests – Comparison with other materials

- To compare the carbon dioxide adsorption results obtained with the best sewage sludge-based activated carbon (**SST6002hN_2_Dry_180**), other materials have been tested;
- The choice fell in another waste material (**ashes**) and a commercial activated carbon (**Norit RST3**).

Adsorption tests – Comparison with other materials



Conclusions and future prospects

- This work has showed how the parameters selected for thermal activation are important to appropriately engineer the biochar samples characteristics;
- The **pyrolysis** process represents an interesting disposal method for the sewage sludges, generating **3 valuable byproducts** (char, pyrolytic oil and gas);
- The **biochar** has demonstrated promising results in terms of carbon dioxide adsorption;
- Anyway, from the preliminary study, the enormous amount of carbon dioxide to yearly manage at plant scale seems to make the adsorption an inappropriate method for the biogas upgrading, since the same issues occurred also for a commercial material;
- Applications with a smaller carbon dioxide (or other substances) concentrations may be examined to find more valorizing solutions;
- The **chemical activation** may represent a further improvement for the biochar preparation if economically sustainable;
- The **pyrolytic oil** and **gas**, due to their interesting heating value, respectively **22,4 - 28,0 MJ kg^{-1}** and **12,0 - 20,0 MJ m^{-3}**, may represent interesting **biofuels** for CHP applications(oil and gas) and duty truck engines in the transport sector (oil).

Grazie dell'attenzione
Domande?

