Technische Universität Berlin

Methods for char characterization

York Neubauer

TU Berlin | Institute of Energy Engineering | NWG-TCKON | µCHP 16 | Bolzano, 02.12.2016

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outline

- **Why bothering with char ?** – a motivation
- **What is char ?** – ‚defining‘ carbon materials
- How can char-like materials be characterized ?

Junior research group „TCKON“

Fundamental examinations and selective influencing of heterogeneous reactions in thermochemical conversion of biomass and robust, continuous on-line monitoring of the organic load on the gas phase.

Main aims:

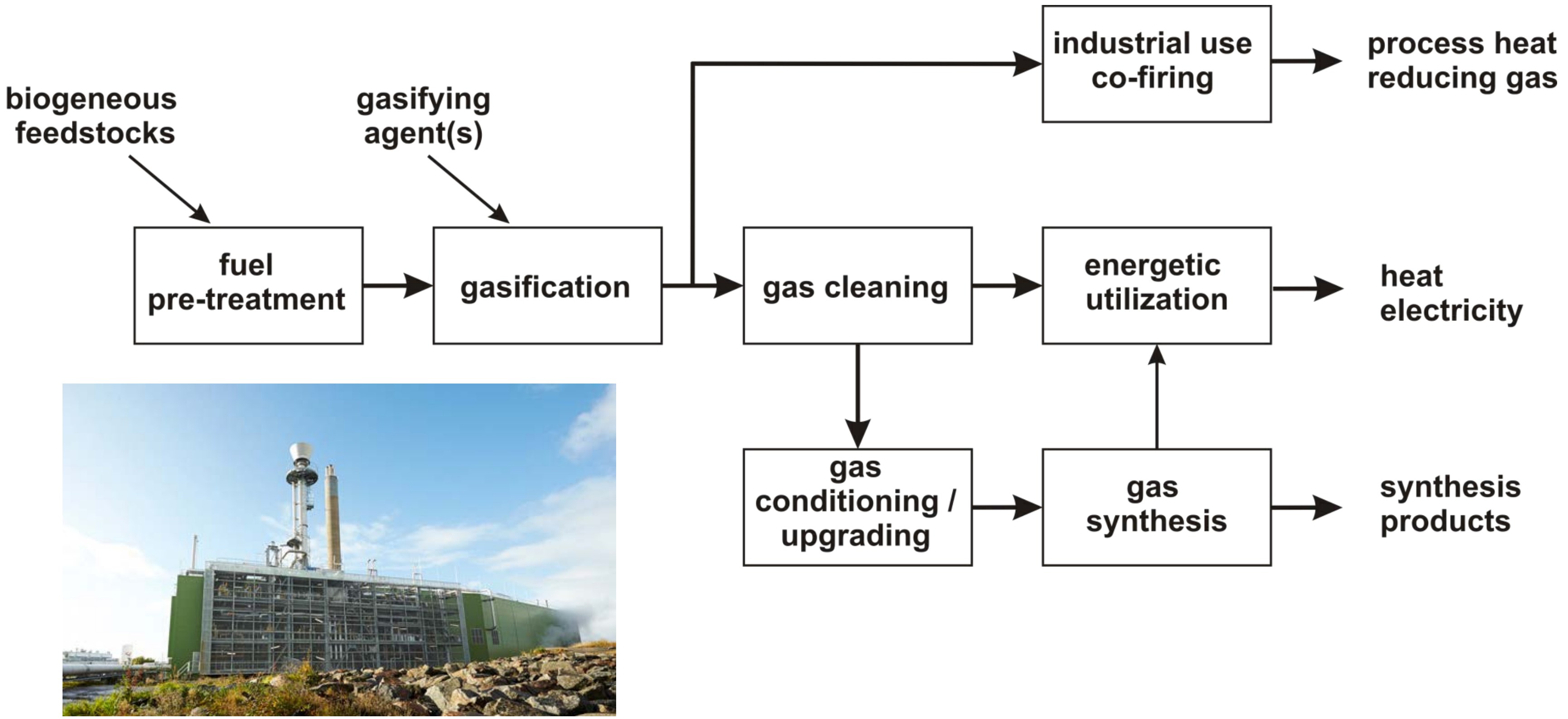
- Actively **influencing of heterogeneous reactions of gas or vapour with the solid surfaces of carbon structures** in the conversion process

- **Selective influencing of char properties and making use of of char generated in the process**

- **Fluorescence measurements** of aromatic multi-component mixtures in hot product gases of Thermochemical conversion processes / development of a robust ‚tar‘ sensor

Process char: just reaction intermediate or activated carbon within gas producer process chains?

Or simply: What are we aiming for?



scheme adapted from: Hofbauer H, Gas production for polygeneration plants. *International Conference on Polygeneration Strategies (ICPS)*, Vienna, Austria (2009)

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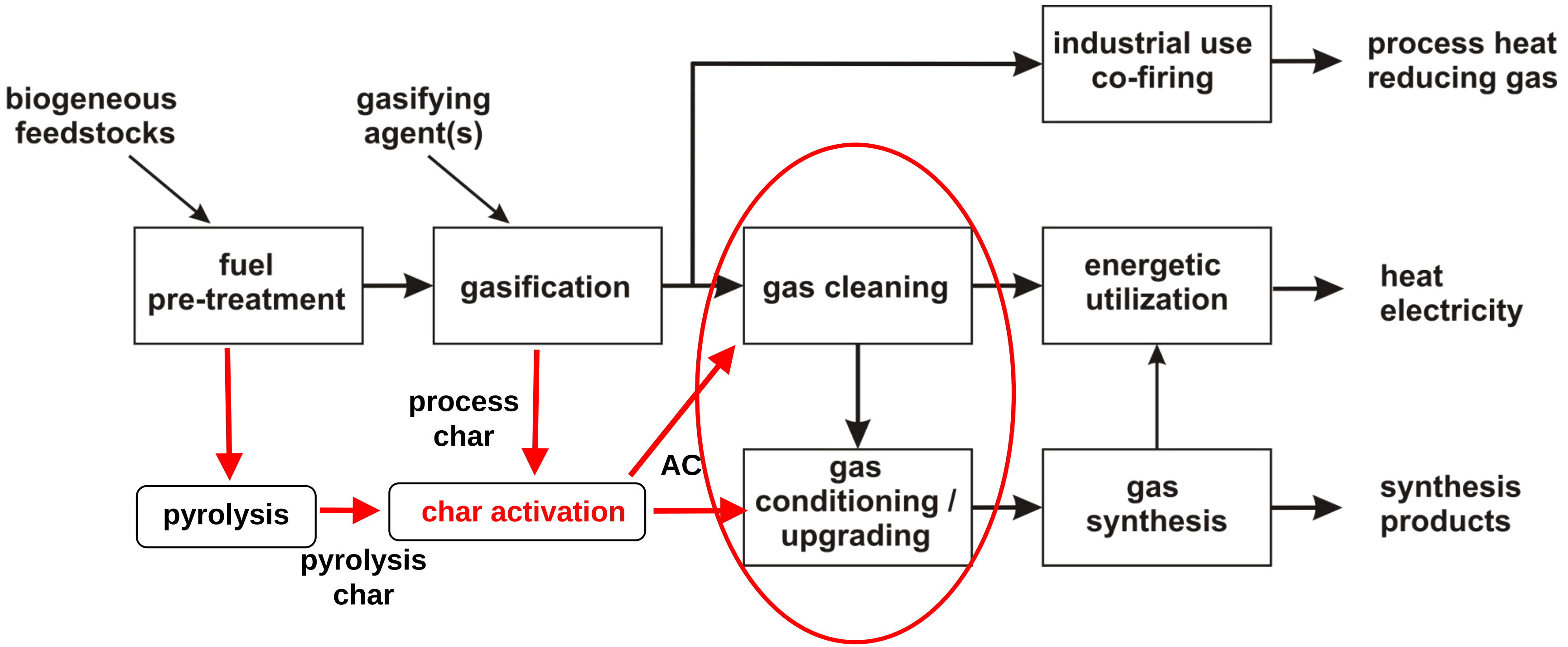

adapted from Hofbauer H, Gas production for polygeneration plants. *International Conference on Polygeneration Strategies (ICPS)*, Vienna, Austria (2009)

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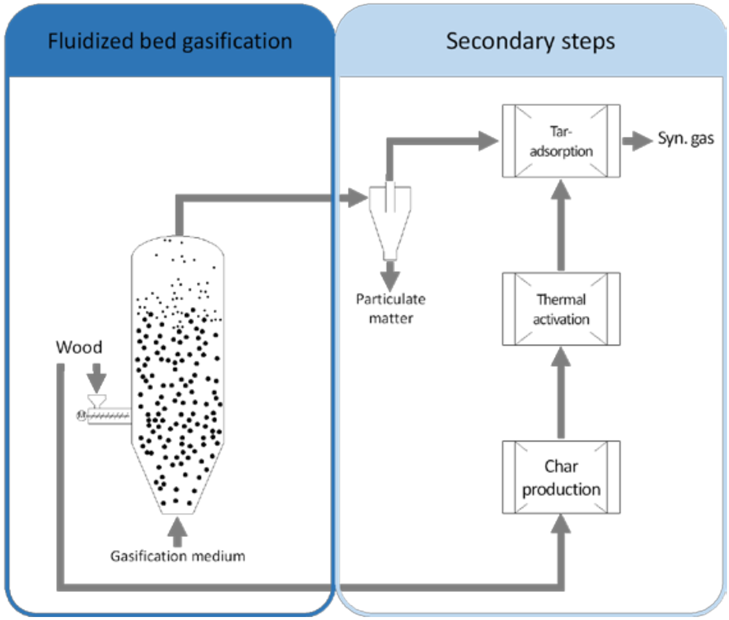
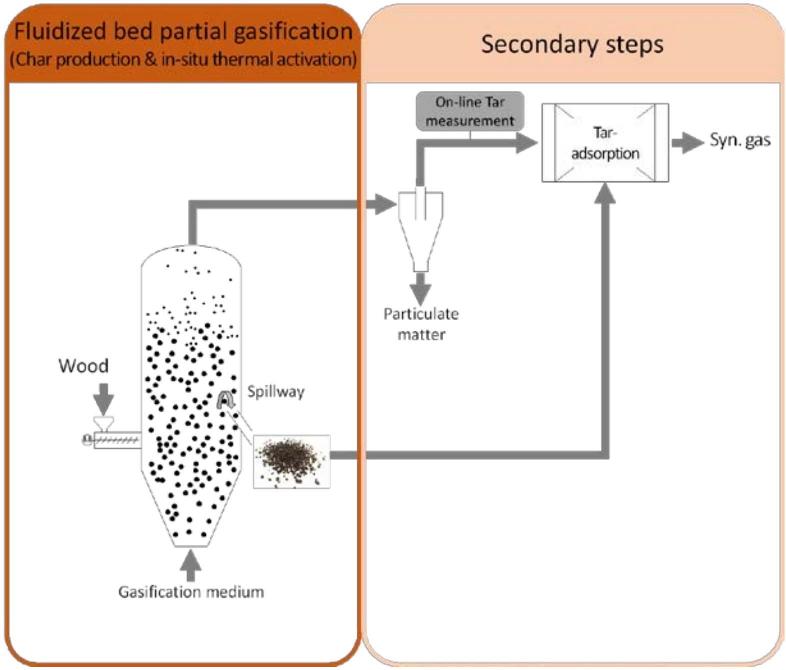
Our approach @ TU Berlin





