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activated hydrochars made from moist-dry biomass mixtures

Grüne Kaskade project meeting

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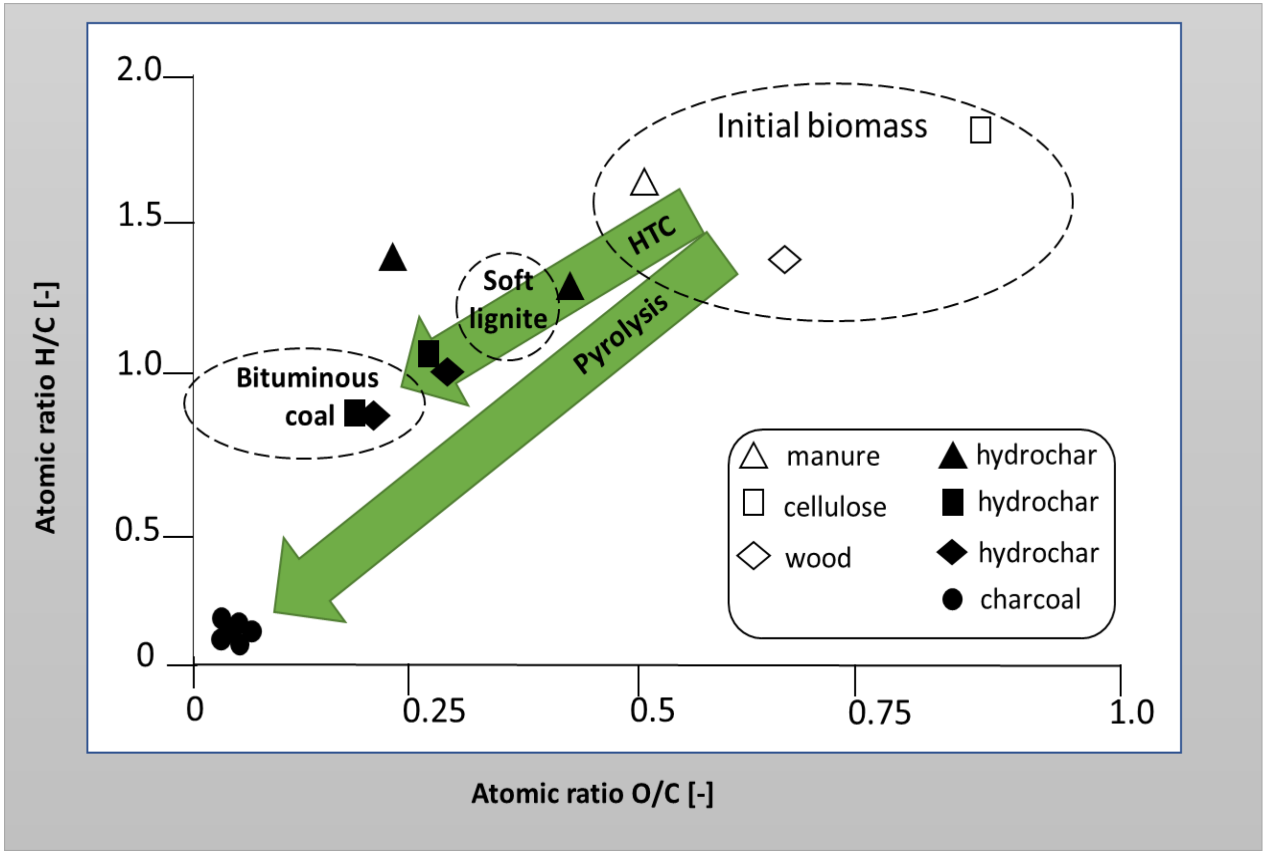
HTC vs. Pyrolysis

- Two general processes to convert biomasses into biochars
  - ➢ pyrolysis
  - ➢ hydrothermal carbonisation (HTC)

- Pyrolysis takes place at high temperatures (> 300 °C)
  - ➢ only dry biomasses
  - ➢ 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



552_44079_HTC.png

- Activation tests in a tube furnace

- Sample in crucible

- Reaction conditions
  - ➢ T = 650 °C
  - ➢ t = 1 h
  - ➢ inert atmosphere

- Water vapor flows through the oven

Bio activated carbon made from pure manure

ss	Reaction time [h]	Temperature [°C]	SSA [qm/g]
re	1	180	70
	4		115
	8		135
	12		169
re	1	220	124
	4		142
	8		137
	12		150

- High temperatures lead to hydrochars with bigger surfaces at lower reaction times
  - ➢ faster polymerization reactions?

- Reaction time of 4 h at 220 °C seems sufficient

Key questions

- Application of produced hydrochars as…
  - ➢ economic adsorbent
  - ➢ electrode material
  - ➢ catalyst carrier

- How can we create hydrochars with surface areas > 10 m^2/g ?