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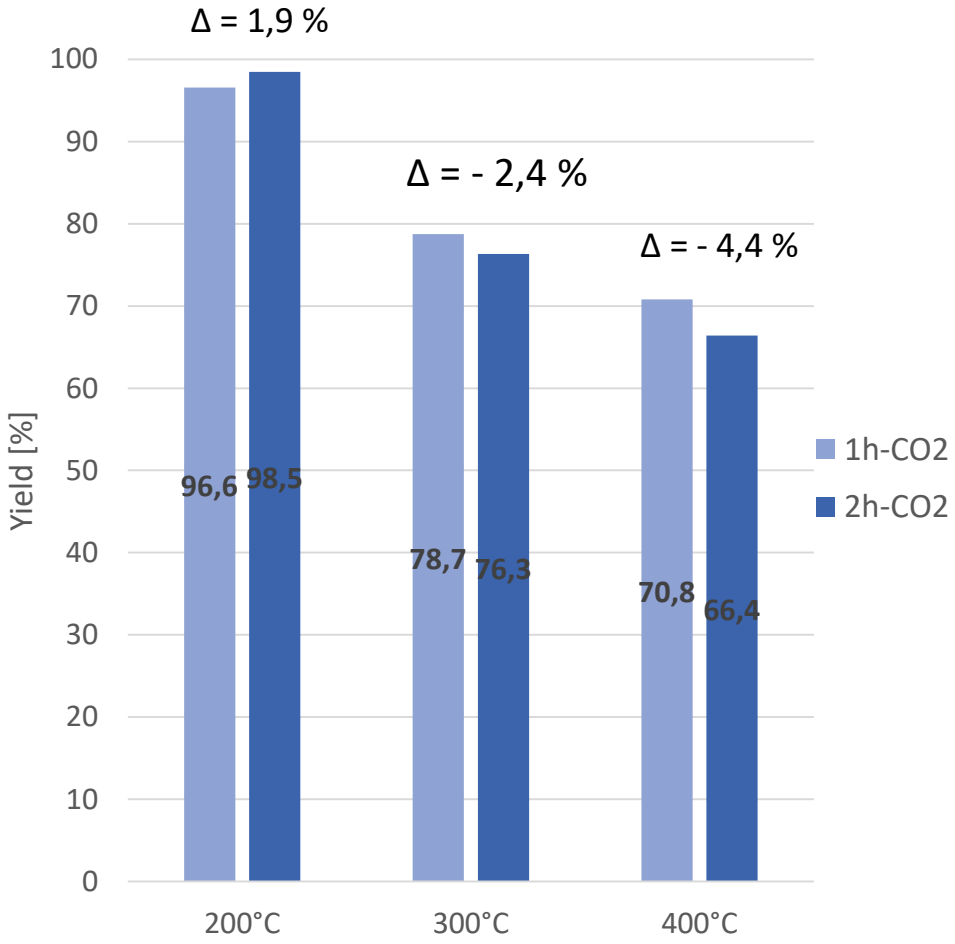
