Porous hydrochars from hydrothermal carbonization of biomasses

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Process of hydrothermal carbonizarion

Biomass + Water → HTC process → Hydro-char + Gas + Liquid phase + Heat

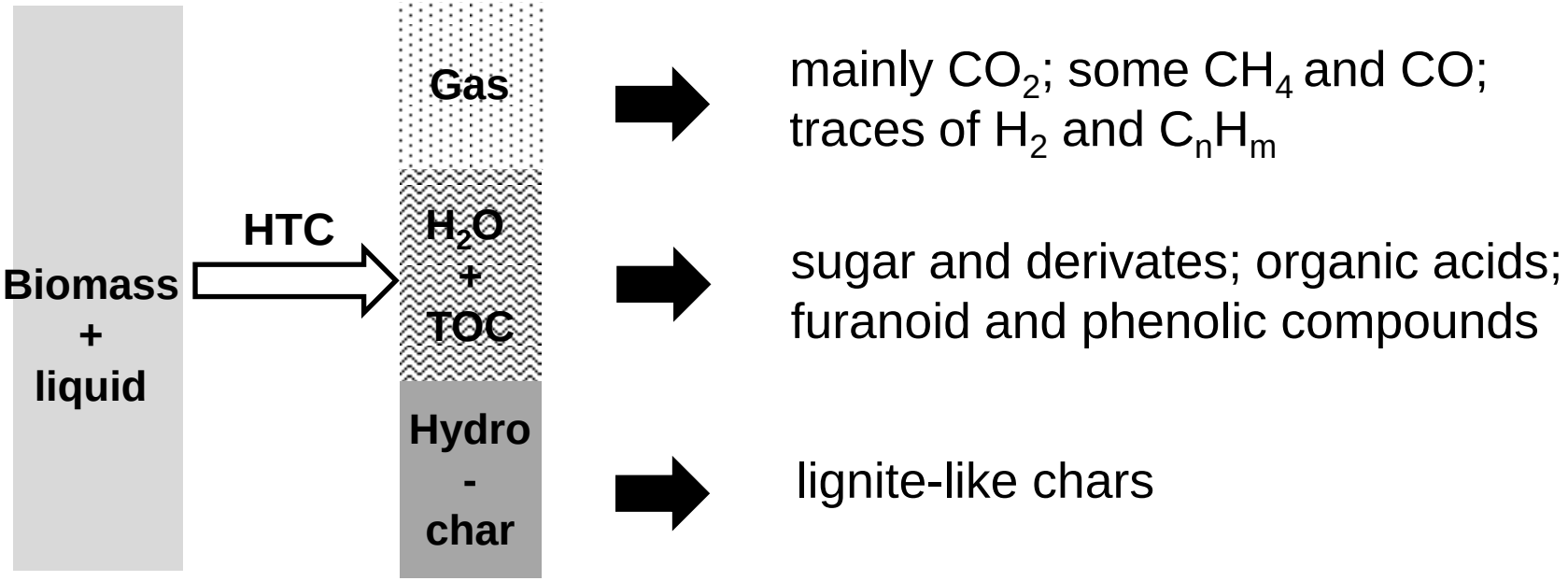
T about 200 ° C
p ca. 20 bar

1 h 3 h 6 h

Fotos: J. Pfingstmann

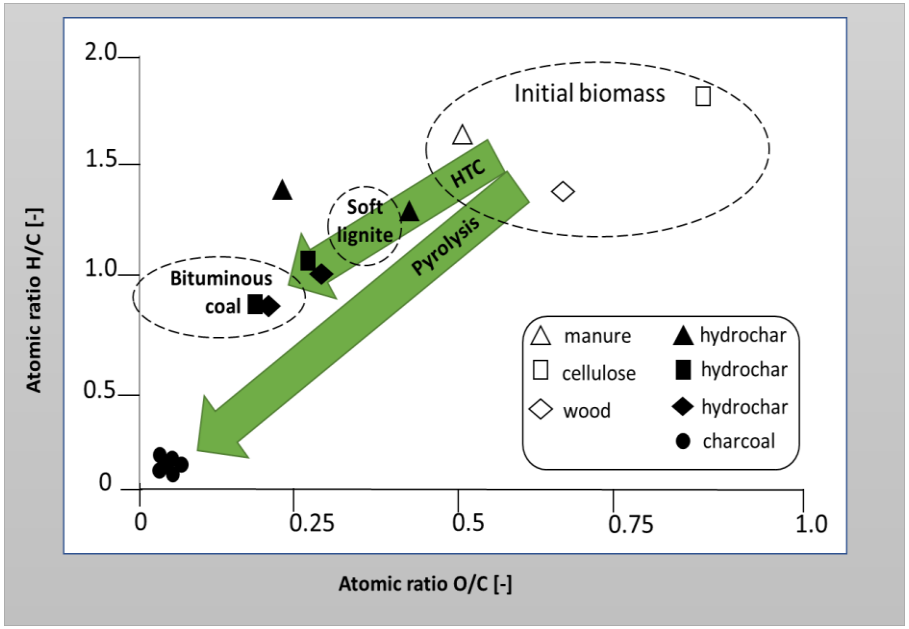
HTC products

- transformation of biomasses and **wet substrates** into biochar
- heating of biomass in aqueous suspensions to **180 – 250 °C** under elevated pressure
- chars with **high amount of functional groups** and small surface area (< 10 m^2/g)

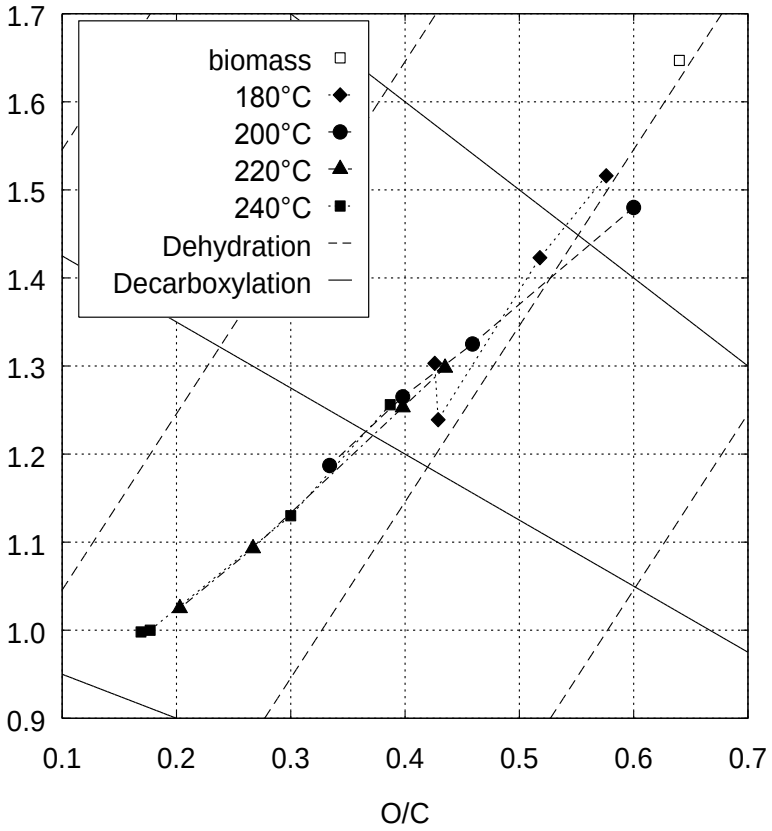


HTC vs. Pyrolysis

- Pyrolysis takes place at temperatures > 300 °C
  - lower H/C ratio
  - high aromatic content
- HTC takes place under pressure (~ 20 bar) and moderate temperature (~ 200 °C)
  - higher O/C ratio
  - high functionality

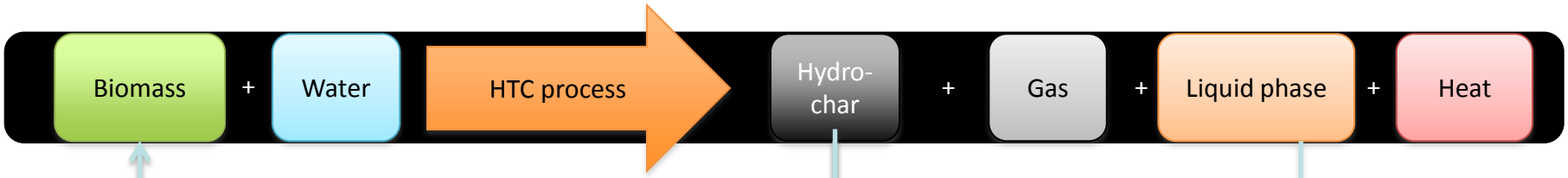


HTC of landscape management biomass

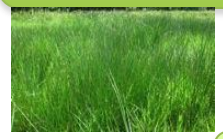


M. Röhrdanz, T. Rebling, J. Ohlert, J. Jasper, T. Greve, R. Buchwald, P. von Frieling, M. Wark,
Journal of Environmental Management 173 (2016), 72-78,
"Hydrothermal carbonization of biomass from landscape management - Influence of process parameters on soil properties of hydrochars"

HTC – Possibilities and challenges



Grass, leafs, maize silage, etc.