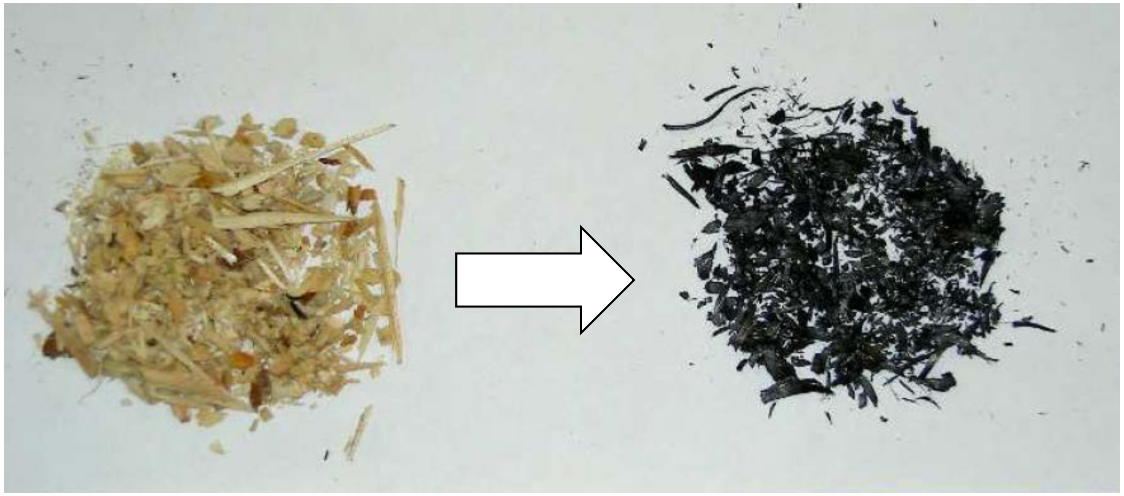
<u>Objectives</u>:

- Creating a suitable pore structure for 'tar' adsorption from fuel-type materials (e.g. woodchips)
- Study on the effects of the gasification product gases on the pore structure
- Investigations on PAH adsorption by activated process char (carbon)

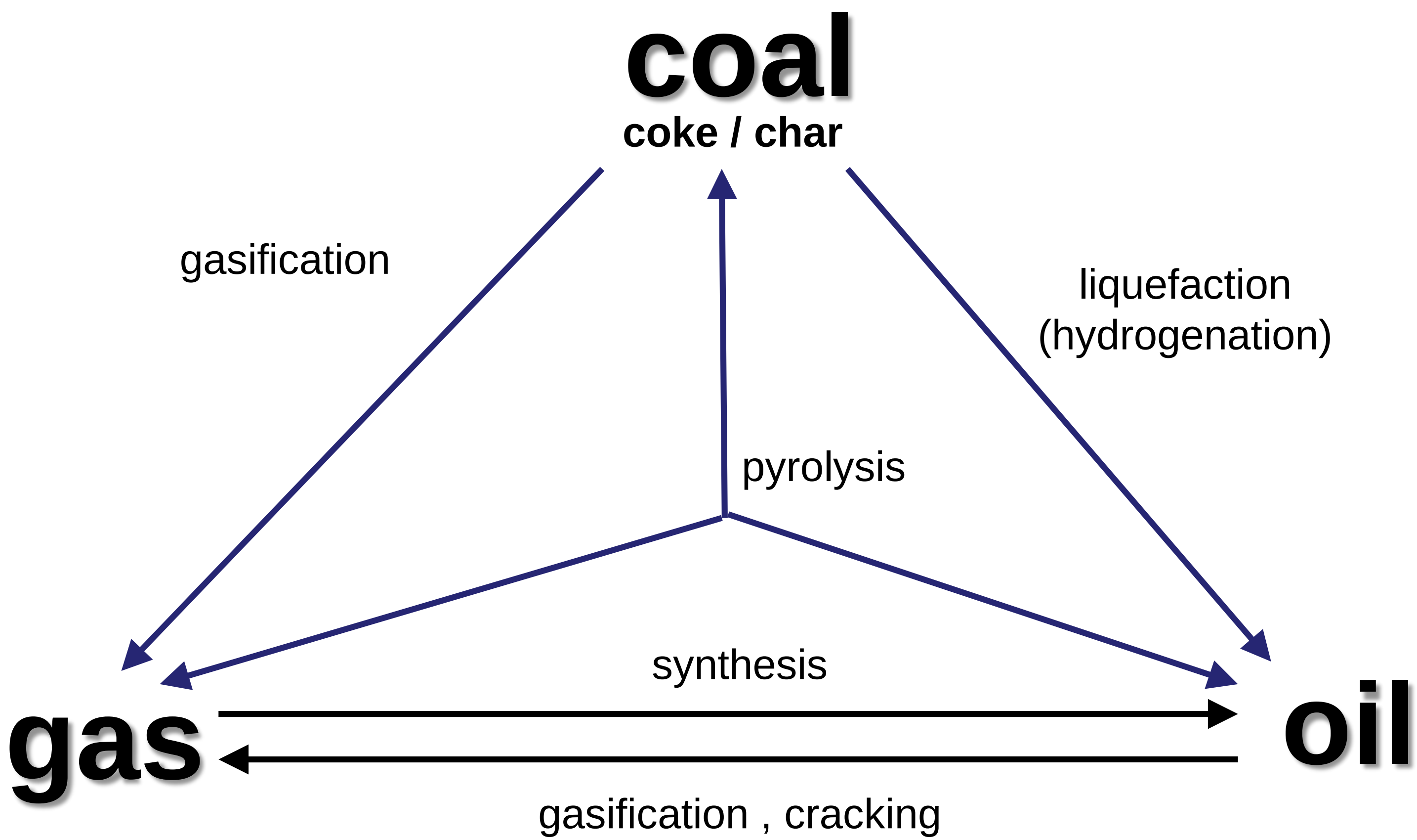
- Characterization of the fluidized bed char
- Feasibility study on activation of the fluidized bed process-char

outline

- **Why bothering with char ?** – a motivation
- **What is char ?** – ‚defining' carbon materials
- How can charry materials be characterized ?

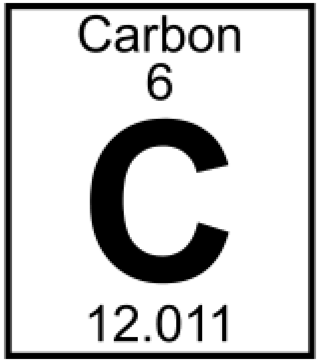


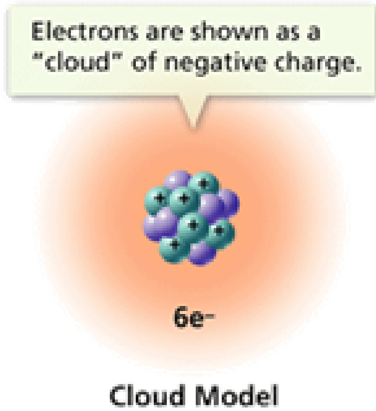
Carbon conversion routes

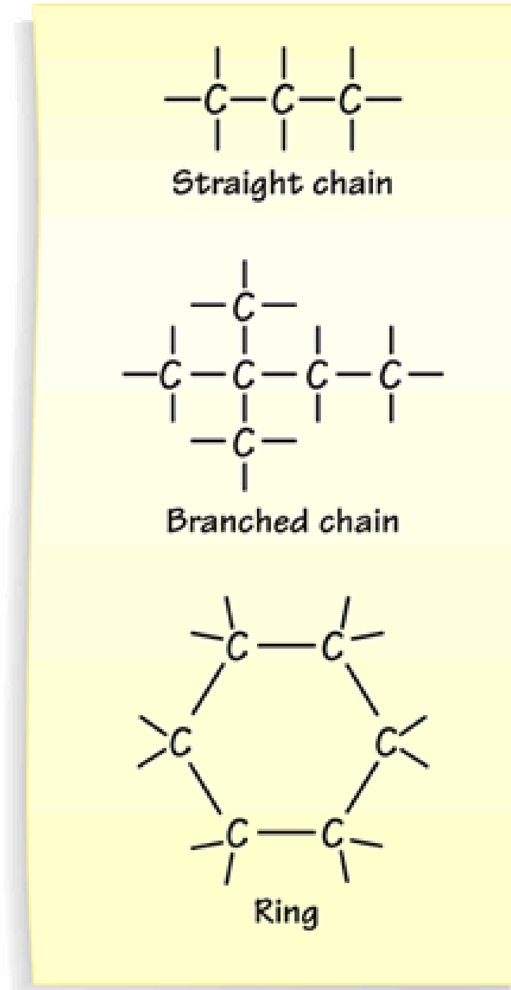


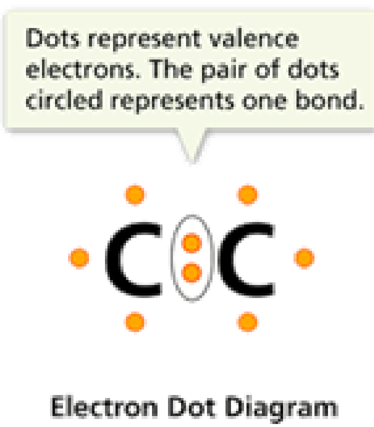
Adapted from Reimert, R., Die thermochemische Kohleveredlung. *in:* Schmalfeld, J. (Ed.), Die Veredlung und Umwandlung von Kohle. Technologien und Projekte 1970-2000 in Deutschland. (2008) Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V.

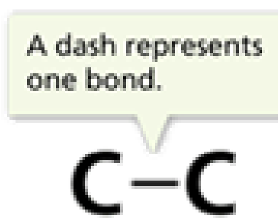
Carbon – the element





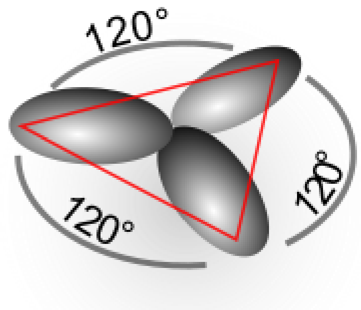


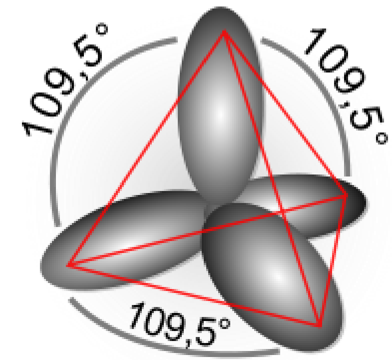


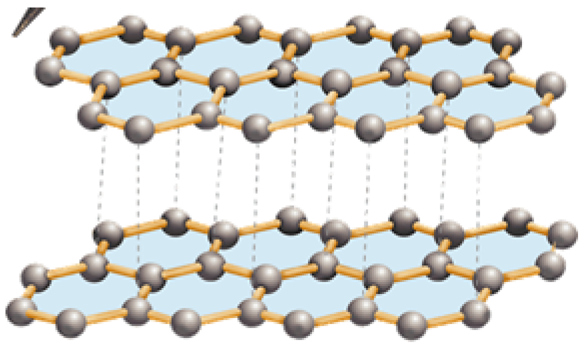


P. K. McKenzie, Carbon Chemistry Properties of Carbon. http://slideplayer.com/slide/7017396/

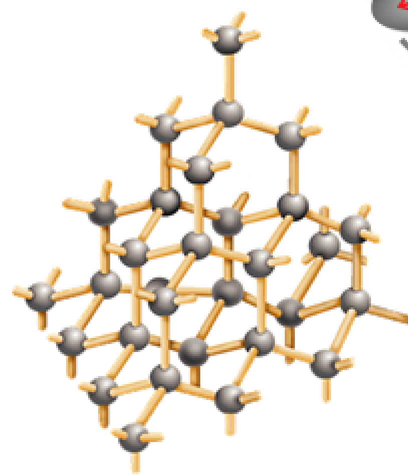
Forms of pure carbon







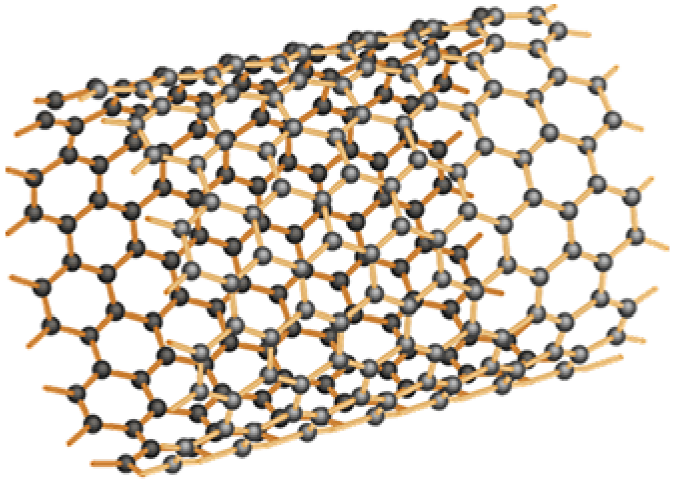
Layered Structure of a Graphite
The carbon atoms in graphite are arranged in layers. The dashed lines show the weak bonds between the layers.