- Increased carbon content benefits activation processes in the gaseous phase
  - ➢ dry content in manure is round about 10 %
  - ➢ surface enlargement with the use of corrosive, chemical agents like acids or salts

- What about the use of lignin rich biomasses as additives in the HTC process?

Bio activated carbon made from coconut shell / manure mixtures

s	Reaction time [h]	Coconut shell [wt.%]	SSA [qm/g]	Coconut shell [wt.%]	SSA [sm/g]
e	1	0	125	25	294
		25	401	50	364
e	4	0	142	10	335
		25	365	50	397
e	8	0	137	10	207
		25	279	50	194

- Specific surface decreases with longer reaction times and / or enlarged amounts of coconut shell
- What about the mechanism regarding HTC test wit manure and coconut shell as additives?

Chemical composition of hydrochars made from coconut shell – manure mixture

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- Use of coconut shell as additive leads to an increase of the carbon content up to 65 % and a reduction of the reaction time from 12 h down to 4 h

- Second carbonization step is done by a subsequent activation step and generates hydrochars with a carbon content up to 65%

- Activated hydrochars made from manure-coconut shell mixtures are similar to black coal, as shown in van-Krevelen plot

Structure determination via ${}^{13}C$ solid state NMR

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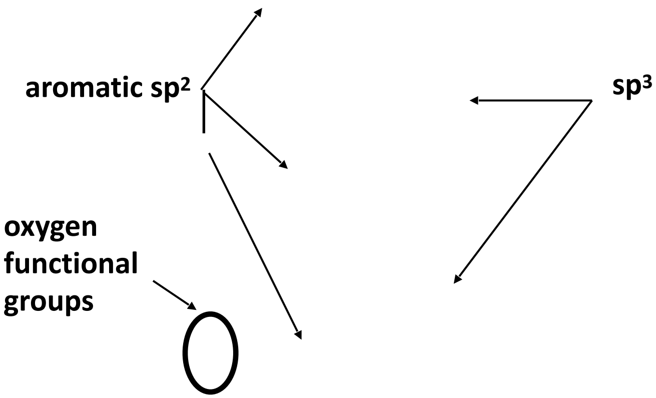
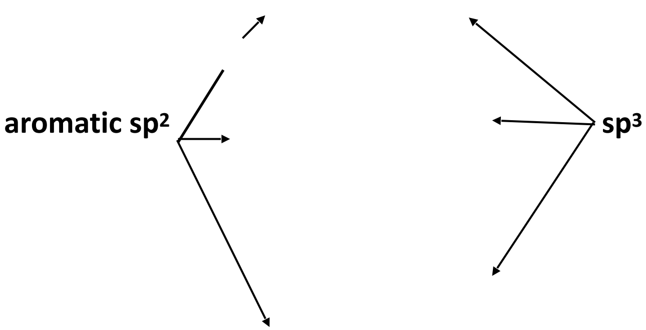


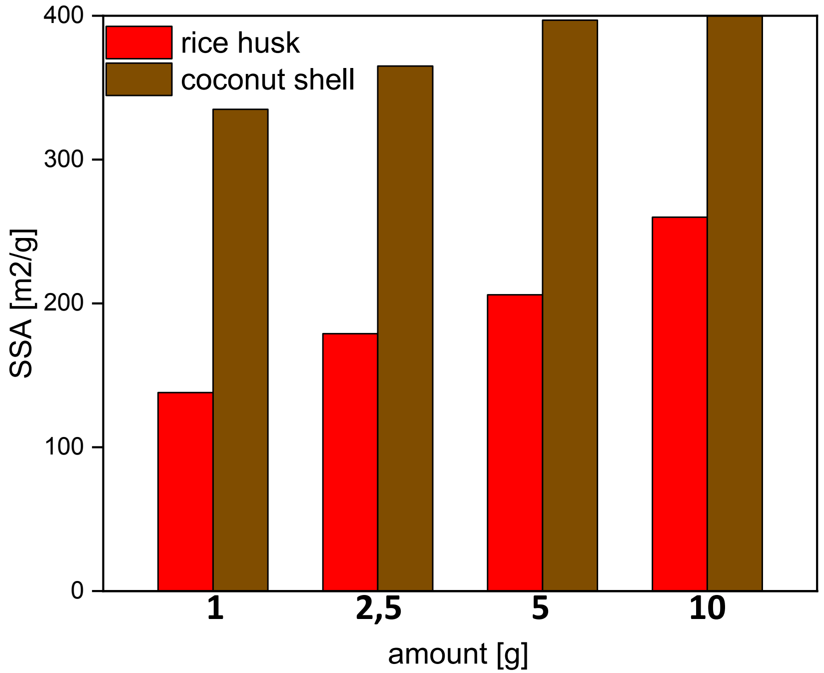
manure



manure + coconut shell

- Loss of oxygen functional groups due to hydrothermal treatment
- Subsequent activation process causes an increased aromatic content
- Interaction between manure and coconut shell
  ➔ degradation of lignin
- Lignin degradation leads to a reduction of inert aromatic content, thus lignin can participate in the HTC process

Does it also work with other dry biomasses?