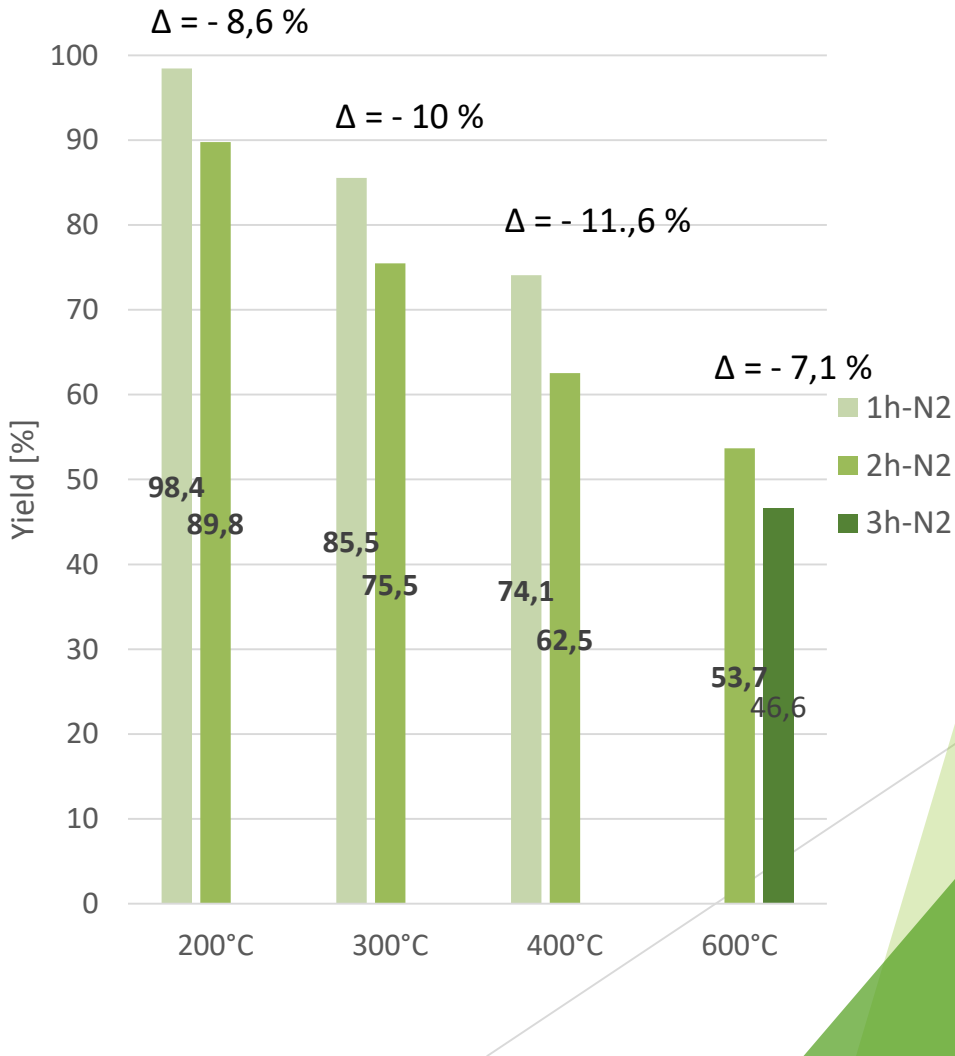
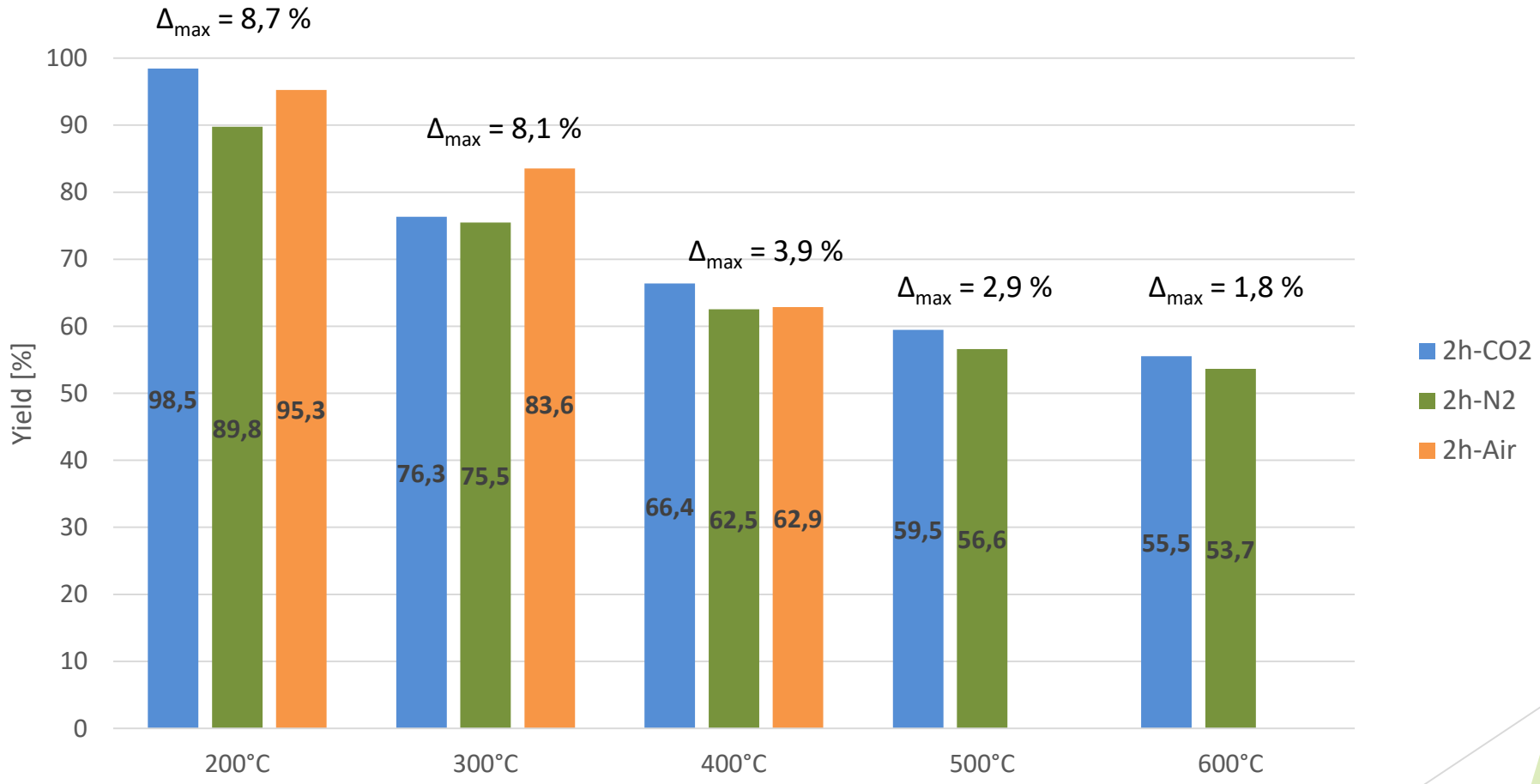
Supplementary material

