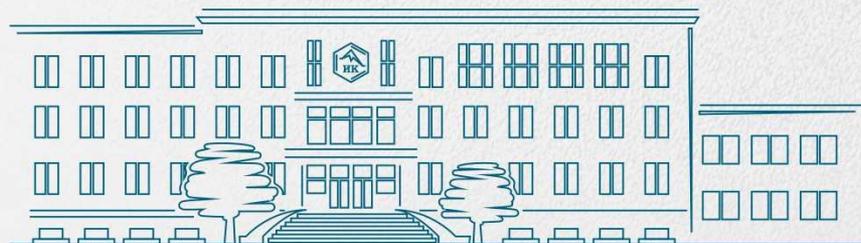# Conversion of vegetable feedstock, peat and coal to porous carbon-mineral composites and carbons via oxidative carbonization in fluidized catalyst bed

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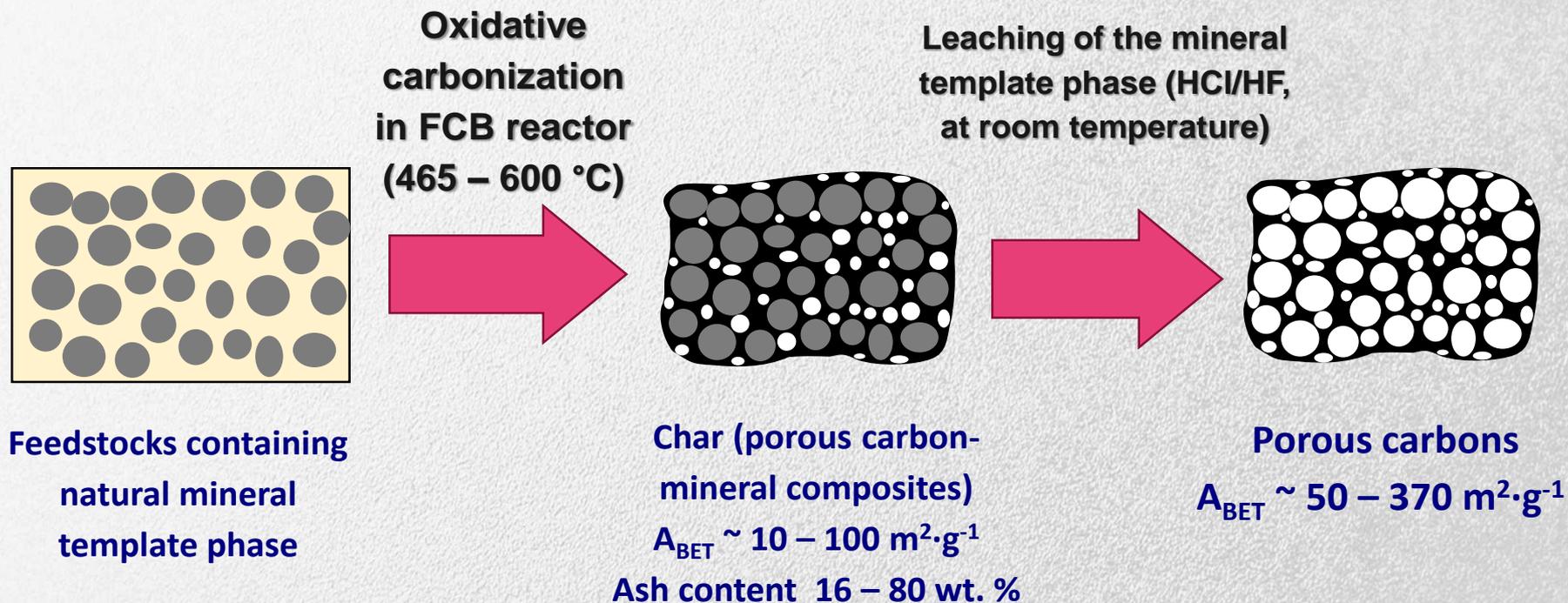September 12 - 17, 2021

Introduction

Currently, biochar production is one of the hottest topics in chemical engineering science that can also be considered as an environmentally friendly approach to carbon dioxide utilization – via the stage of its consumption by a plant. Conventional approaches to biochar production are mainly based on pyrolysis, which is known to be energy consumable and characterized by formation of side polluting products (CO, polyaromatics etc.), which are necessary to be utilized. Compared to pyrolysis, oxidative carbonization of biomass at low temperatures in fluidized catalyst bed (FCB) and air, as the gaseous medium, can allow one to hold the process in autothermal mode, thus avoiding the necessity of creation of inert atmosphere. Furthermore, the use of a deep oxidation catalyst turns the process to clean one since the most of side products undergo complete oxidation to form CO_2 and water.