Additive [-]	Reaction time [h]	Amount [g]	SSA [m²/g]	Micropore area [%]
rice husk	4	1,0	138	36
		2,5	179	41
		5,0	195	54
		10	332	62
coconut Shell	4	1,0	337	39
		2,5	365	51
		5,0	397	64
		10	497	73

- It works and mesoporous hydrochars are also obtained
  - ➢ enlarged mesopores portions with higher amount of rice husk as additive
- Improved surface area due to the combination of manure with rice husk
- Surface area of pure coconut shell is larger as those which were made from manure coconut shell mixtures

Microwave-assisted Hydrothermal Carbonization

	Reaction time [h]	SSA [m²/g]	Reaction time [h]	SSA [m²/g]
ell)	4 h (autoclave)	365	0,5 h (micro wave)	345
)	4 h (autoclave)	177	0,5 h (micro wave)	154
)	4 h (autoclave)	195	0,5 h (micro wave)	173

- Subsequent steam activation is also required for hydrochars obtained from microwave assisted HTC
- Specific surface areas of activated hydrochars derived from microwave-assisted HTC tests are slightly smaller as those derived from autoclave tests
  - ➢ 30 min : 240 min
  - ➢ faster cooling down after microwave assisted test

Application of activated hydrochars

- Emission Partner

  - ➢ activated hydrochars as bio-catalyst carrier
  - ➢ exhaust purifying due to H_2S sorption

  ➔ determination of best sorption tests with different activated hydrochars

- Deutsches Institut für Luft- und Raumfahrt

  - ➢ Pt-doped activated hydrochars as electrode materials in fuel cells
  - ➢ substitution of fossil-based materials

FULL PAPER
Energy Technology
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Hydrothermal Carbonization-Derived Carbon from Waste Biomass as Renewable Pt Support for Fuel Cell Applications: Role of Carbon Activation

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Pt catalysts in proton exchange membrane fuel cells (PEMFCs) typically use carbon blacks such as Vulcan (Vulcan is a registered trademark of the company Cabot Corporation) based on fossil sources. Thus, an important research task is using sustainable supports in PEMFCs. Hydrothermal carbonization (HTC) converts biomasses into chars, which are possible substitutes for fossil-based carbons. Herein, a Pt catalyst derived from HTC of coconut shells is developed for catalysis of O_2 reduction in acidic media. Thermal activation enlarges the specific surface area by factor of 7 to 546 $m^2 g^{-1}$ and generates electrical conductivity making the material suitable for catalysis. Pt particles of 1.8 ± 0.5 nm are distributed well on the activated carbon. Cyclic and CO stripping voltammetry show an electrochemical surface area (ECSA) of 69 ± 21 $m^2 g_{Pt}^{-1}$, almost identical to that of the commercial catalyst using Vulcan (69 ± 6 $m^2 g_{Pt}^{-1}$). Although ECSAs are highly comparable, the activity for O_2 reduction is lower compared with the commercial catalyst. HTC-derived carbon has a lower degree of graphitization, less functional oxygen groups on its surface, and a lower electrical conductivity than Vulcan. This suggests different Pt–support interactions.

petroleum-based products. It is estimated that 118 billion tons of biomass is available each year as dry matter and therefore represents an abundant feedstock.[4] Furthermore, biomasses are potential carbon sinks due to CO_2 binding in plants.[5,6] Especially, the transformation of waste products into high-quality products such as activated carbons has gained high importance during the last years.[7–9] Hydrothermal carbonization (HTC) has advantages compared with other carbonization methods such as pyrolysis[10–12] or hydrothermal liquification.[13–15] HTC takes place in autoclaves at reaction temperatures <300 °C and allows the direct carbonization of wet biomasses (e.g., manure, sewage sludge) without any drying step.[16] The obtained chars are lignite-like products characterized by a high number of

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Summary

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- Substitution of corrosive, chemical agents for surface improvement by the use of lignin rich biomasses

- Manure interacts with coconut shell in a positively way, which leads properly to a lignin degradation, so lignin can participate in the HTC process
  - ➢ increased carbon content, which benefits activation reactions
  - ➢ disappearing of oxygen functional groups (IR-spectroscopy) and methylene groups and accordingly the formation of aromatic compounds (solid state NMR)
  - ➢ TGA measurements confirm assumption regarding lignin degradation due to reduced thermal stability

- Surface measurements for activated hydrochars via N_2 sorption confirm lignin degradation, due to the smaller specific surface and pores at high temperatures and / or high coconut shell amounts

- Enlarged ash content exhibits activated carbons with small surface areas, due to inhibition of activation processes in the gaseous phase

Thank you for your kind attention