Physical Activations – Influence of the Dwell Time on the char Yield

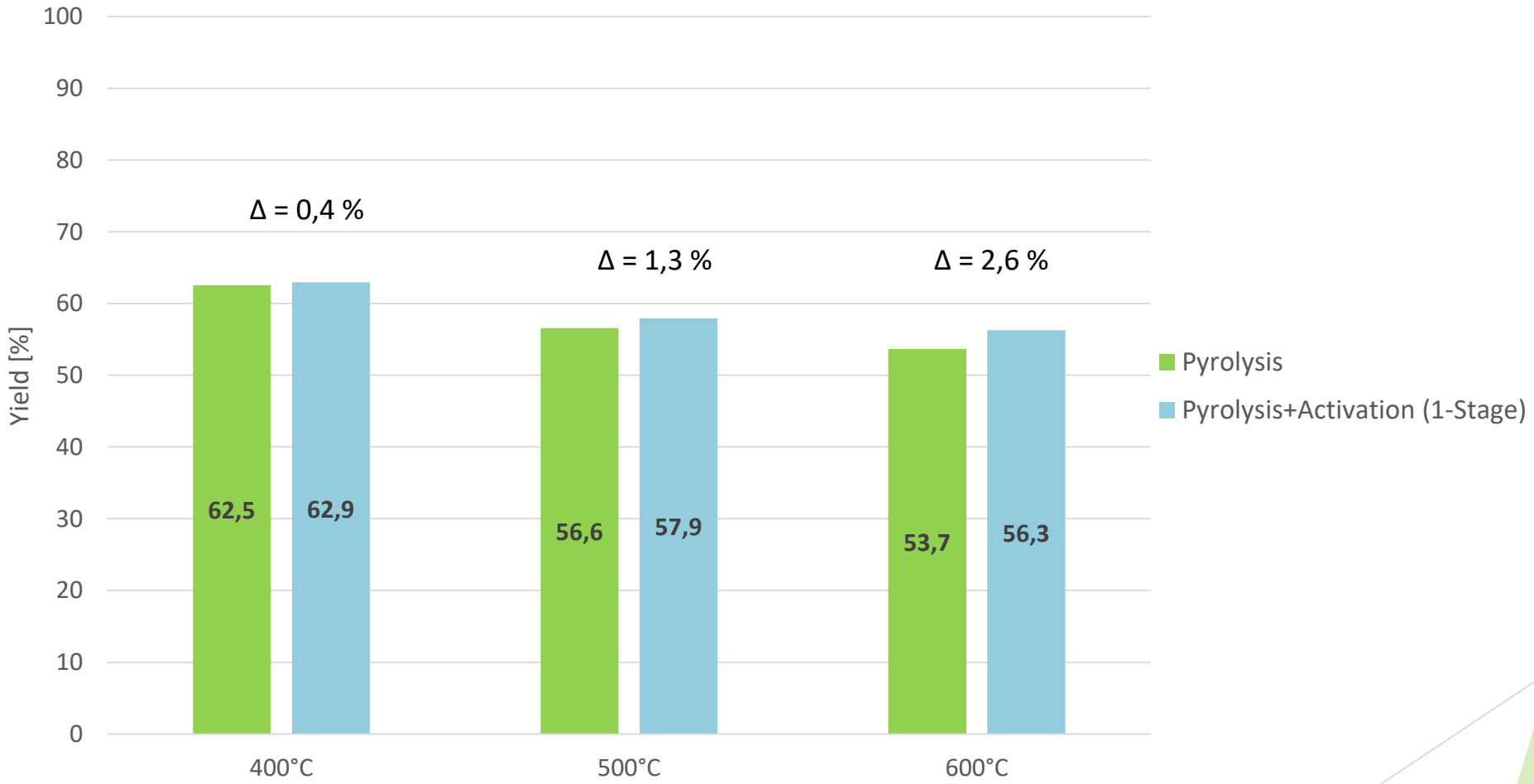




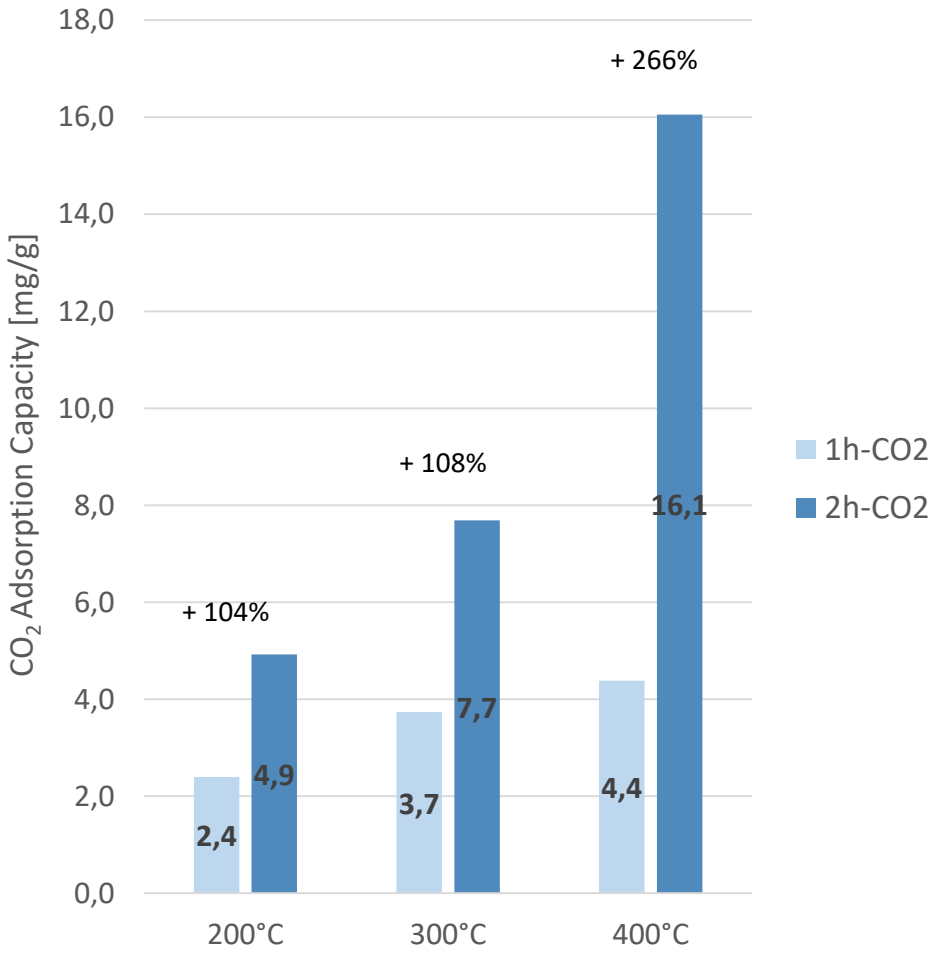
Physical Activations – Influence of the Atmosphere on the char Yield