Digestate

Manure

Electrode material, Catalyst support

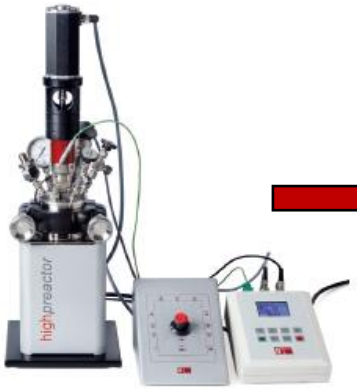
Additive for Bio-Polymers

Porous materiai/ adsorbens, filter

Peat substitute/ Soil improvement

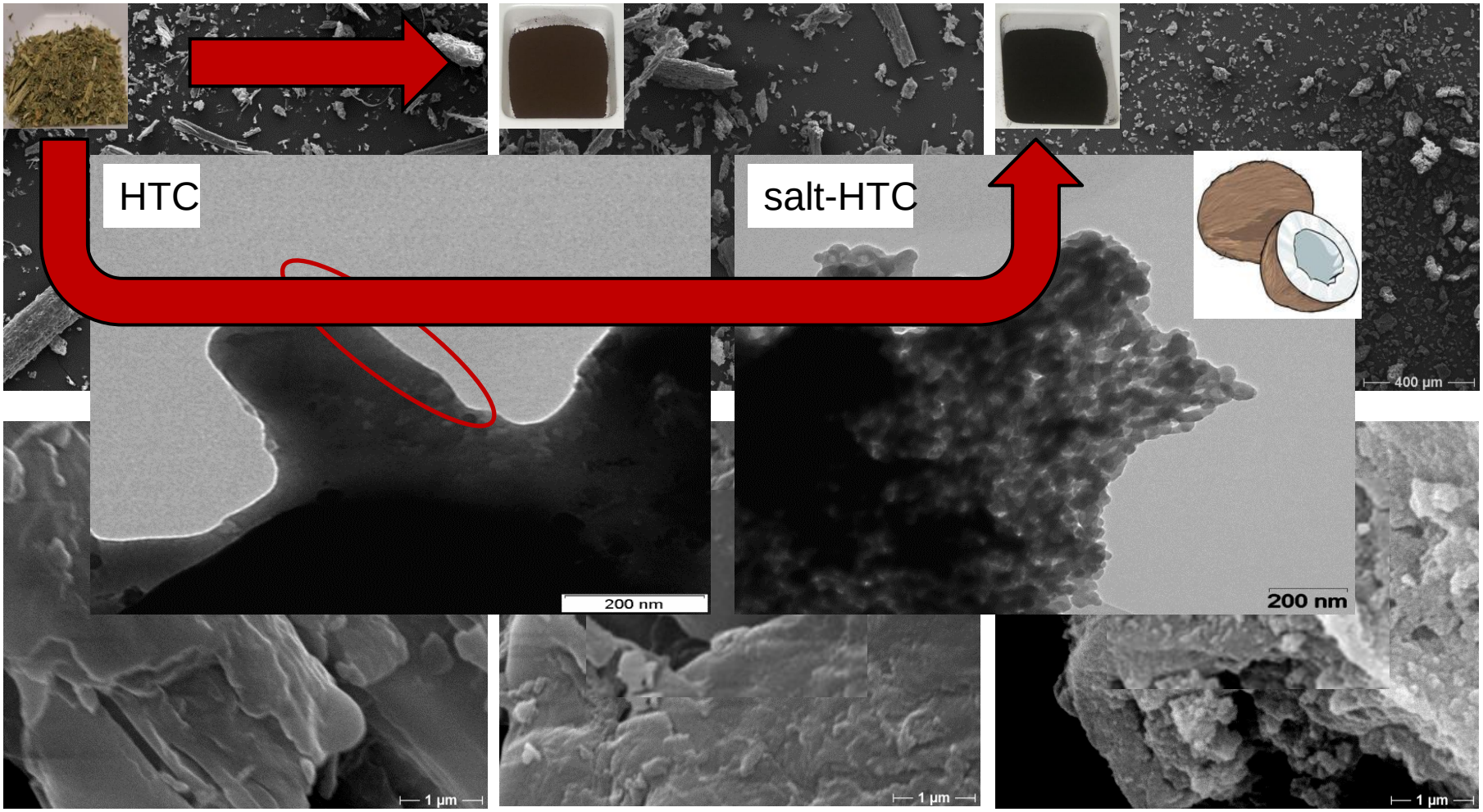
Process water treatment
- Analysis,
- Recirculation,
- Use in Biogas plants
- Use as fertilizer
- Feeding of algae
- Photocatalytic degradation

HTC with salt additives

Biomass, water, additive	HTC	Processing	Hydrochars
			
Glucose, HMF, Cellulose, Lignin, Grasses, Coconut shell, Rice husks, Dandelion leaves, Algae, Sawdust LiCl, NaCl, KCl, $ZnCl_2$, $MgCl_2$, Na_2SO_4, Na_2CO_3, ...	180-220 °C 4-36 h 200-2000 mL	Washing, drying, milling	EA, SEM/TEM, XRD, SS-MAS-NMR, FTIR, XPS, gas sorption, TGA, ...