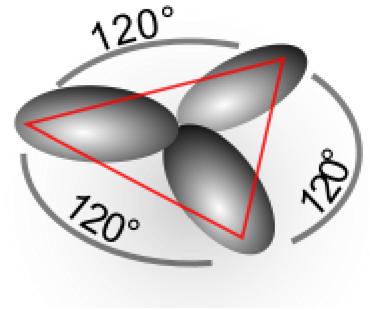
Crystal Structure of a Diamond
The carbon atoms in a diamond are arranged in a crystal structure.

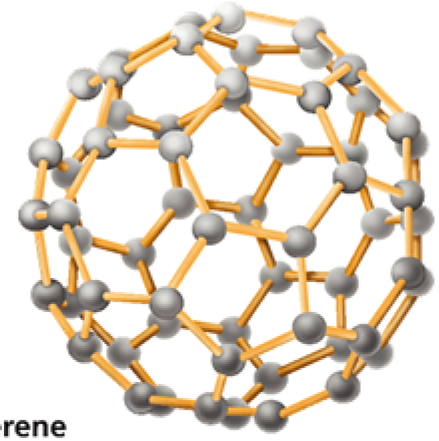
P. K. McKenzie, Carbon Chemistry Properties of Carbon. http://slideplayer.com/slide/7017396/

Forms of pure carbon



Cylindrical Structure of a Nanotube
The carbon atoms in a nanotube are arranged in a cylinder.

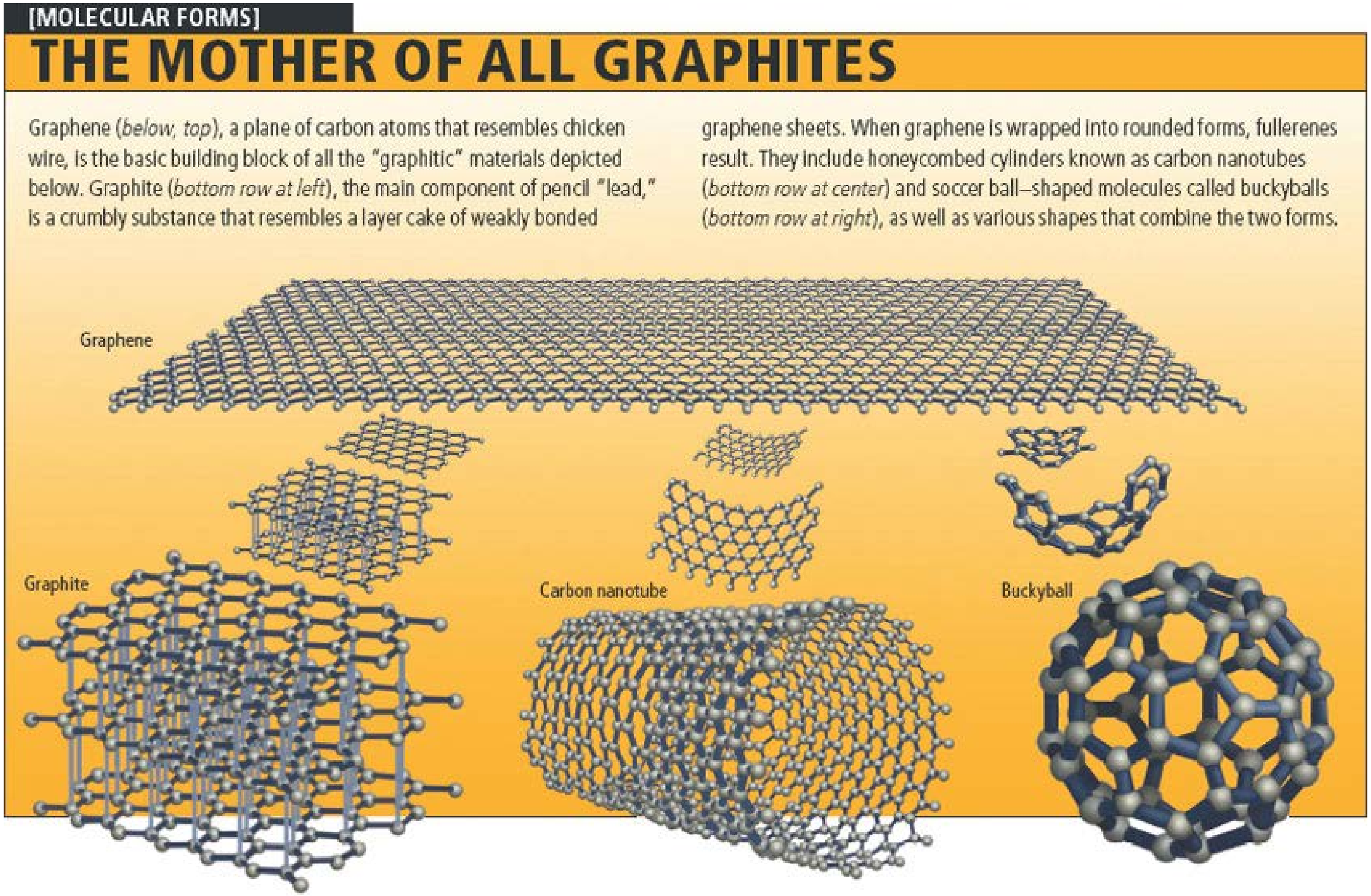




Spherical Structure of a Fullerene
The carbon atoms in a fullerene form a sphere that resembles a geodesic dome.

P. K. McKenzie, Carbon Chemistry Properties of Carbon. http://slideplayer.com/slide/7017396/

Carbon Structures



A. K. Geim and P. Kim, Carbon Wonderland, Scientific American 298, 90 - 97 (2008) doi:10.1038/scientificamerican0408-90

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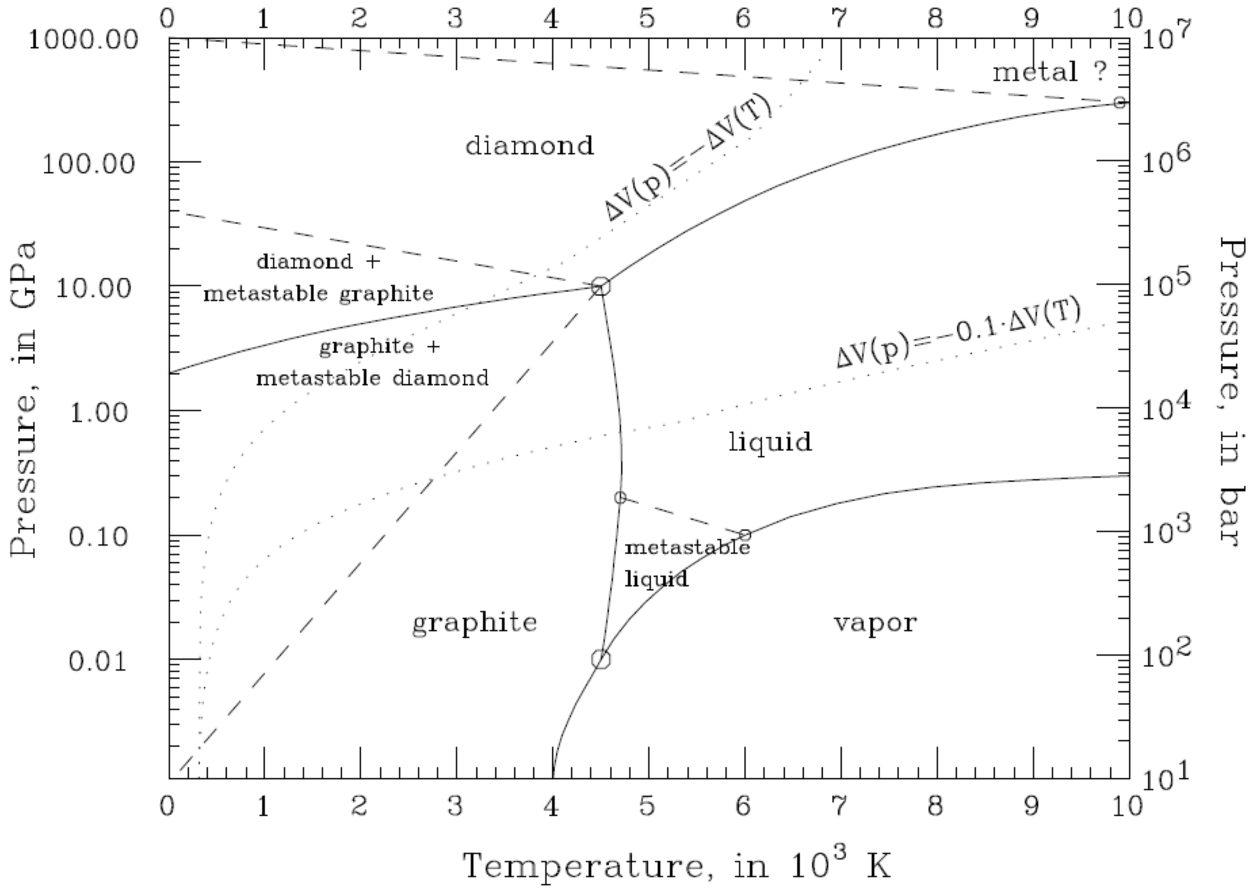
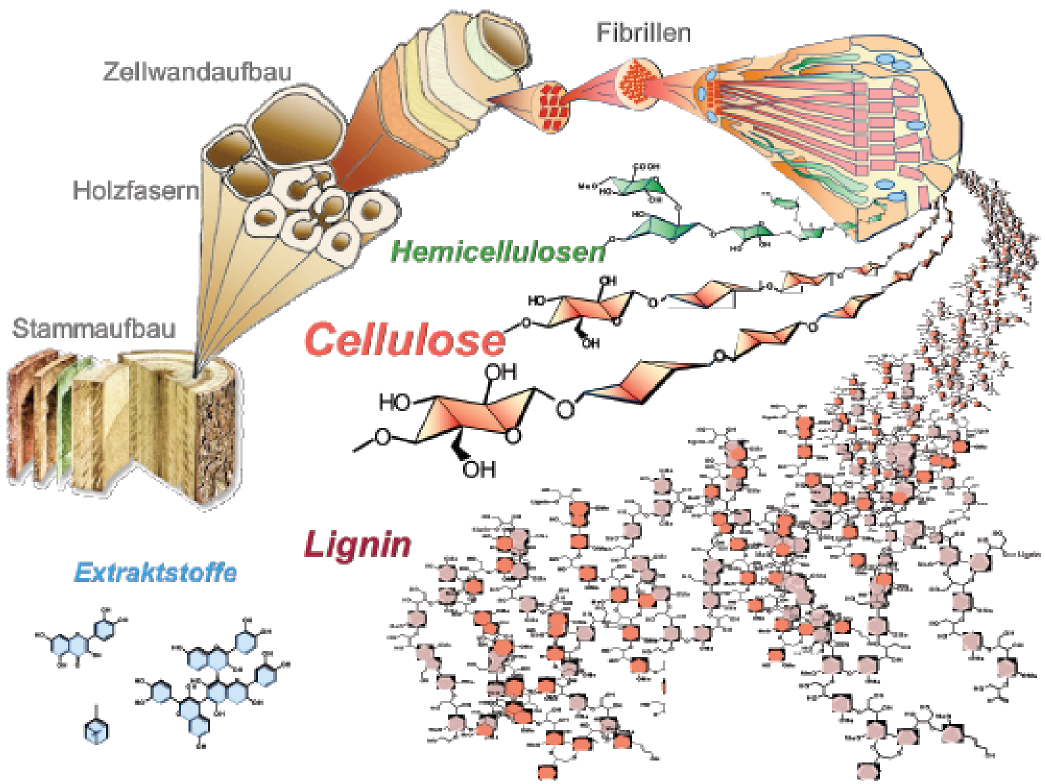
Phase diagram of carbon



J. M. Zazula, On Graphite Transformations at High Temperature and Pressure Induced by Absorption of the LHC Beam. LHC Projekt Note 78/79, 1997