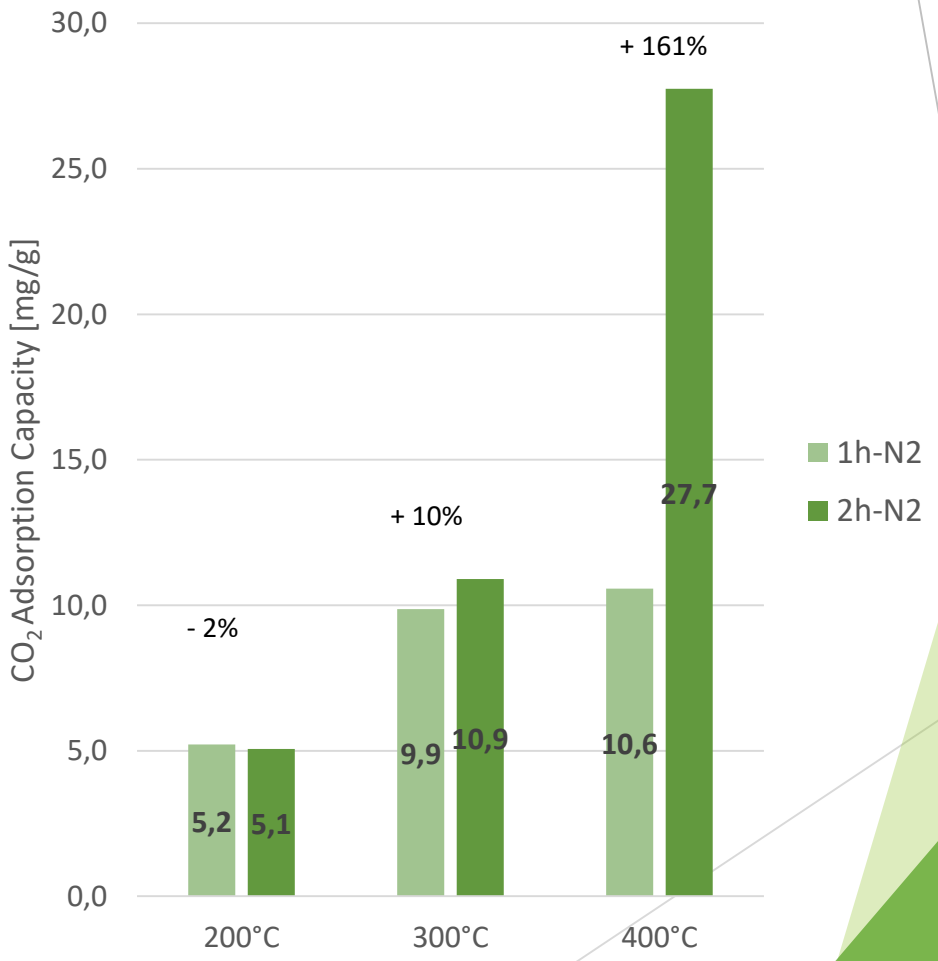


Physical Activations – Influence of the Activation Method on the char Yield

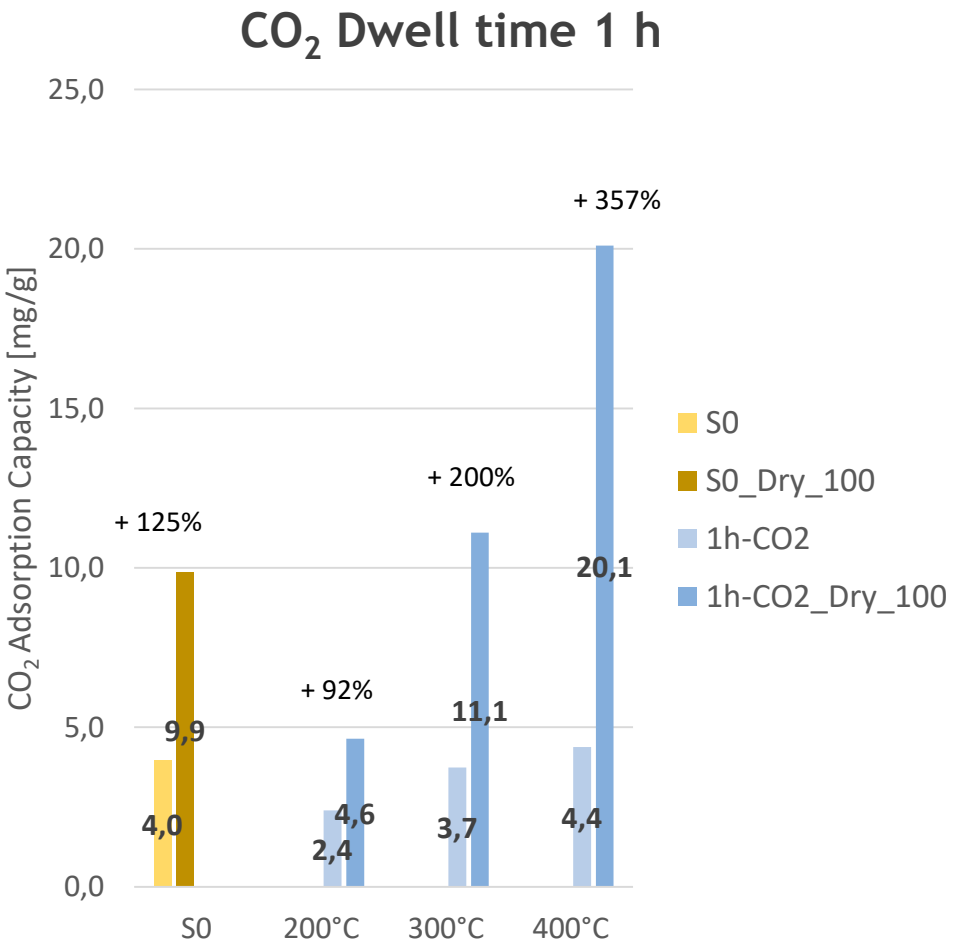