Influence of additives on the morphology

Biomass (grass mixture) Hydrochar Salt-Hydrochar

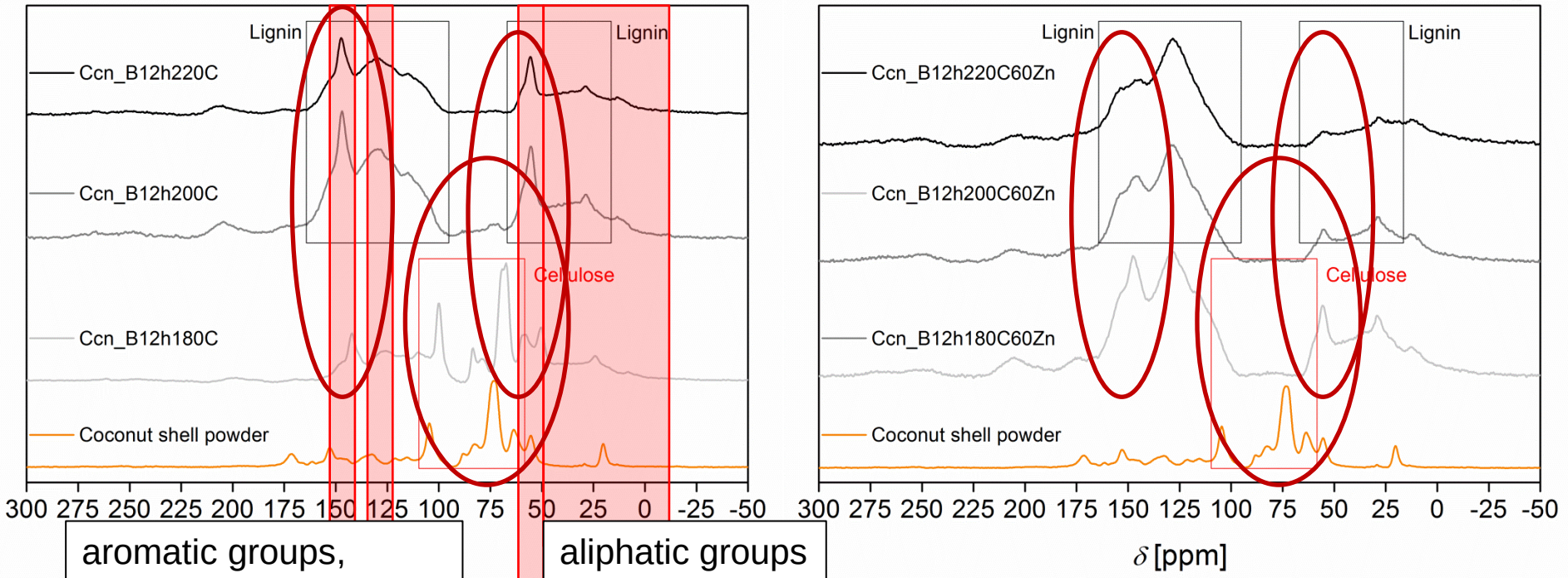


HTC-Biochar: Structure by Solid State NMR

HTC

^{13}C-solid state MAS-NMR spectra

Salt-HTC



aromatic groups, bound to lignin

aliphatic groups

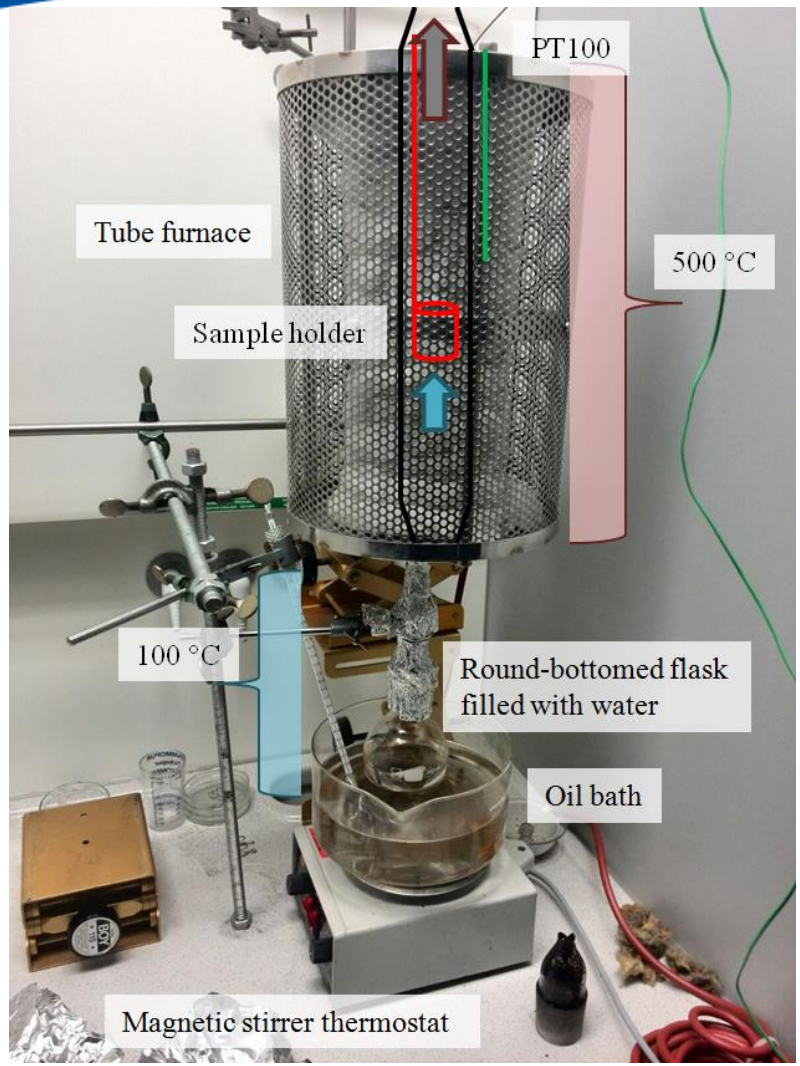
methoxy groups in lignin

sp^2 -carbon

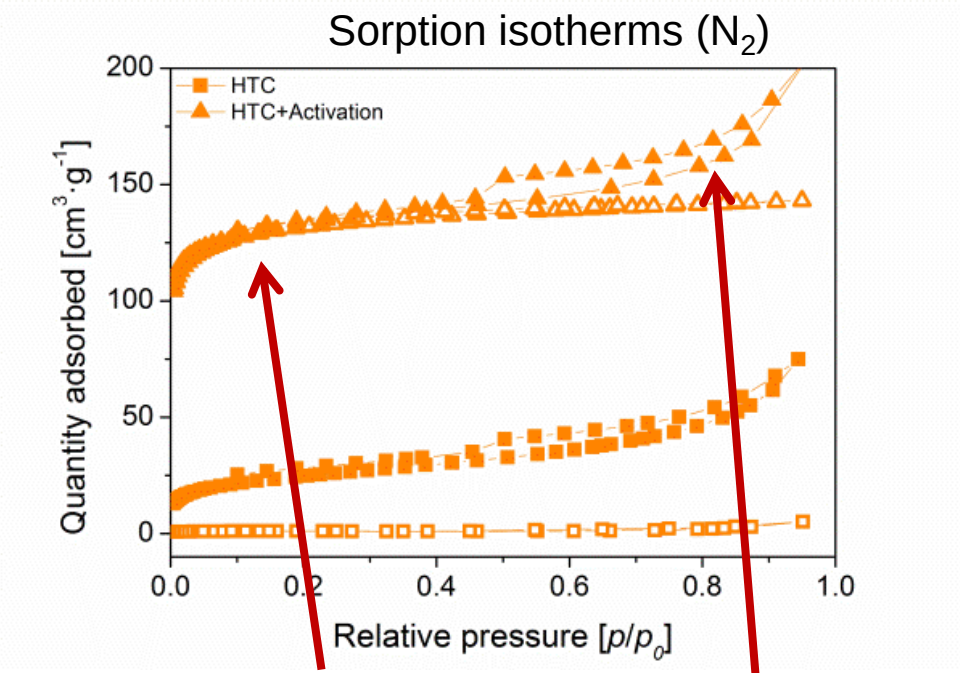
Effects of salt addition:

- Cellulose degradation at lower temperatures
- Degradation of lignin: Start at decreased temperature

Increased porosity by steam activation



- Sample in crucible
- Tube furnace (e.g. 500 ° C)
- Water vapor flows through the oven
- Yield: 20-30%



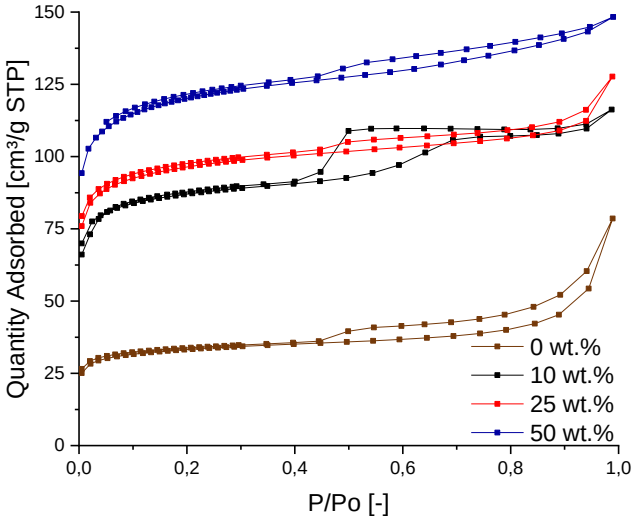
HTC, steam activated: microporous
Salt-HTC, steam act.: micro- and mesoporous