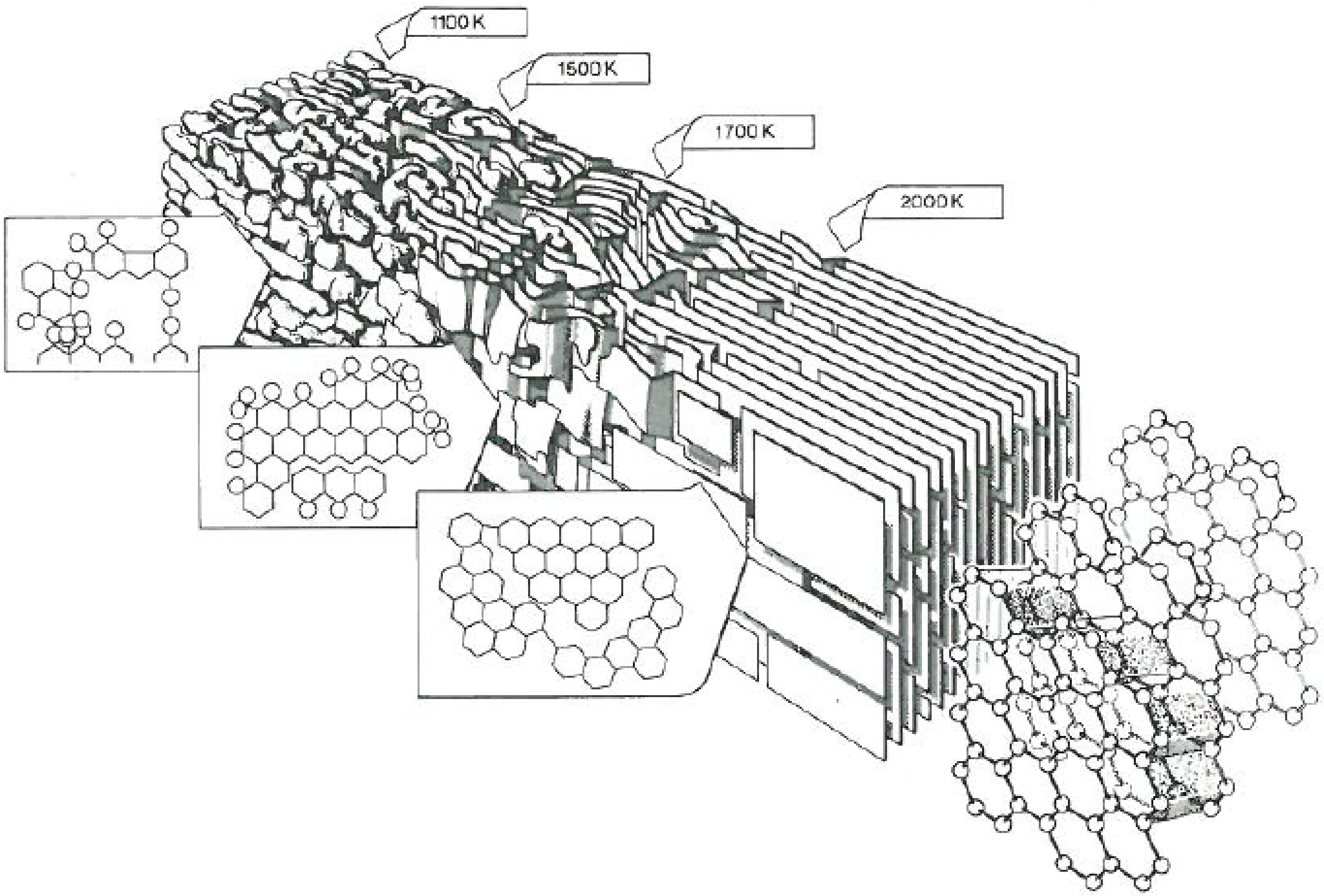
Carbon Precursors – terrestrial plants



$CH_{1,4}O_{0,7}$

	Cellulose	Hemicellulose	Lignin	Extraktstoffe/Asche
Laubholz	40-42	30-35	20-22	2-3
Nadelholz	40-43	21-23	27-28	3-5
Einjährige Pflanzen	38-42	25-30	15-21	5-10

Carbon Structure



Edwards, I. A. S.: Structure in Carbons and Carbon Forms. *in:* Marsh, H. (ed.): Introduction to Carbon Science, p.107-152, Butterworths, London, 1989

‘Defining’ Carbon

Definitions given by ICCTC starting in 1982

Anon: **International Committee for Characterization and Terminology of Carbon** "First publication of 30 tentative definitions“. *Carbon,* 1982*, 20*, 445-449

Anon: International committee for characterization and terminology of carbon First publication of further 24 tentative definitions'. Carbon, 1983, 21, 517-519

Köchling, K.-H.; McEnaney, B.; Müller, S.. Fitzer, E.: International committee for characterization and terminology of carbon ‘First publication of 14 further tentative definitions’. Carbon, 1985, 23, 601-603

Koechling, K.-H.; McEnaney, B.; Mueller, S., Fitzer, E.: International committee for characterization and terminology of carbon ‘First publication of 9 further tentative definitions’. Carbon, 1986, 24, 246-247

‘Defining’ Carbon

In the meantime more than 100 terms defined by the “International committee for characterization and terminology of carbon (ICCTC)”

1. Carbon
2. Diamond
3. Graphite

   ….

14. Carbonization
15. Coalification

   ….

16. Coke

   ….

42. Char
43. Charcoal

   ….

44. Activated Carbon

   ….

Carbonization

14. Carbonization

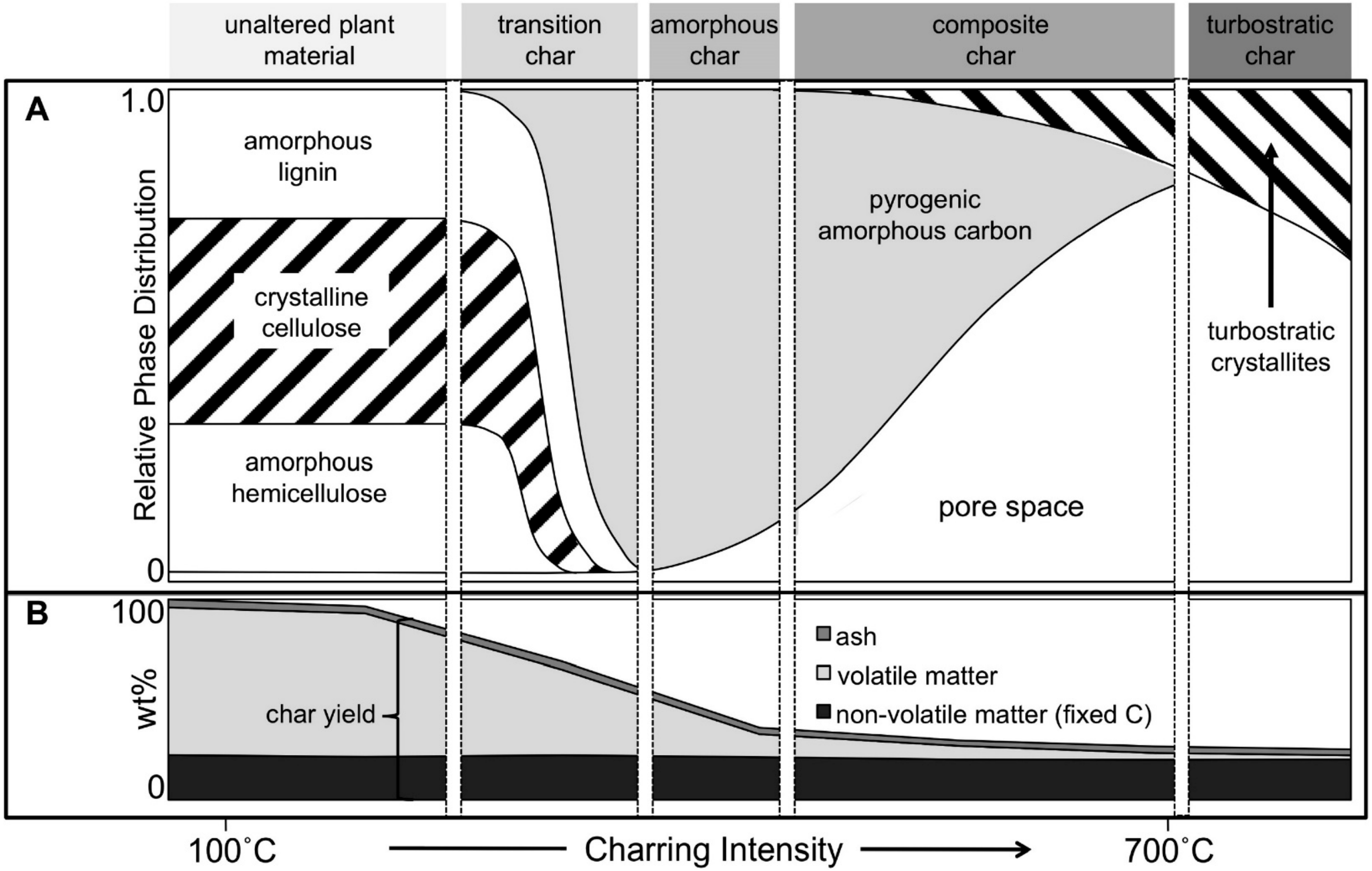
Carbonization is a process of formation of material with increasing carbon content from organic material, usually by pyrolysis, ending with an almost pure carbon residue at temperatures up to about 1600 K.

Notes. **As with all pyrolytic reactions, Carbonization is a complex process in which many reactions take place concurrently, such as dehydrogenation, condensation, H-transfer and isomerization.** It differs from Coalification in that its reaction rate is faster by many orders of magnitude.

The **final pyrolysis temperature** applied controls the **Degree of Carbonization** and the remaining content of foreign elements, e.g. at *T* - 1200 K the carbon content of the residue exceeds 90 wt/%, whereas at *T* – 1600 K, 99 wt/% carbon is found (see Coalification, Degree of Carbonization), (see also Raw Coke, Calcinized Coke).

Anon: International committee for characterization and terminology of carbon "First publication of 30 tentative definitions“. *Carbon,* 1982*, 20*, 445-449

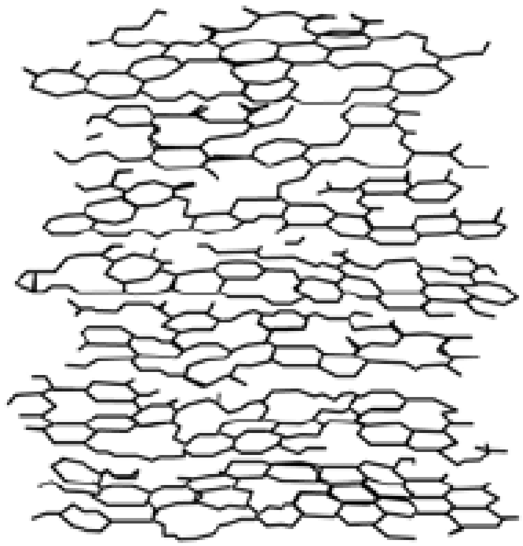
Carbonization - structure of carbon



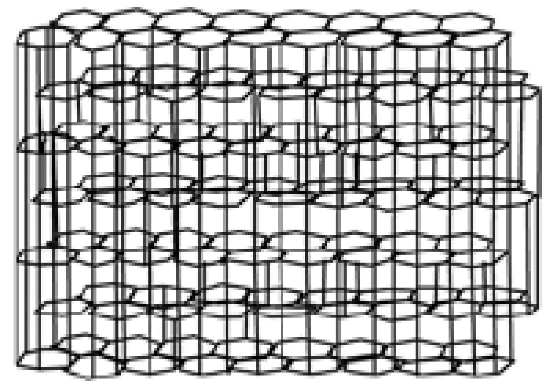
Keiluweit, M. et al.: Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar).
Environmental Science & Technology, 2010, *44*, 1247-1253

Char and char structure

Turbostratic structure



Graphite structure



Source: Schimmelpfennig, S., Glaser, B.: One Step Forward toward Characterization: Some Important Material Properties to Distinguish Biochars. J Environ Qual. 2012 Jul-Aug;41(4):1001-13. doi: 10.2134/jeq2011.0146.