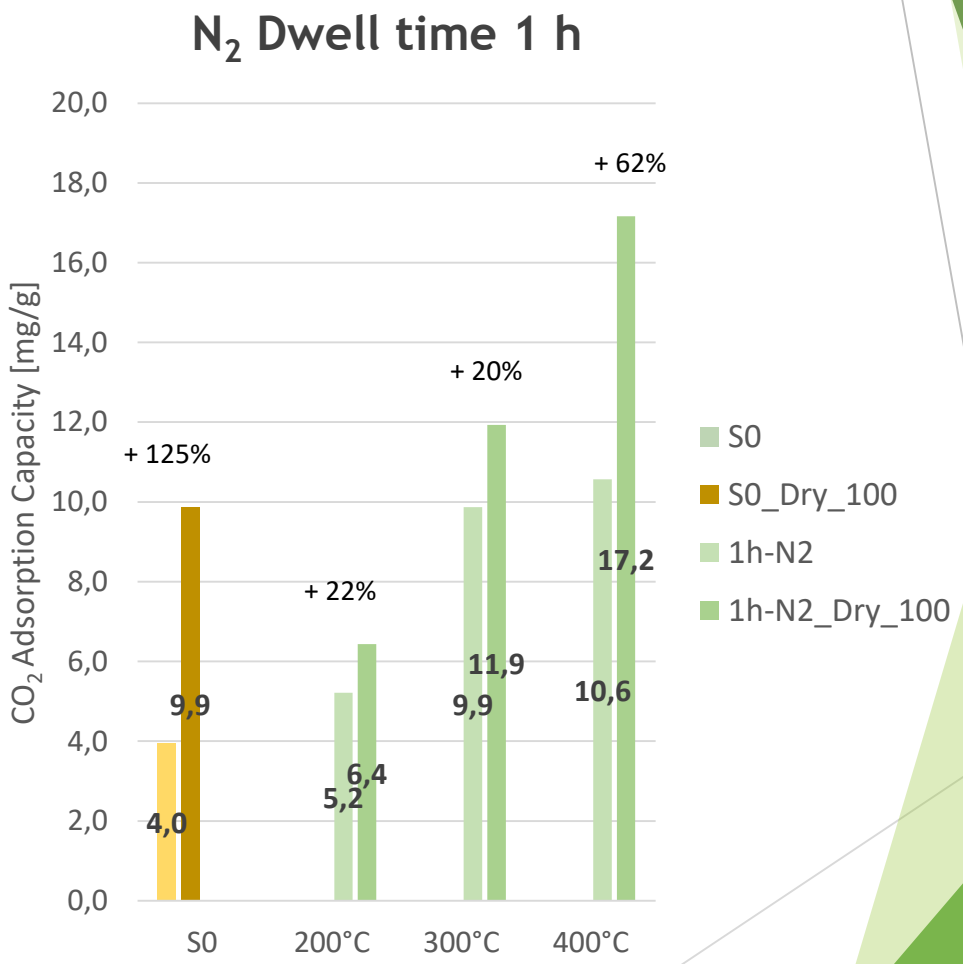
Adsorption tests – Influence of the Dwell Time on the Adsorption Capacity (variable water content)