Mixtures of pig manure and coconut shell

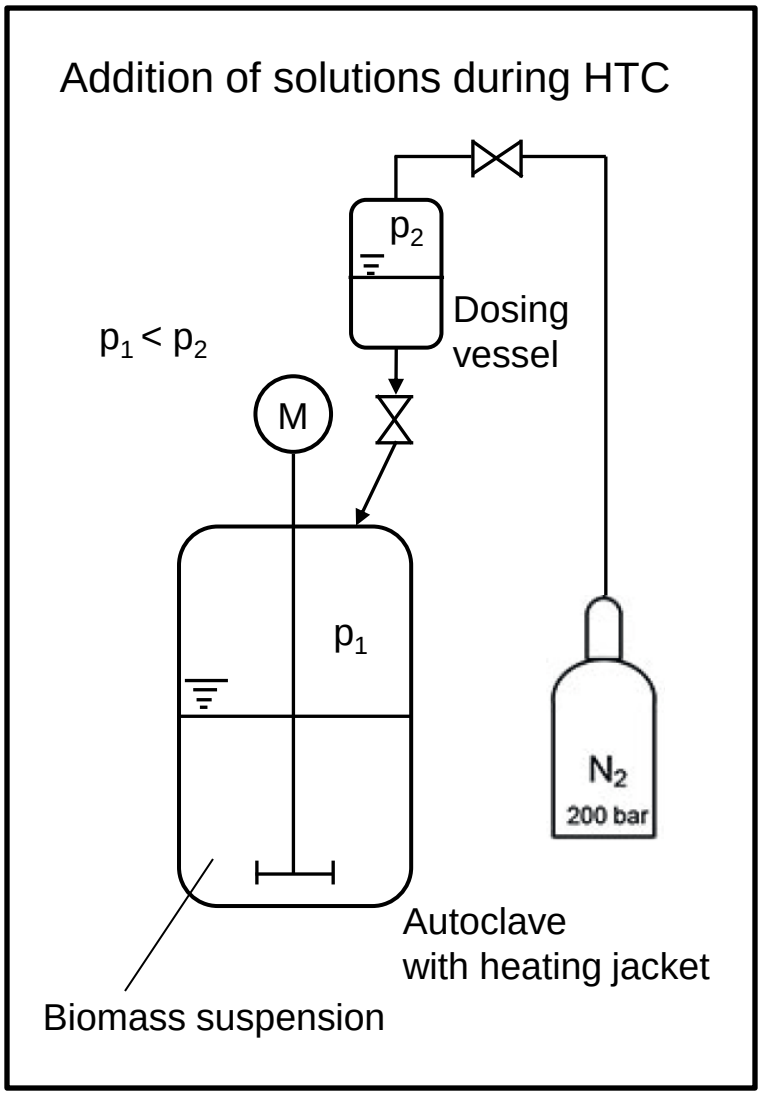
Biomass [-]	Reaction time [h]	Amount of Coconut shell [wt.%]	Surface area [m²/g]
Manure	1	0	143
		10	294
		25	401
		50	364
Manure	4	0	125
		10	335
		25	365
		50	454

- Hydrochars from mixtures of soft and hard biomass:
  - Higher surface areas (N_2 sorption) than hydrochars from HTC of pure pig manure
  - Comparable properties to hydrochars obtained with salts as additives

4 h ; 220 °C



HTC in presence of bases and/or acids



- Making use of sand (SiO_2 source) – being present in the biomass – for creating porosity (as hard template)
- HTC under alkaline and acidic conditions via addition of NaOH and H_2SO_4

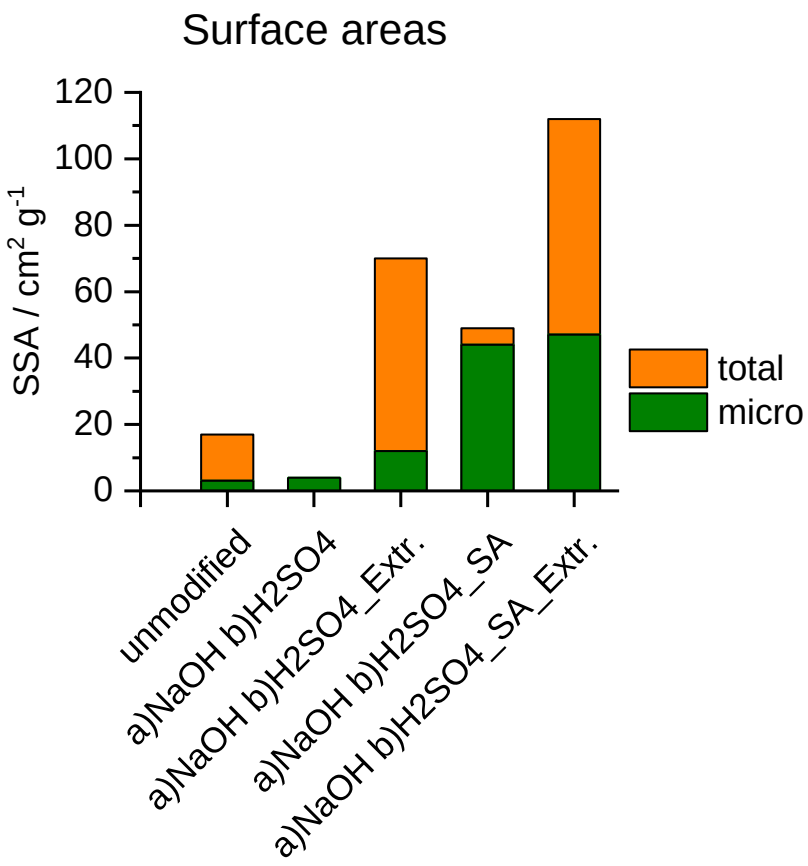
→ Alkaline and acidic one-pot HTC

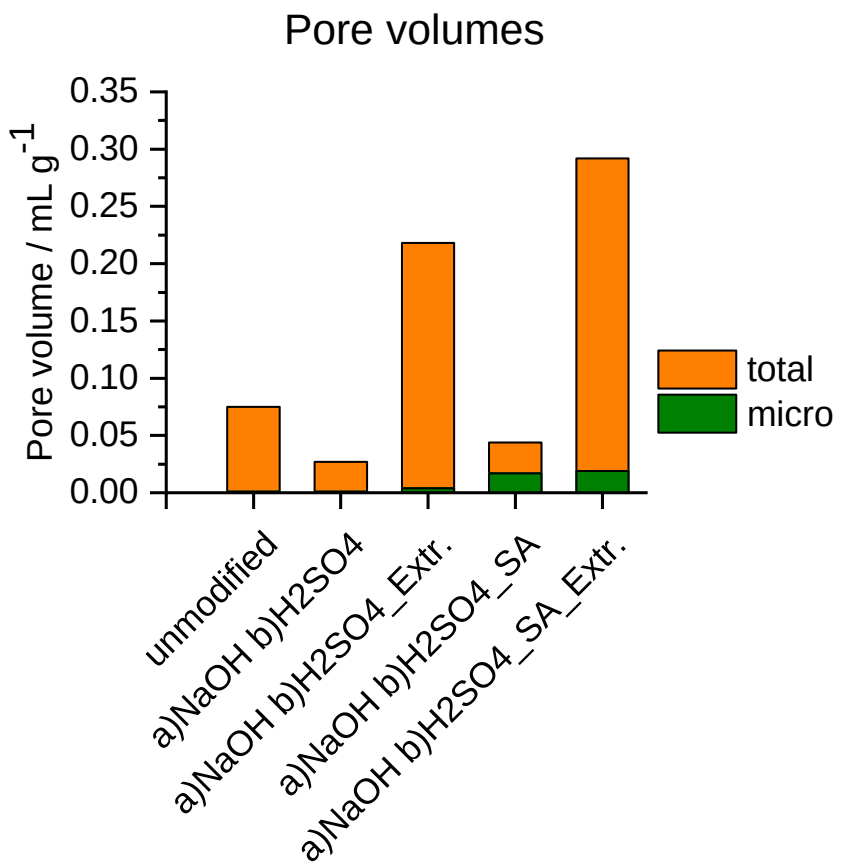
Experiments

Abbreviation	Discription
SA	Subsequent Steam activation, 650 °C, 1h
Extr.	Subsequent Suspension in 0.5 M NaOH solution overnight
NaOH	HTC in 1 M NaOH
H_2SO_4	HTC in 0.5 M H_2SO_4
a) NaOH b)H_2SO_4	HTC in 1 M NaOH, addition of 1 equiv. H_2SO_4 after 9.5 h, cooling down after 12 h