Originally from Dasgupta, K. and Sathiyamoorthy, D., Disordered carbon–its preparation, structure, and characterisation Materials Science And Technology 19 , 2003, doi: 10.1179/026708303225004693

coke

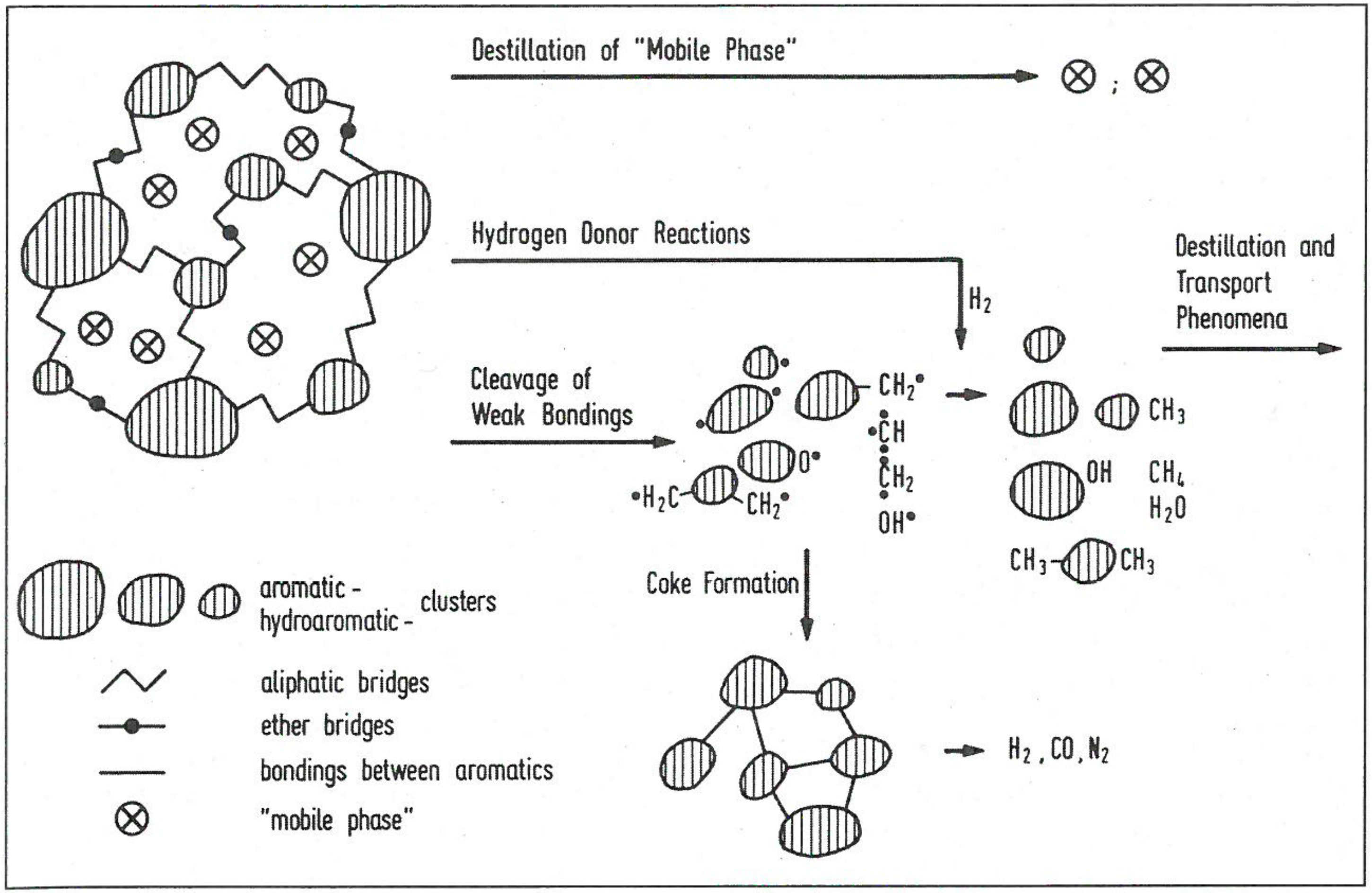
16. coke

Coke is a **highly carbonaceous product** of pyrolysis of organic material at least parts of which have **passed through a liquid or liquid-crystalline state during the Carbonization process** and which consists of Non-Graphitic Carbon (see Carbonization, Non-Graphitic Carbon).

Notes. As some parts at least of the Carbonization product have passed through a liquid or liquid crystalline state, the resulting Non-Graphitic Carbon is of the graphitizable variety. From a structural viewpoint, the term Coke characterizes the state of a Graphitizable Carbon before the beginning of Graphitization (see Carbonization, Non-Graphitic Carbon, Graphitization, Graphitizable Carbon).

Source: Anon: International committee for characterization and terminology of carbon first publication of further 24 tentative definitions'. Carbon, 1983, 21, 517-519

Coal structure and reaction mechanisms of pyrolysis and hydropyrolysis



Wanzl, W., Grundlagen der Verkokung und Pyrolyse. *in:* Schmalfeld, J. (Ed.), Die Veredlung und Umwandlung von Kohle. Technologien und Projekte 1970-2000 in Deutschland. (2008) Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V.

Char

42. Char

Char is a **Carbonization product** of a natural or synthetic organic material, **which has <u>not</u> passed through a fluid stage** during carbonization.

Notes. Because the precursor has not passed through a fluid stage, the Char often retains the shape of the precursor (although becoming of smaller size).
For such material the term “pseudomorphous” has been used.
Some simple organic compounds, e.g. sugar, melt at an early stage of decomposition and then polymerise during Carbonization to produce Chars (see Carbonization, Graphitizable Carbon, Pseudomorphous Carbon).

Anon: International committee for characterization and terminology of carbon first publication of further 24 tentative definitions'. Carbon, 1983, 21, 517-519

Charcoal

43. Charcoal

Charcoal is a **traditional term for a Char** obtained **from wood** and some related natural organic materials (see Char).

Notes. Charcoal has or had a variety of uses e.g. in ferrous metallurgy and in gunpowder (minor uses: medical and paint materials).

Anon: International committee for characterization and terminology of carbon first publication of further 24 tentative definitions'. Carbon, 1983, 21, 517-519

Activated carbon

44. Activated Carbon

Activated Carbon is a **porous carbon material, a Char**, which has been subjected to **reaction with gases**, sometimes adding chemicals, e.g. ZnCl, during or after Carbonization in order to **increase its porosity** (see Carbonization, Char).

Notes. Activated Carbons have a large adsorption capacity and are used for purification of liquids and gases. By controlling the process of Carbonisation and activation a variety of active carbons having different pore sizes can be obtained. Activated Carbons are used mainly in granular form, but can also be produced in textile form by controlled Carbonization and activation of textile precursors. Other terms used in the literature active carbons, active charcoals (see Carbonization).

Anon: International committee for characterization and terminology of carbon first publication of further 24 tentative definitions'. Carbon, 1983, 21, 517-519

outline

- **Why bothering with char ?** – a motivation
- **What is char ?** – ‚defining‘ carbon materials
- **How can char-like materials be characterized ?**

Analysis of carbon

Good laboratory praxis

Manufacturers of analytical instruments

Carbon community

- Journal ‚Carbon'
- Carbon 2011X -conference

ISPAC

- International society of polycyclic aromatic compounds

Biomass gasification, pyrolysis combustion communities

- EUBCE tcbiomas ……

standards

- DIN EN ISO ASTM

Characterizing chars (physical & chemical properties)

microscopy
- SEM, TEM

thermogravimetry
- reactivity

porosimetry
- pore sizes macropores – e.g. by mercury

extraction
- Soxleth
- ASE
- GC/MS analysis

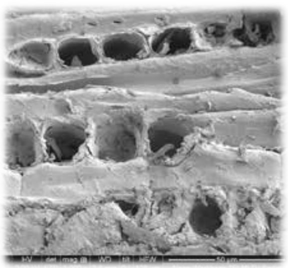
proximate analysis
- content of volatiles,
- moisture,
- and ash

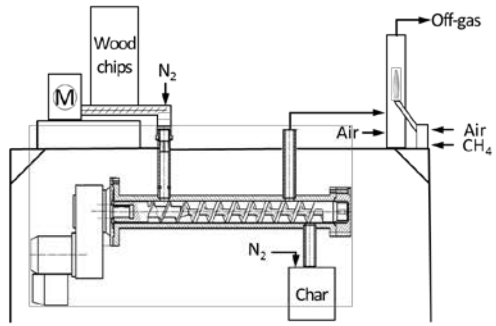
gas-sorption
- specific surface area - BET
- pore size distribution- BJH, DFT

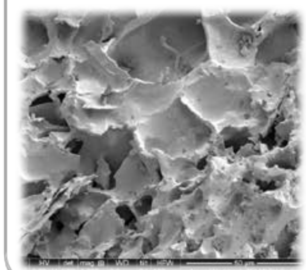
elemental composition (ultimate analysis)
- elemental analysis - CH(O)NS
- ICP-OES
- AAS
- XRD

adsorption (AC‘s)
- adsorption capacity, break through behavior

Step I: pyrolysis







starting material

oak woodchips
trunk wood without bark
granulometric fraction 2-4 mm

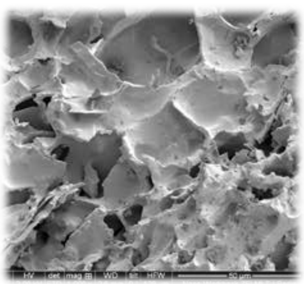
process (1st stage)

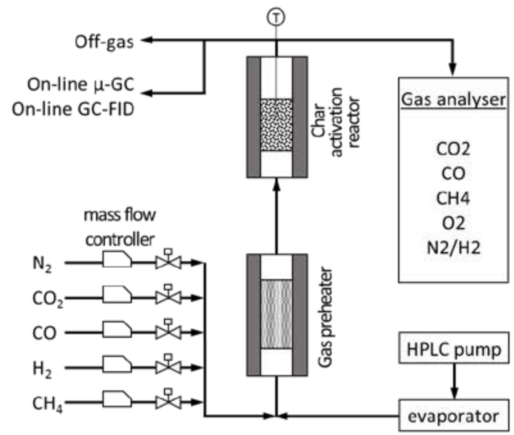
screw type pyrolysis reactor
temperature 300-400°C
N_2 -atmosphere

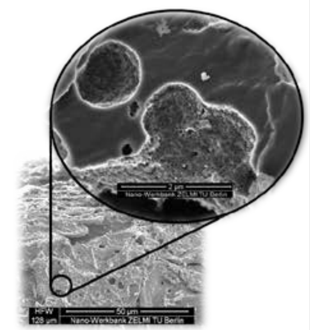
product (1st stage)

pyrolysis char
ash 0,7-2 % / volitile 7-15 %
granulometric fraction 1,4-2,8 mm

Step II: char activation







<u>product (1st stage)</u>

pyrolysis char
ash 0,7-2 % / volitile 7-15 %
granulometric fraction 1,4-2,8 mm

<u>process (2nd stage)</u>

fixed bed partial gasification (activation)
temperature 800-900°C
activating medium CO_2, steam , gas mix

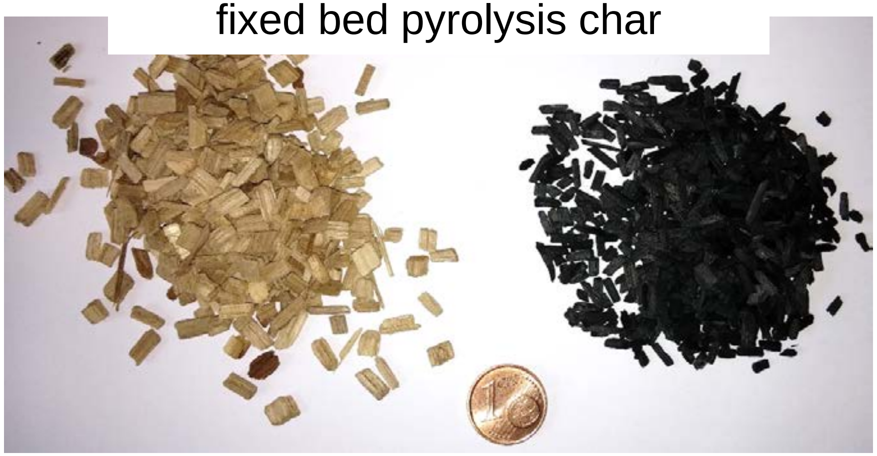
<u>product (2nd stage)</u>

activated carbon
burnoff 35-60%
granulometric fraction 1,0-2,8 mm

Starting materials and activated char (activated carbon – AC)

fluidized bed gasifier char

fixed bed pyrolysis char



samples	reaction temperature	Proximate analysis (dry basis, %)			Ultimate analysis (dry & ash free basis, %)				
		volatile matter	ash	fixed carbon	C	H	N	O	S
Fluid.-bed pine char	800-820°C	5,0	7,7	87,3	87,65	0,30	0,21	3,89	0,25
Fixed bed pine char	600°C	7,6	0,7	91,7	91,02	1,95	0,10	6,15	0,01
activated pine char (27% burn-off)	850°C	n/a	n/a	n/a	93,35	0,60	0,16	5,84	0,05
Fixed bed oak-char (Räuchergold)	600°C	15,1	1,5	83,4	83,05	2,89	0,32	12,06	0,18

Characterisation – specific surface area and pore size distribution

BET

Stephen **B**runauer, P.H. **E**mmett, Edward **T**eller,
Adsorption of gases in multi-molecular layers,
J. Am. Chem. Soc. 60 (**1938**) 309–319.