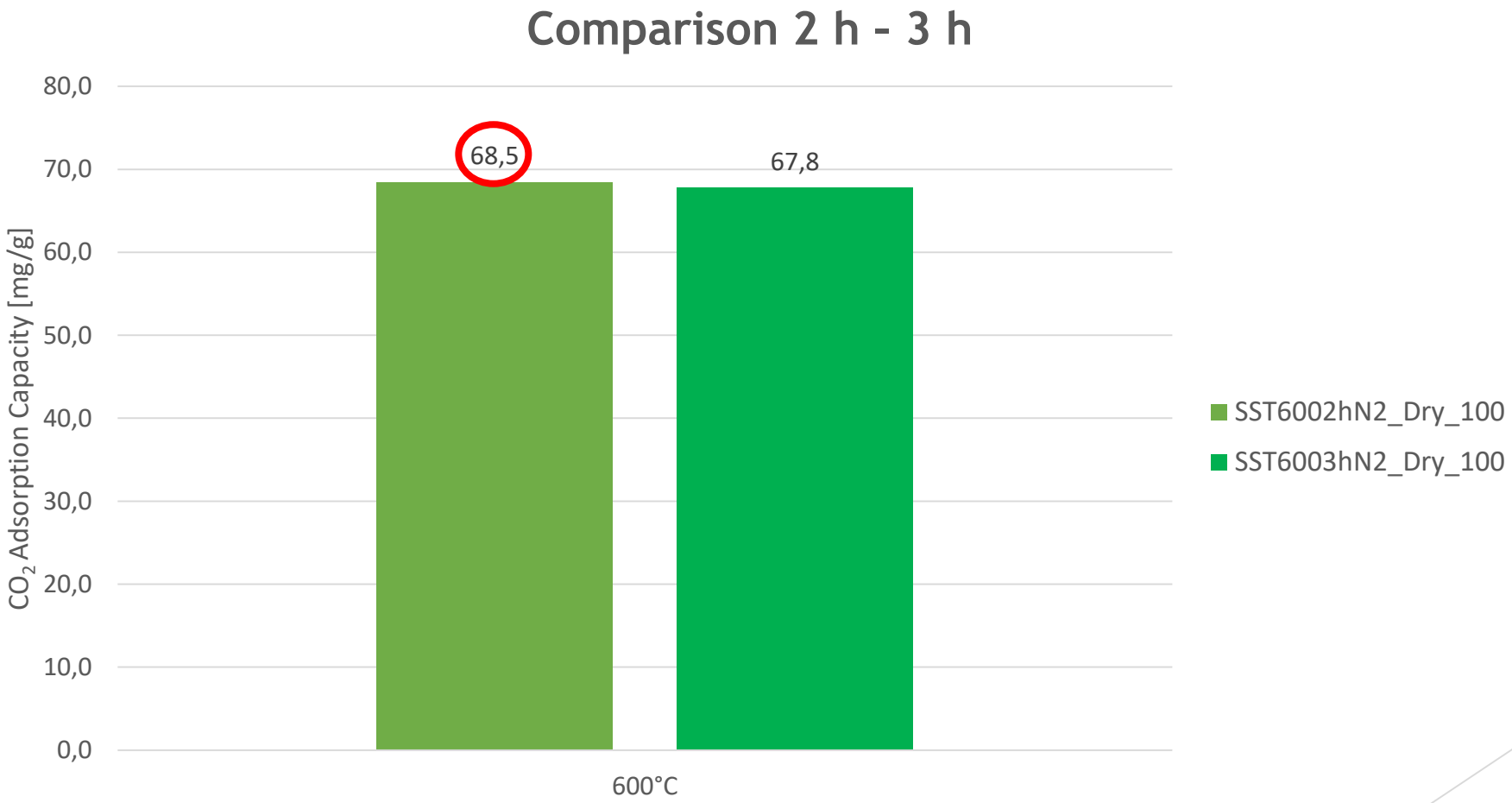
Adsorption tests – Influence of the Water Content