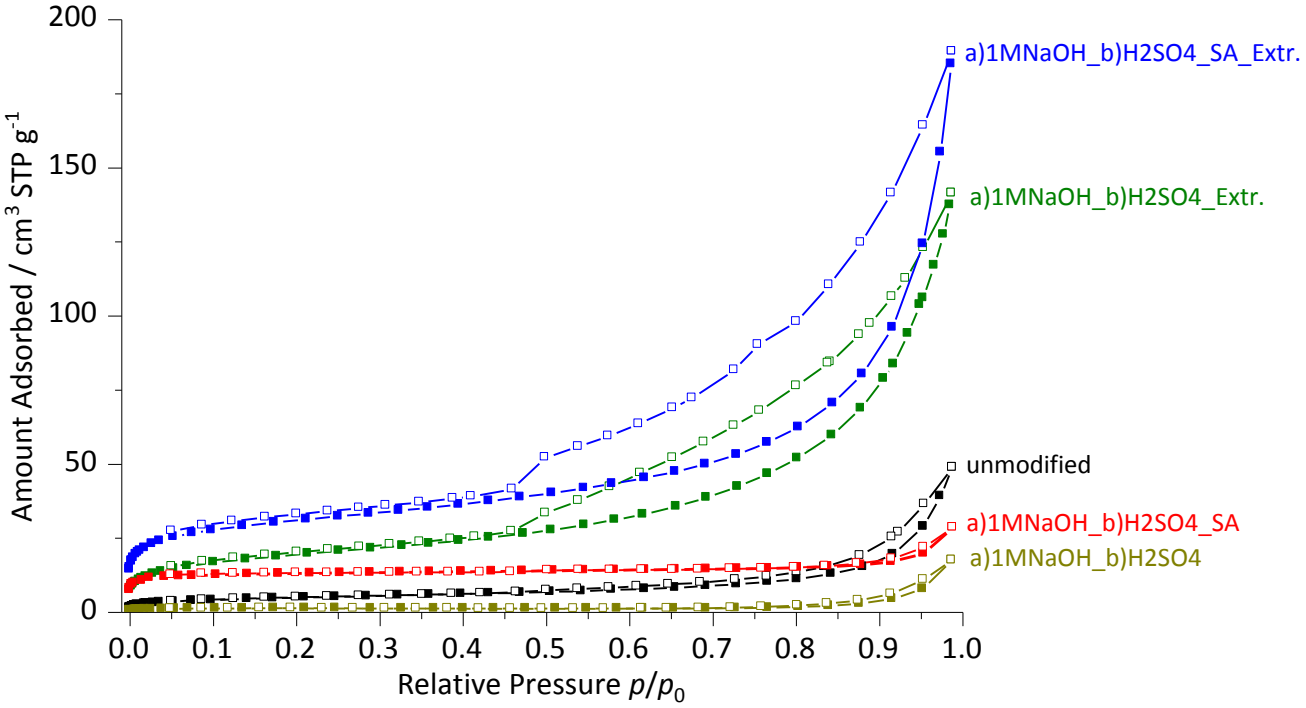
HTC of digestates with base/acid

Use of fermentation residues from a biogas plant (provided by Heidekreis)





HTC of digestates with base/acid



Sample	SSA_{total} / m^2 g^{-1}	SSA_{micro} / m^2 g^{-1}
Unmodified	17	3
a) NaOH, b) H_2SO_4	4	4
a) NaOH, b) H_2SO_4_Extr.	70	12
a) NaOH, b) H_2SO_4_SA	49	44
a) NaOH, b) H_2SO_4_SA_Extr.	112	47

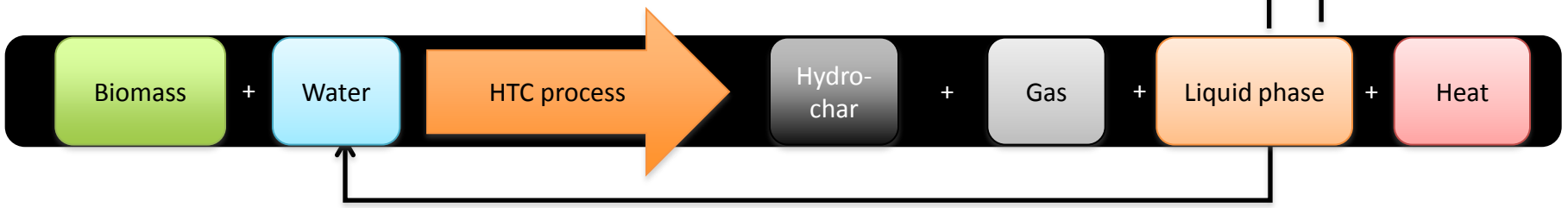
Cleaning of the HTC water phase

- Direct from HTC process:
  Chemical oxygen demand (COD): 10 – 70 g/l
- Required: COD < 1 g/l
- Solution: extraction of valued products,
  degradation of organics?

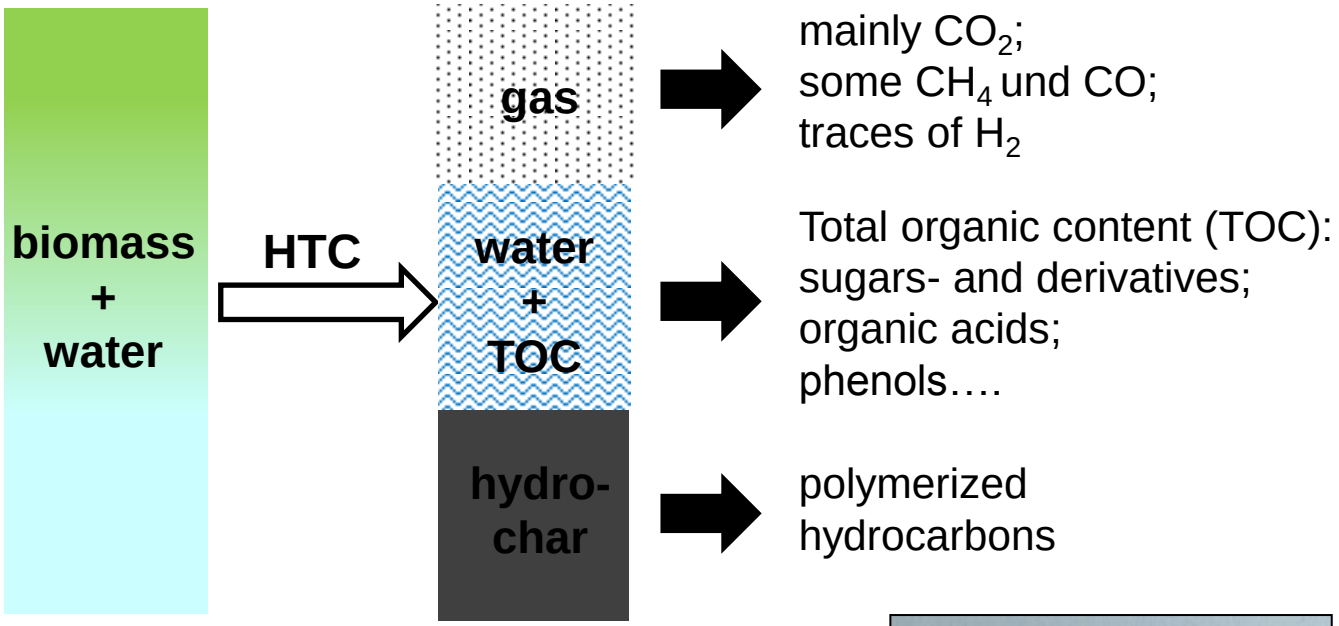
Extraction of chemicals, , e.g. 5-HMF, phenols

Water	200°C 15 min	200°C 60 min

Make-up:
By chemistry? physics? biology?