BJH

Elliott P. **B**arrett, Leslie G. **J**oyner, Paul P. **H**alenda, BJH
The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms,
J. Am. Chem. Soc. 73 (**1951**) 373–380.

DFT

N.A. Seaton, J. Walton, N. Quirke, A new analysis method for the determination of the pore-size distribution of porous carbons from nitrogen adsorption measurements,
Carbon 27 (**1989**) 853–861.

DFT - Density Functional Theory

NLDFT - Non-local density functional theory

QSDFT - Quenched solid density functional theory

Characterisation – pore size distribution

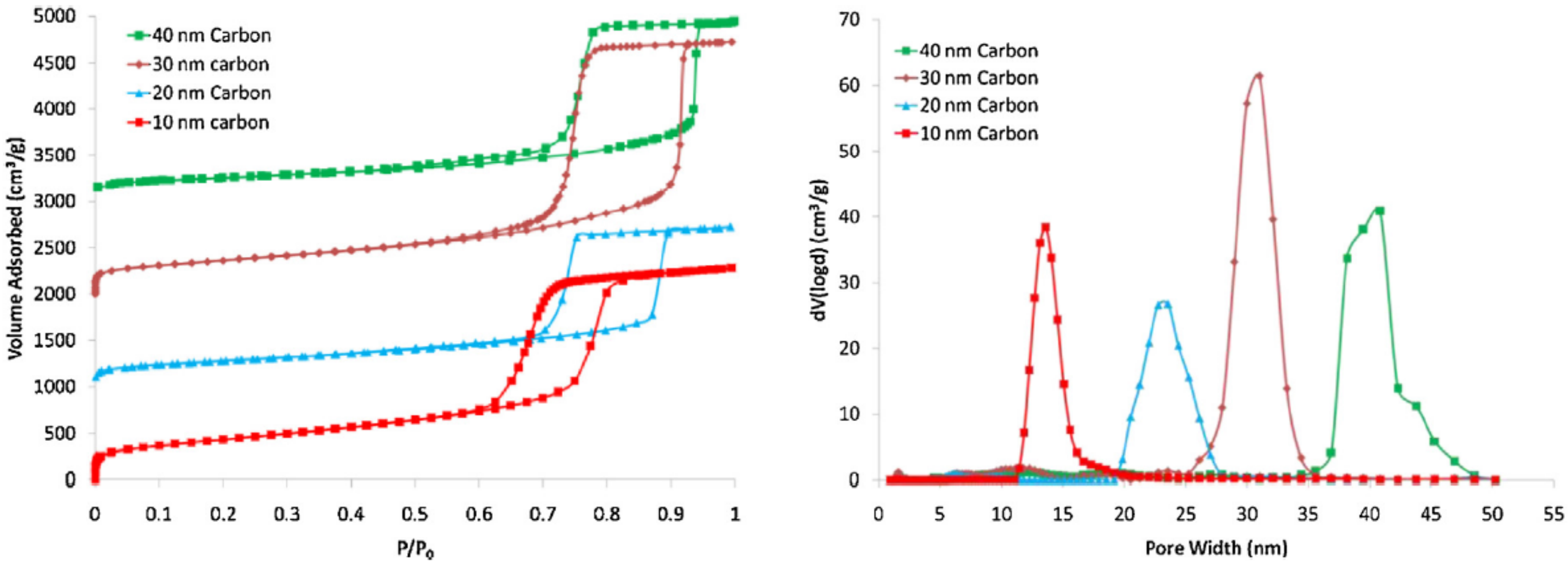
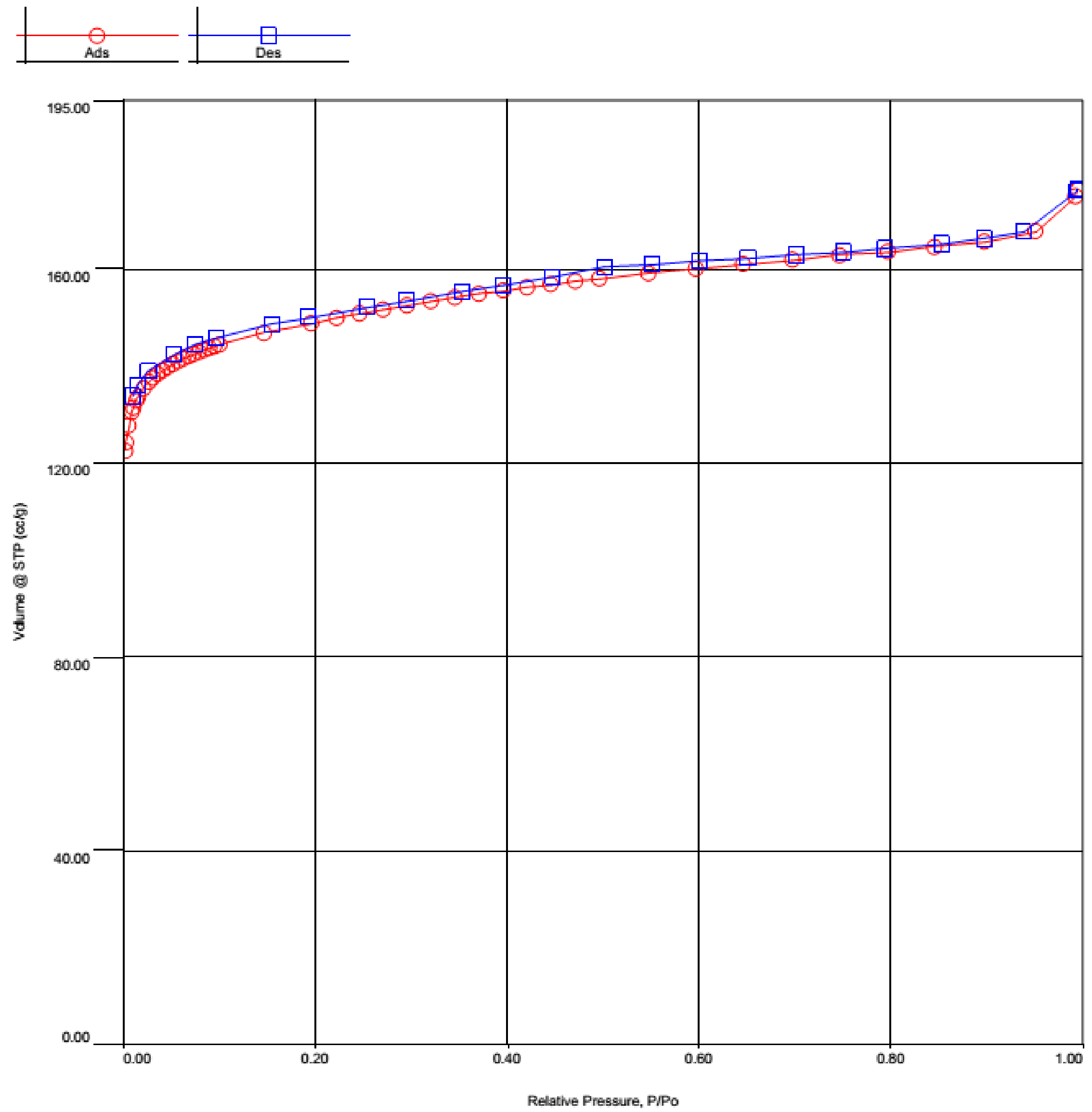


Fig. 13. Isotherm (left) and corresponding pore size distribution (right) for 3DOm materials of varying pore sizes.

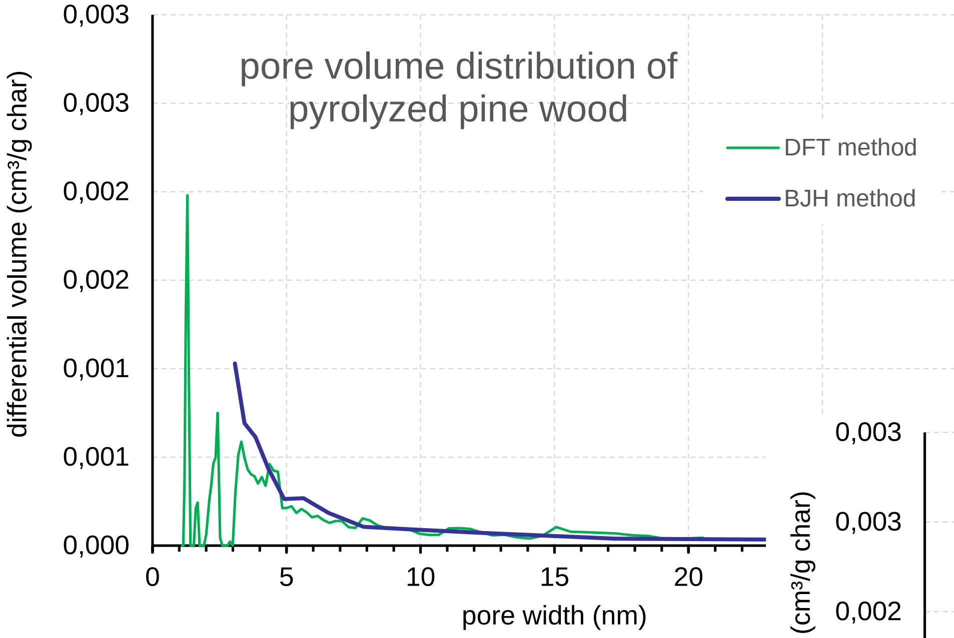
Source: Landers, J., Gor, G. Y., Neimark, A. V., Density functional theory methods for characterization of porous materials. Colloids and Surfaces A: Physicochem. Eng. Aspects 437 (2013) 3–32

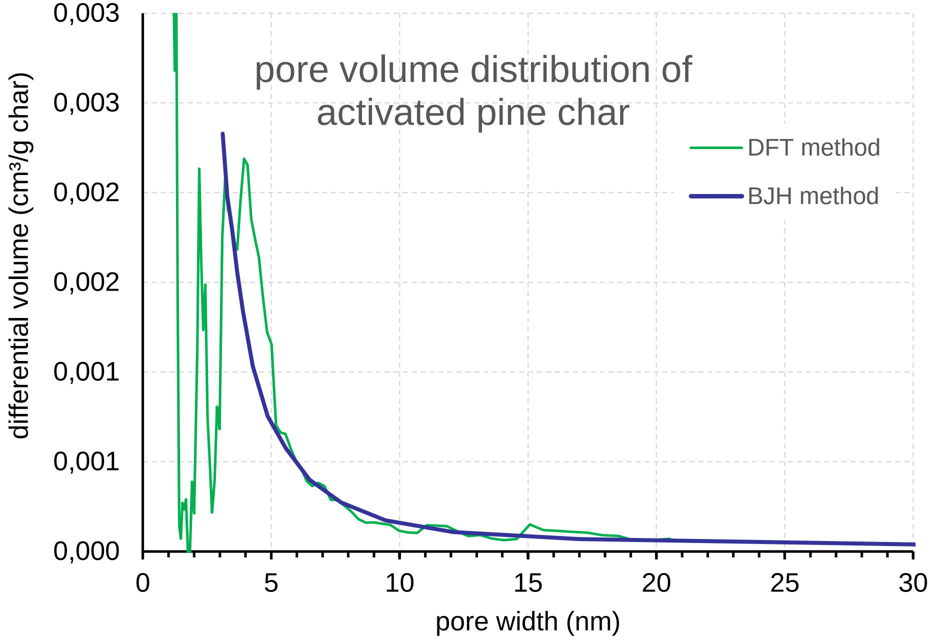
starting materials and activated char

Sample	spec surface area S_{BET} m^2/g	pore size distribution (cm^3/g) micropores <2 nm	mesopores 2 – 50 nm	total <250 nm
Fluidized-bed pine char				
Burn-off 0%	170	0,038	0,078	0,160
Spruce/Fir char				
Burn-off 0%	474	0,167	0,026	0,216
Burn-off 36% (by CO_2)	638	0,209	0,089	0,344
oak-char				
Burn-off 0%	151	0,043	0,035	0,096
Burn-off 46% (by CO_2)	716	0,257	0,033	0,323
Burn-off 52% (by CO_2)	766	0,274	0,035	0,344
Burn-off 60% (by CO_2)	819	0,293	0,037	0,367