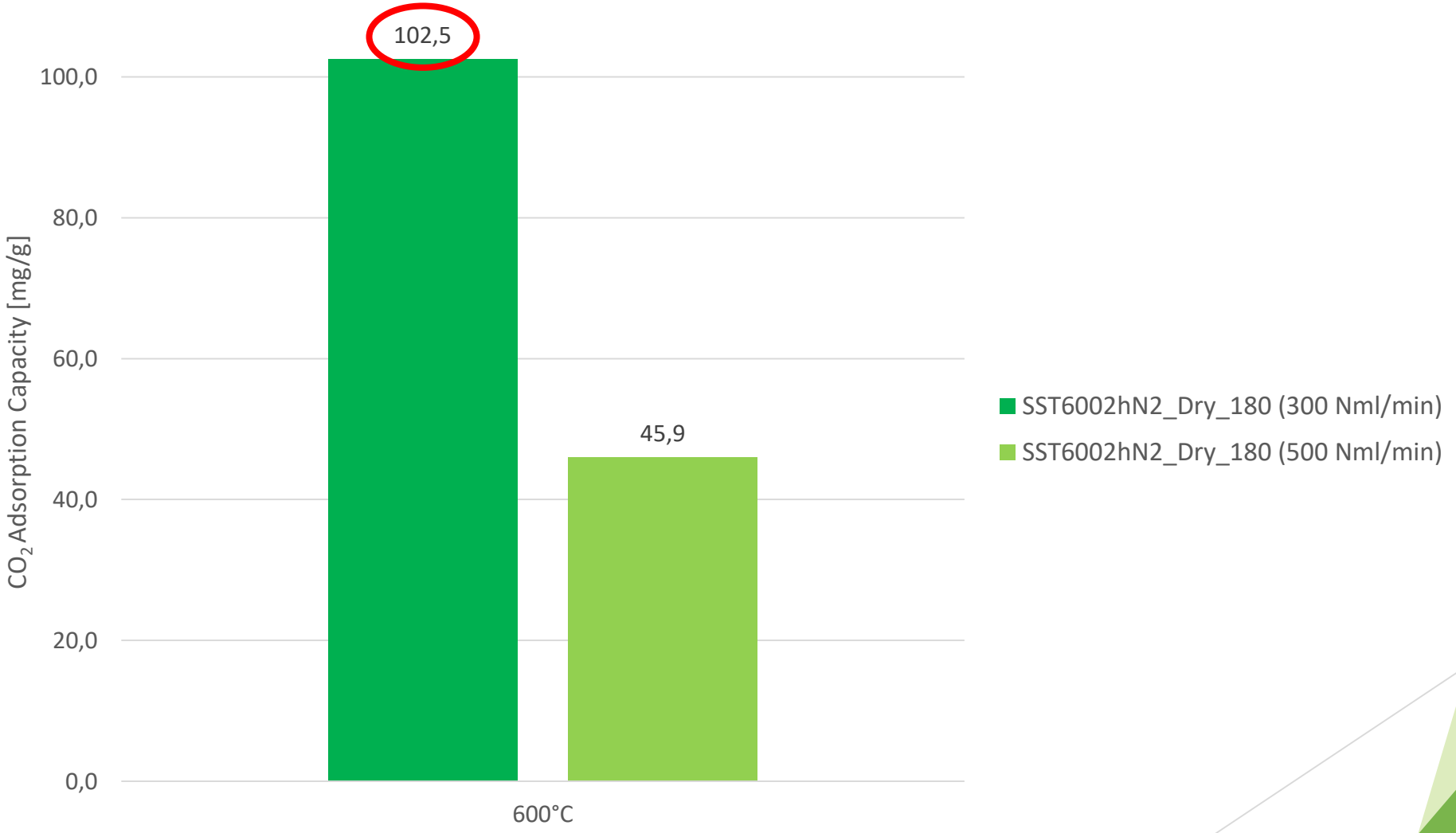


The legend “Dry_100” is referred to the dehydration of the related sample at the temperature of 100 – 110 °C.

Adsorption tests – Optimization – Dwell Time



Adsorption tests – Optimization – Activation Flow rate (300-500 Nml min^{-1})



Adsorption tests – Optimization – Activation Heating rate (10 – 20 °C min^{-1})