Phases in HTC

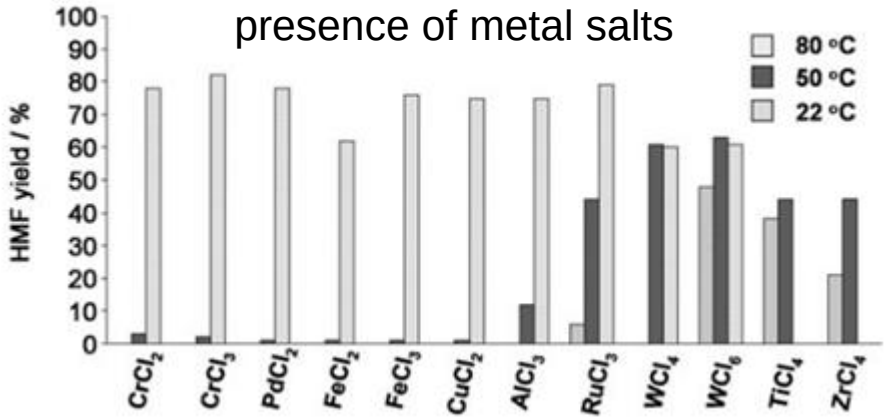


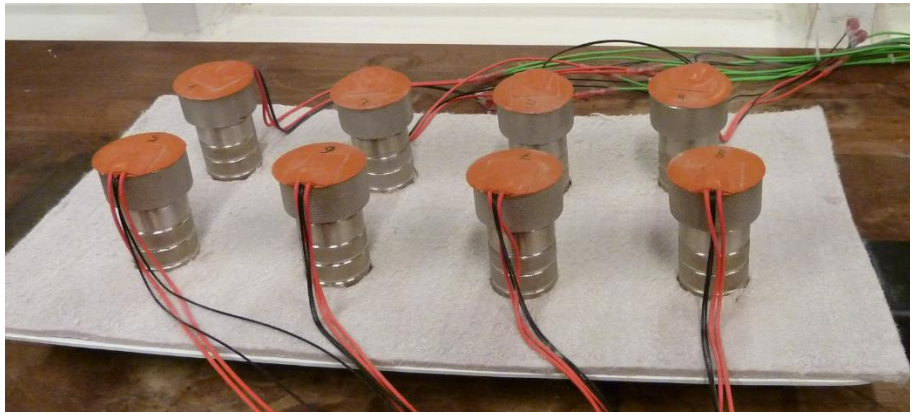
Main research
→ Qualitative and quantitative analysis of the aqueous HTC process water

Main aims
→ Reduction of TOC
→ Getting information about it‘s composition

First results to 5-HMF extraction

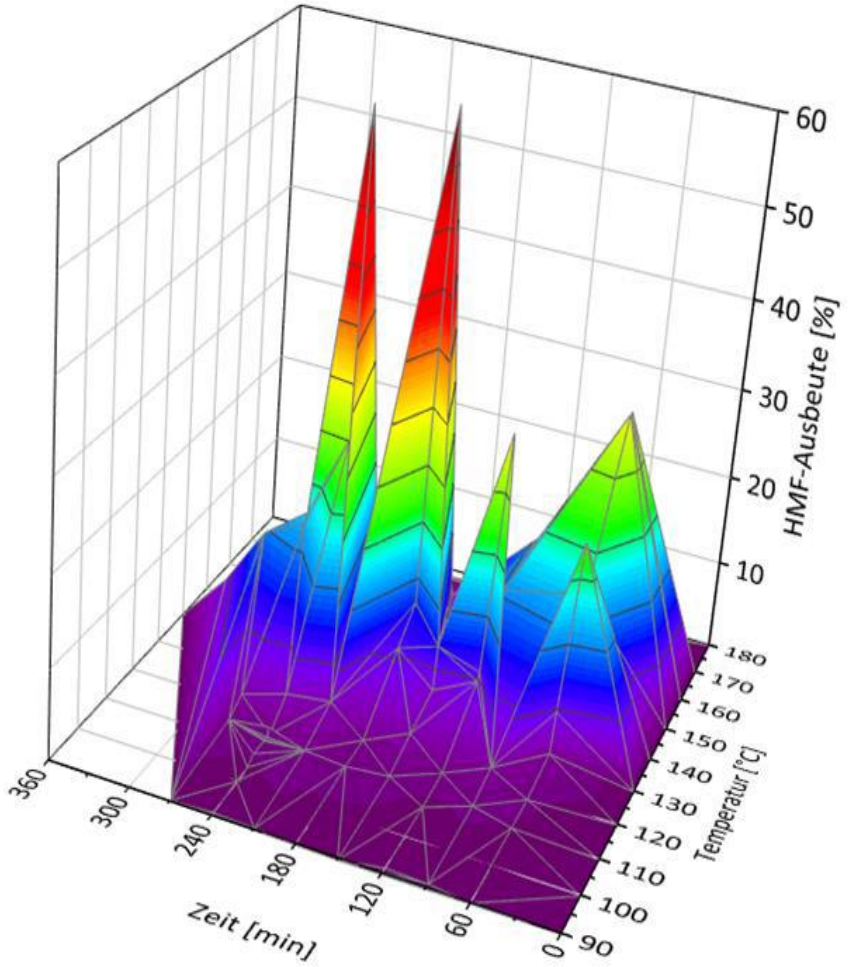
5-HMF extraction in presence of metal salts



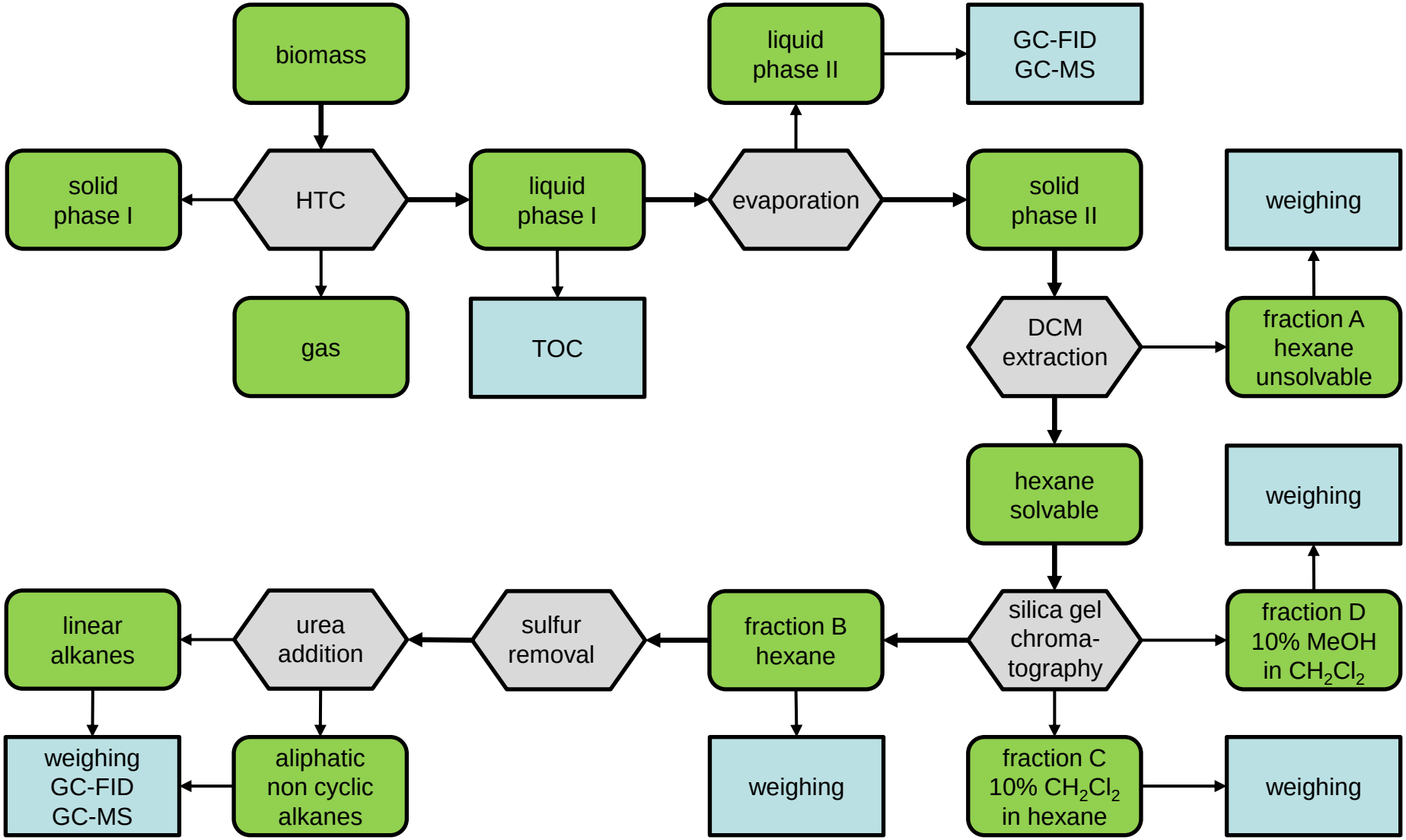


Multi-autoclave setup for Hydrolyzation
10 ml volume Teflon® inlet
Energy comes from a heating plate