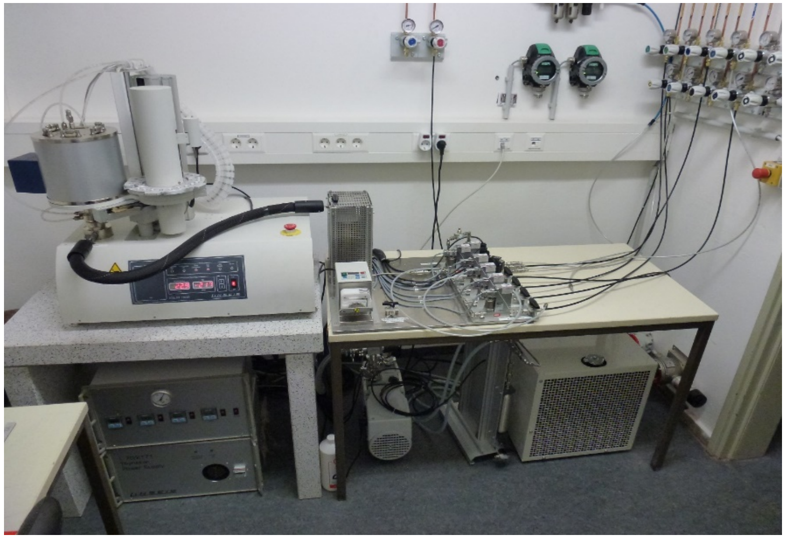

Ads
Des
195.00
160.00
120.00
80.00
40.00
0.00
Volume @ STP (cc/g)
0.00
0.20
0.40
0.60
0.80
1.00
Relative Pressure, P/Po

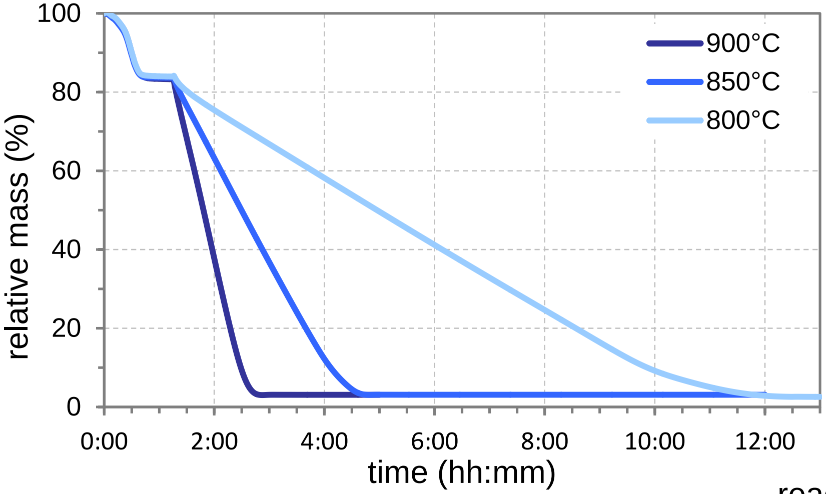
Characterisation of process chars – pore size distribution

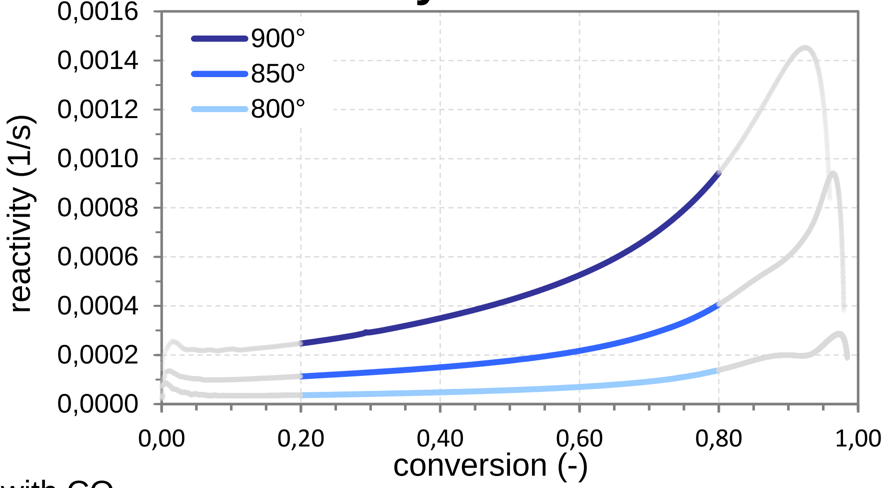




Thermogravimetric analysis







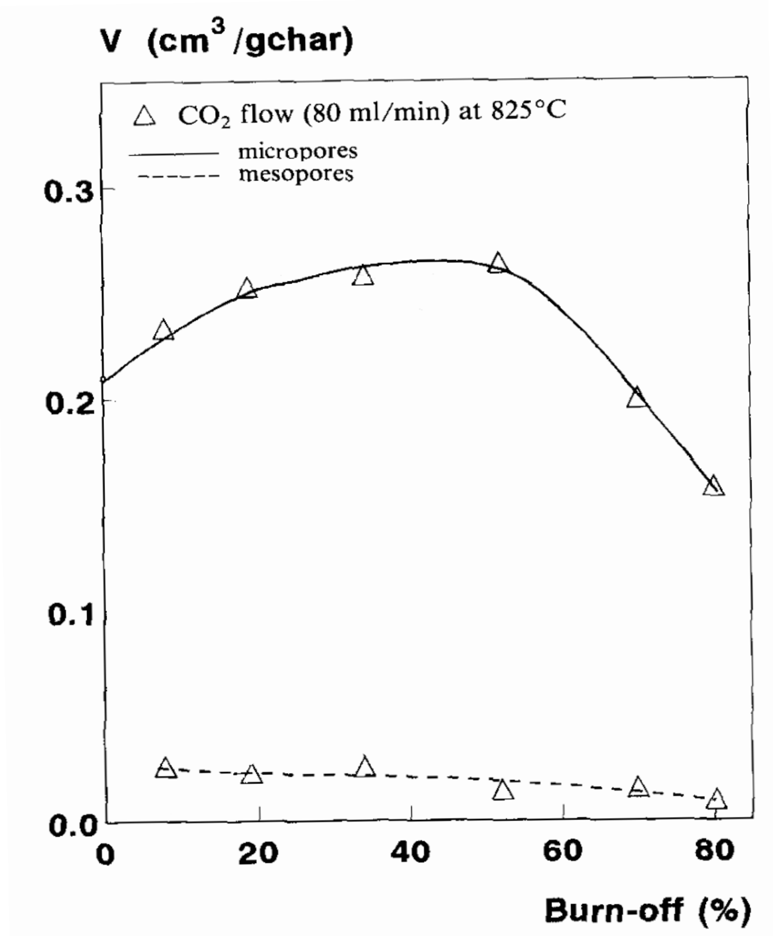
reactions with CO_2

PAH adsorption

Quantitative study of PAH adsorption on activated carbon from model compounds by Mastral et al.[2]:

total microporosity is the main factor controlling the adsorption process

- a micropore size distribution higher than 0.7 nm, where PAH molecules do not find diffusional problems favors the adsorption
- High development of the mesoporosity not only drive the adsorbate molecules to the micropores but also promote the multilayer interactions increasing the equilibrium adsorption capacity
- low surface acidity, due to both the hydrophobic nature and the lower humidity adsorption capacity of the PAH

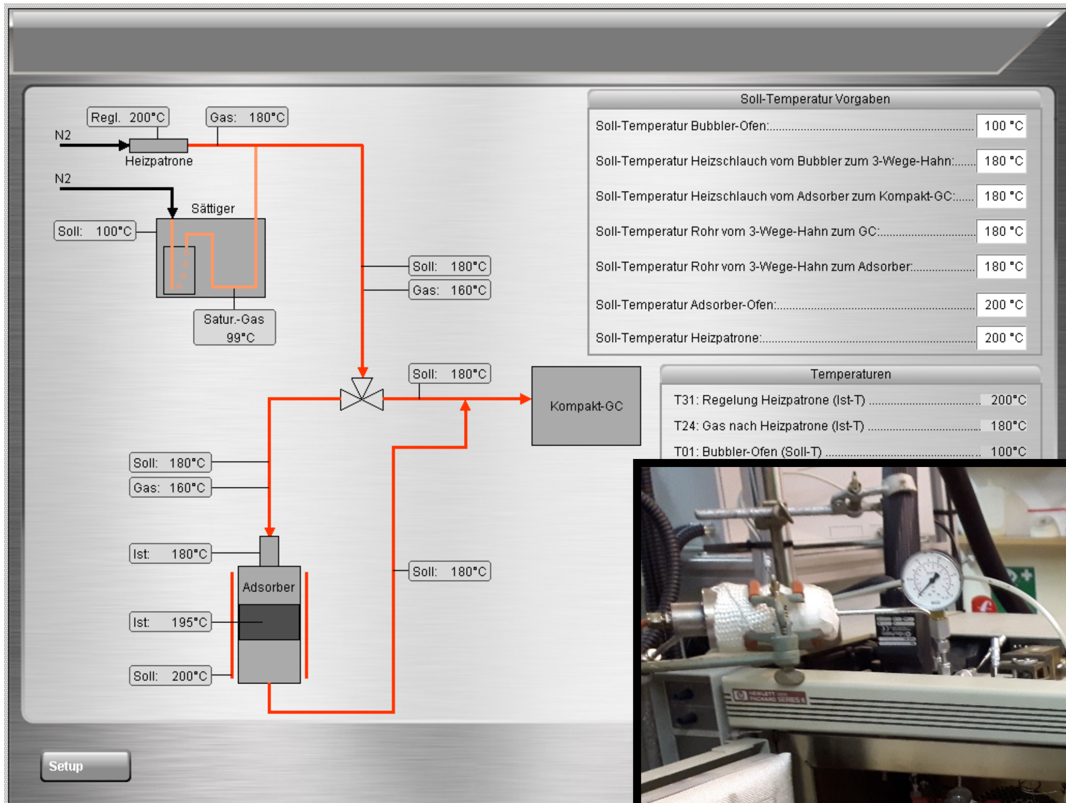


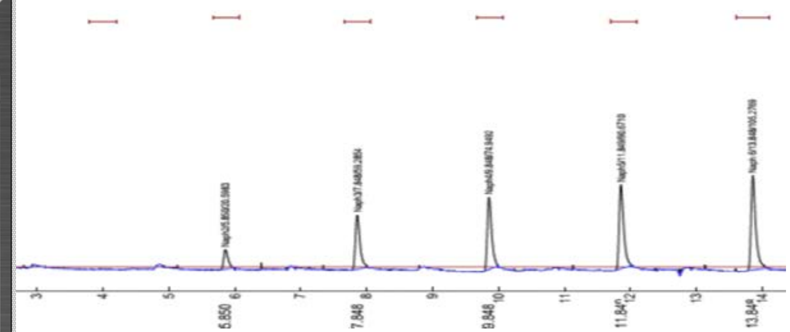
Evolution of pore volume per gram of starting char as a function of burn-off (char obtained from olive stones) [3]

[2] A. M. Mastral et. al. Development of Efficient Adsorbent Materials for PAH Cleaning from AFBC Hot Gas. Energy & Fuels 18, 2004