Results of the extraction of 5-HMF from HTC waste water

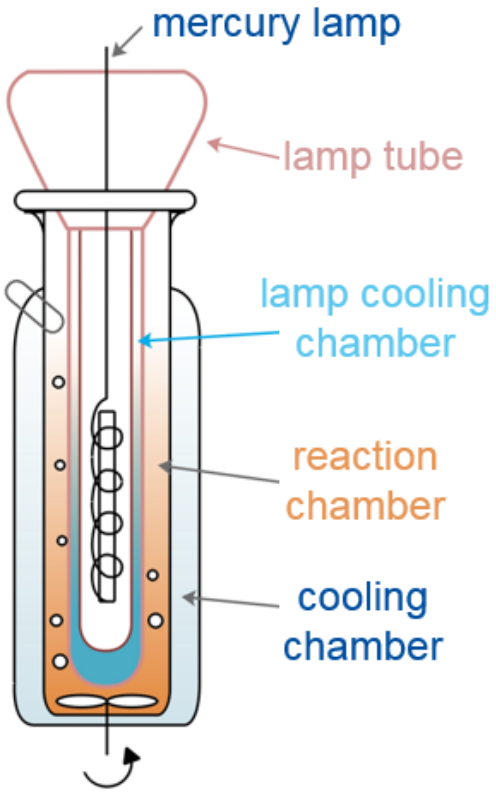


Fractioning of organics in HTC water phase



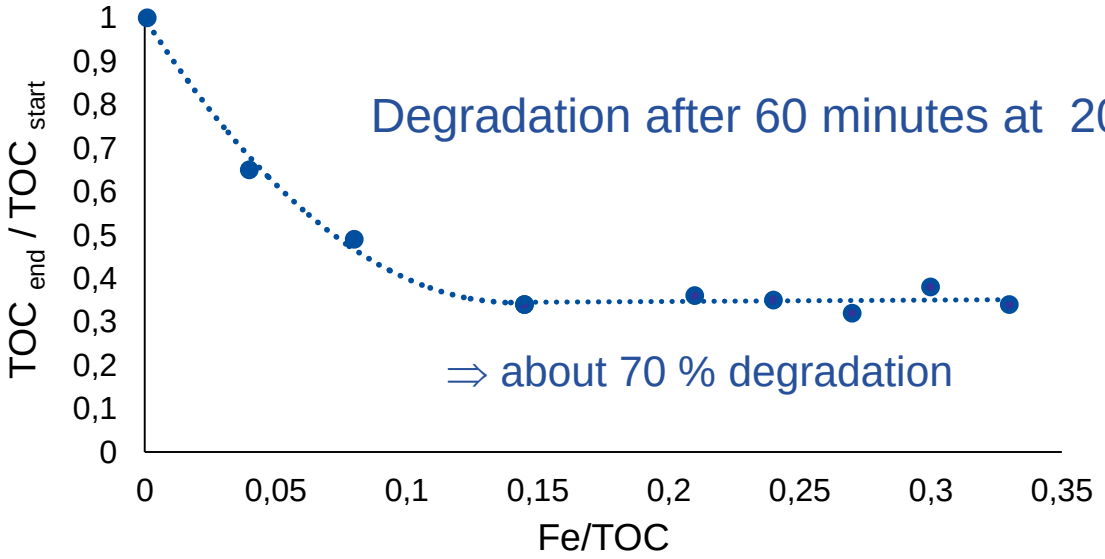
Degradation of the organic compounds: Photo-Fenton reaction

700 mL Volumen

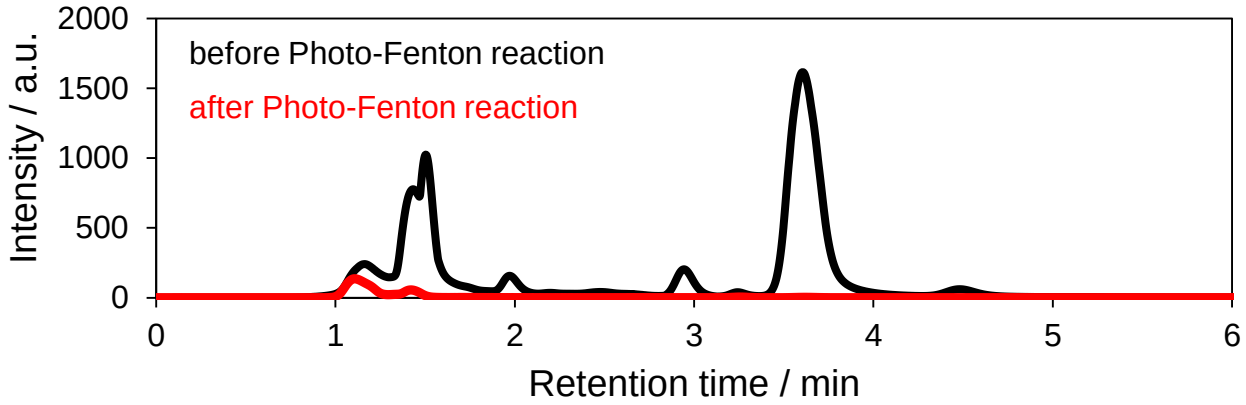


Reagents:

- HTC water phase
- Fe(II) salt
- H_2O_2

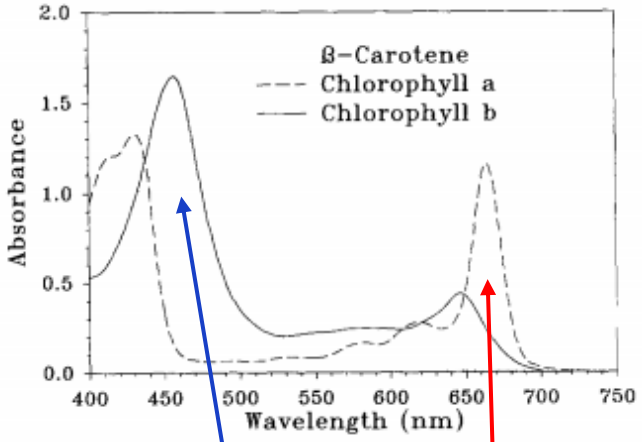


Gas chromatography analysis

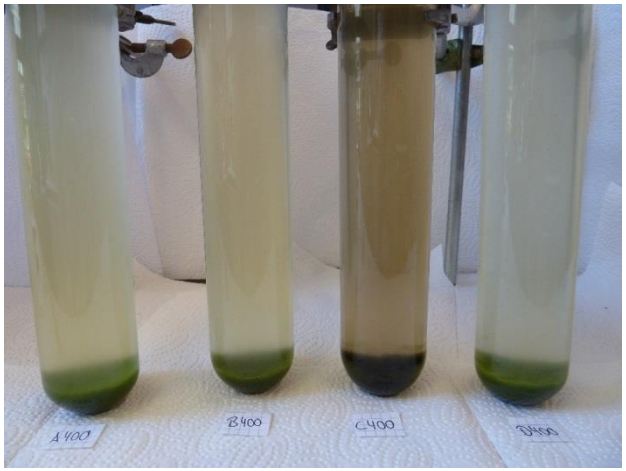


- peak areas decrease by about 95%,
- some compounds are not UV active ⇒ not detectable