[3] F. Rodriguez-Reinoso et. al. The use of steam and CO2 as activating agents in the preparation of activated carbons. Carbon Vol. 33, No. 1, 1995

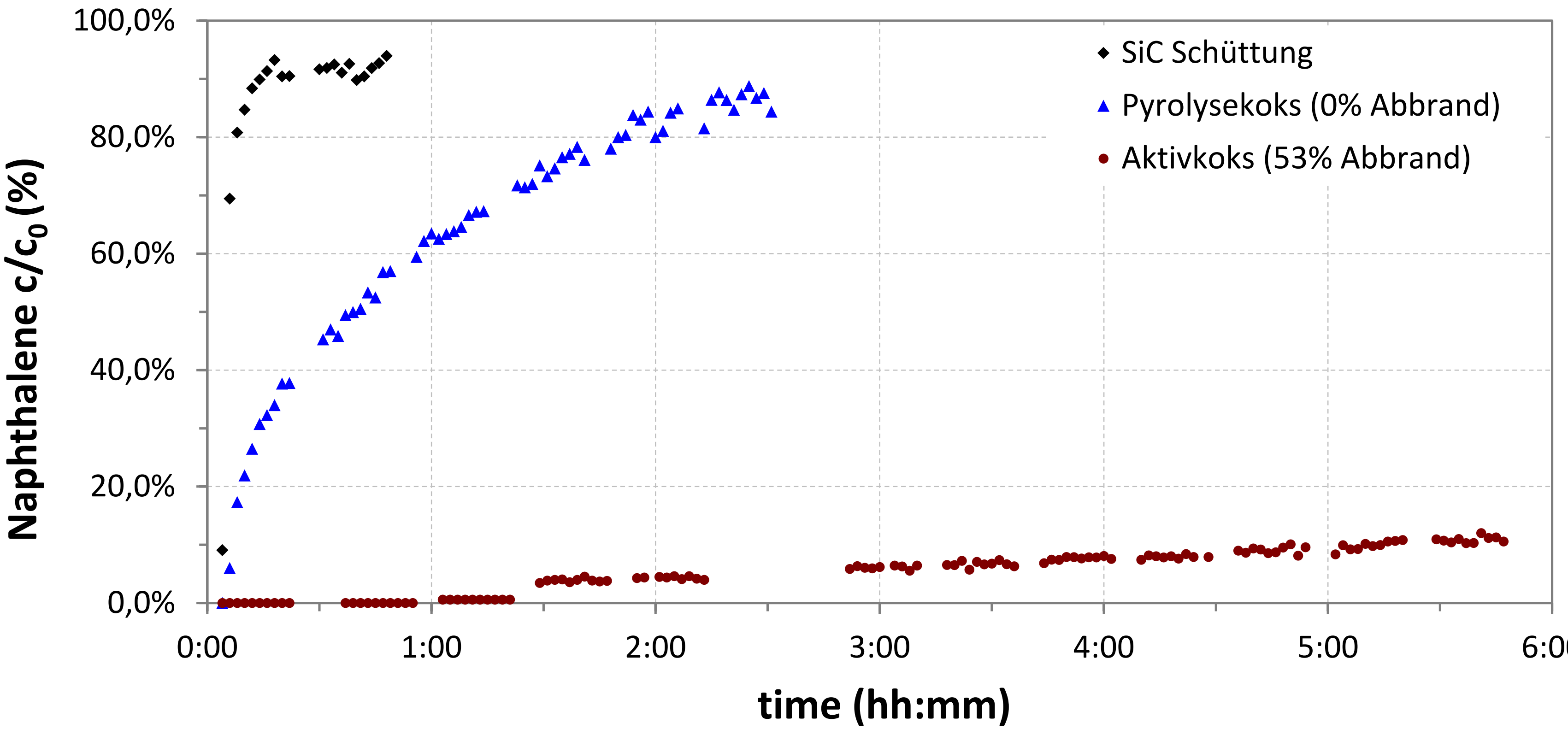
Test stand: PAH adsorption



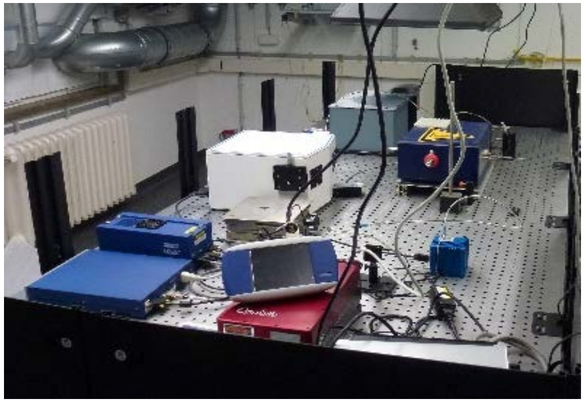


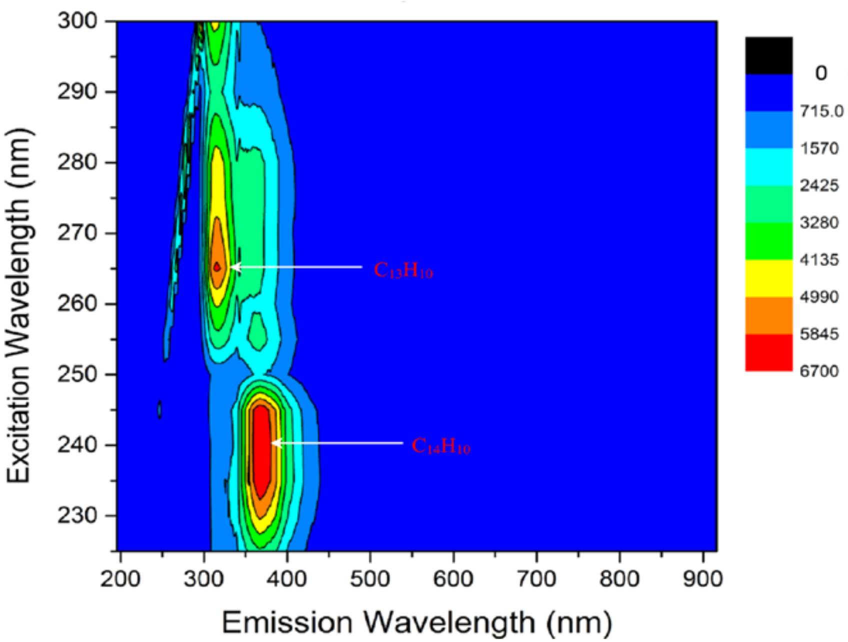
PAH-Adsorption – breakthrough of adsorbents

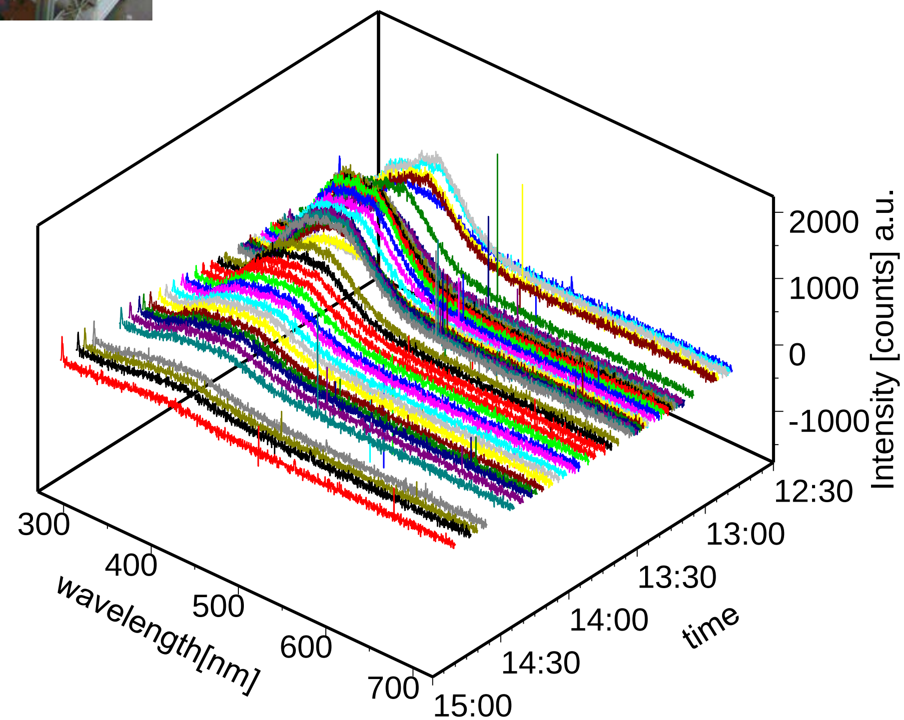
• Adsorptionstemperatur:	150 °C
• Load of naphthalene in the gas	1.500 mg/Nm³
• adsorptive material	4 g
• Gas flow	500 ml/min



Sppecies break through on-line detection in absorption-tests with laser-induced fluorescence



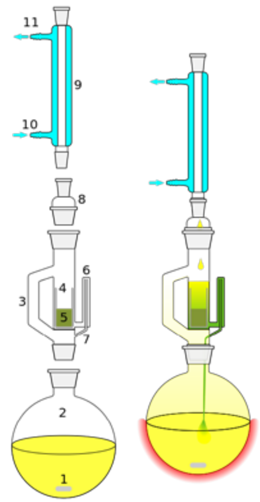


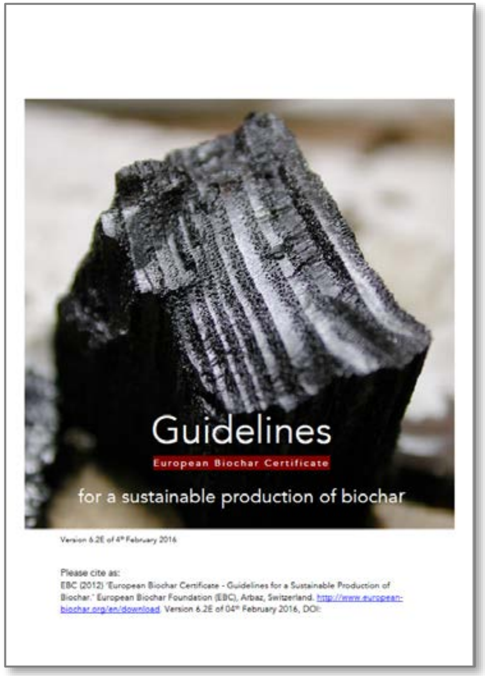


Adsorbed contaminants (BTX, PAH,…)

Extraction of organics (shaking in solvent, Soxhlet, ASE)
and subsequent analysis with GC/MS, GC/FID, (U)HPLC

- Choice of solvent and extraction conditions strongly effect amount of recovered species !
- Highest values are obtained with toluene and hot extraction
- threshold values in working safety, soil applications or for disposal of residues as ‚waste' apply and there are several standards / norms





http://www.european-biochar.org/biochar/media/doc/ebc-guidelines.pdf

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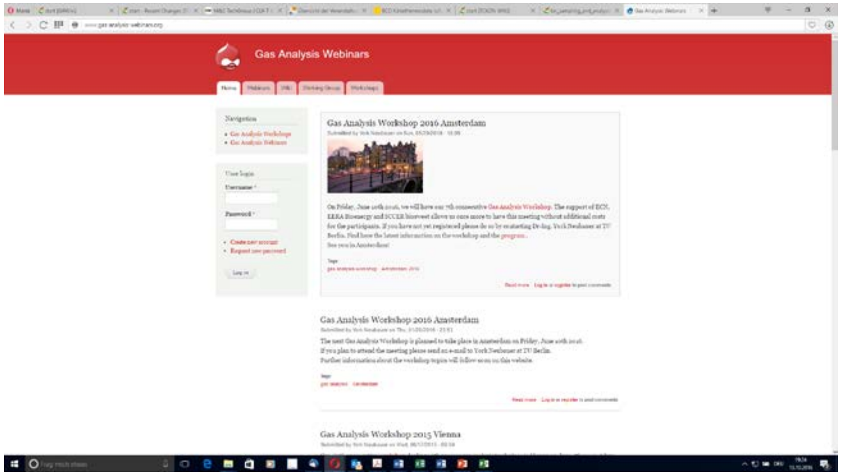

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