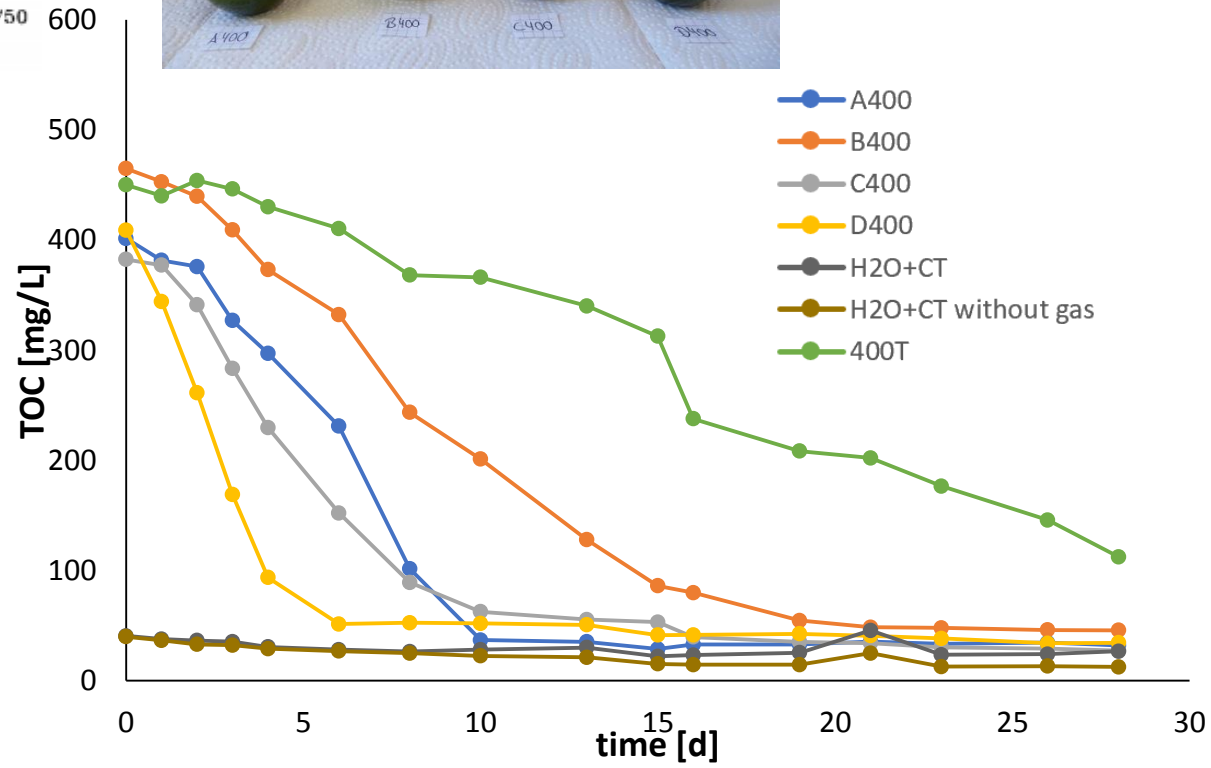
Degradation of the organic phase by algae



LED	blue	green	red
λ [nm]	467-470	570-575	620-625
Status	max	off	max



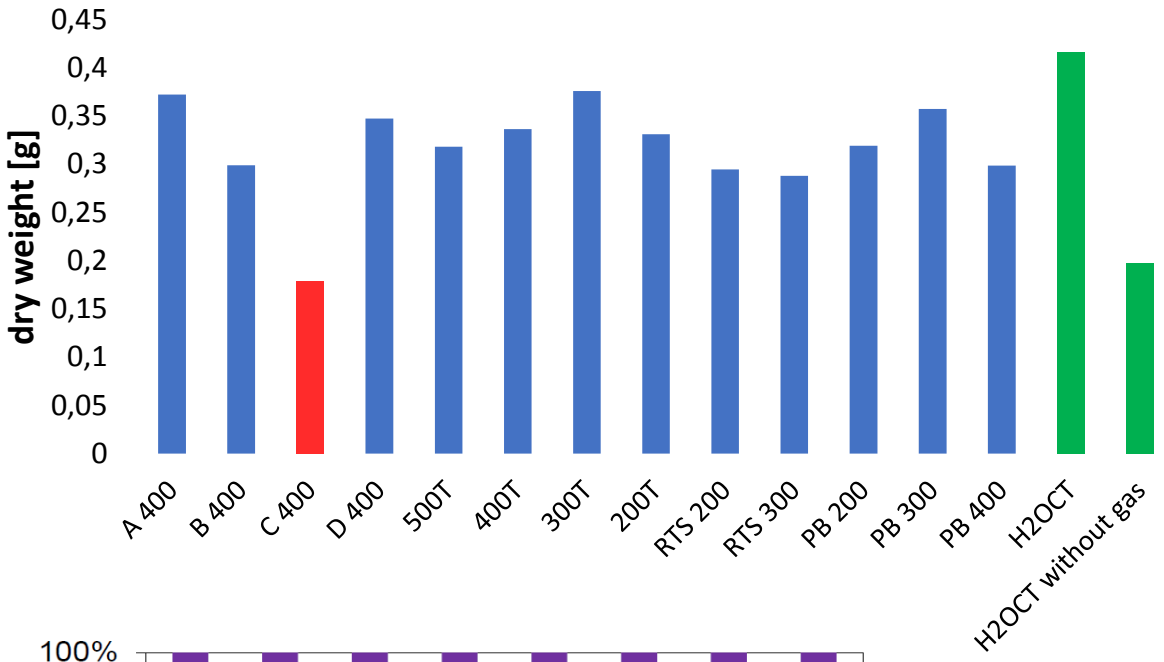
A	insoluble in hexane
B	non-polar
C	aromatics
D	NSO compounds

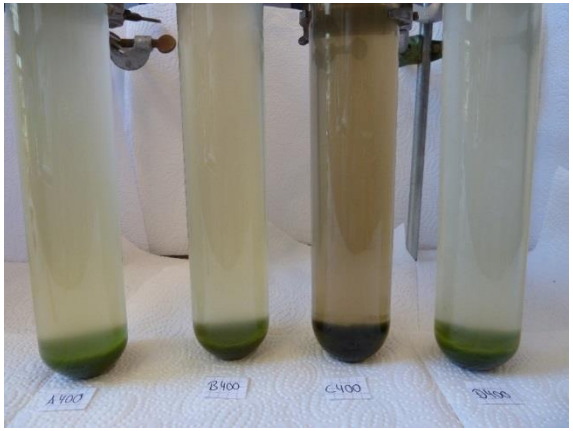


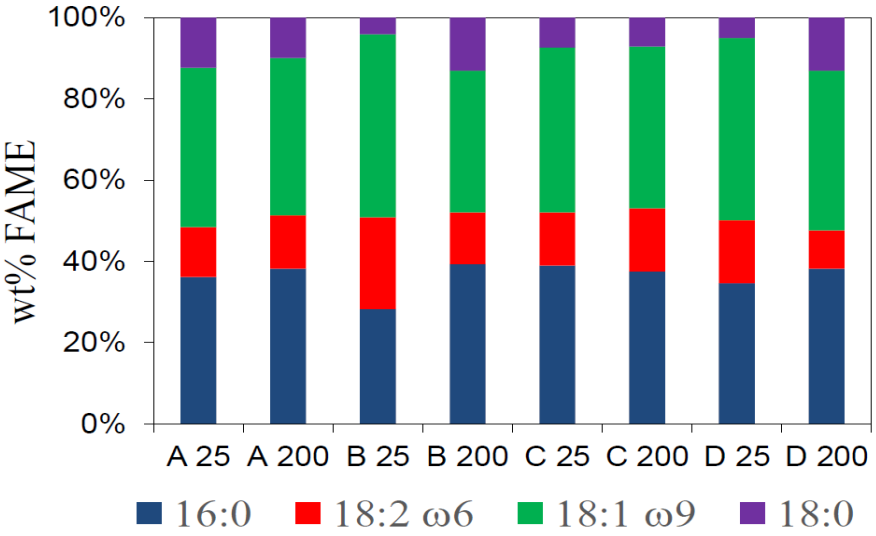
Dry mass of the grown algae

Organic phases for feeding the algae:

A	insoluble in hexane
B	non-polar
C	aromatics
D	NSO compounds
T	terephthalic acid
RTS	pig manure
PB	cattle manure







Composition of the formed fatty acids

Summary

- Hydrothermal Carbonization leads to hydrochars with more chemical functionality (functional groups for interaction with other species) than biochar from pyrolysis.
- HTC hydrochars are peat or brown coal (lignite) like.
- HTC hydrochars show a potential for applications as „green activated carbons“ (adsorption of gases, dyes, herbicides, pesticides, etc.), filter materials, catalyst supports, …
- Tailored mixtures of soft and hard biomasses can create porosity / inner surface without use of additives after activation with steam. Lignin structures act possibly as internal templating agent. However, the chemical functionality is partly lost due to the treatment with steam.
- The total organic content (TOC) of the HTC water phase can be lowered significantly by Photo-Fenton reaction (requiring hydrogen peroxide) or the use of algae. The (somewhat stressed) algae produce more fatty acids than under ideal growth conditions.
- Extraction of valued products like 5-HMF from the organic contaminants of the HTC waters seems to be possible.

Many thanks for your kind attention