The goal of this work is to study an opportunity of conversion of three types of renewable raw materials (wheat bran, rice husk, and highly mineralized peat Sukhovskoy), as well as, for the comparison - brown coal, into chars, representing porous carbon-mineral composites, through oxidative carbonization in fluidized catalyst bed reactor at low temperatures (465 – 600 °C). Since such materials are enriched with natural mineral phase that can play a role of template, another idea is estimation of possibility of synthesis of porous carbons via leaching this phase without any additional activation.

Introduction

Scheme of the process

Oxidative carbonization in FCB reactor (465 – 600 °C)

Leaching of the mineral template phase (HCl/HF, at room temperature)

Feedstocks containing natural mineral template phase

Char (porous carbon-mineral composites)
$A_{BET} \sim 10 - 100$ m^2·g^{-1}
Ash content 16 – 80 wt. %

Porous carbons
$A_{BET} \sim 50 - 370$ m^2·g^{-1}

Experimental setup and conditions

Experimental conditions of the carbonization process

- d(reactor) = 75 mm
- h(cat. bed) = 1000 mm
- T = 465, 550 and 600 °C
- catalyst CuO-Cr_2O_3/γ-Al_2O_3
- (Cr_2O_3 − 6.5 wt. %, CuO − 3.5 wt. %, d = 2 − 3 mm, A_{BET} = 115 $m^2 \cdot g^{-1}$)
- τ = 1 − 1.5 s
- α ~ 1.9
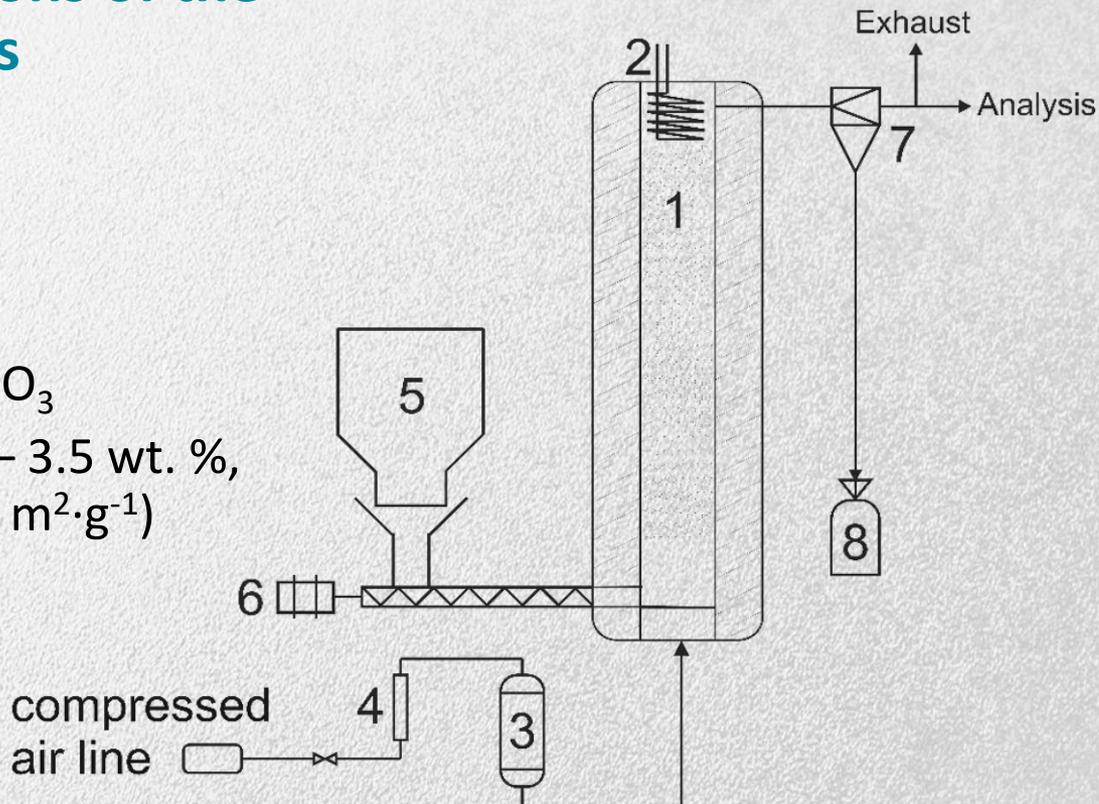
Scheme of the laboratory installation for combustion of solid fuels in a fluidized bed of catalyst. 1 – reactor; 2 – heat exchanger; 3 – electric air heater; 4 – rotameter; 5 – feedstock tank; 6 – screw feeder; 7 – cyclone; 8 – carbonized feedstock collection tank

Experimental setup and conditions

Conditions of acid leaching

▶ Room temperature

▶ Magnetic stirrer

▶ Washing of carbonized wheat bran and highly-mineralized peat by: 1) ca. 10-fold excess of HCl (concentrated, analytical grade, diluted by half); 2) deionized water up to neutral pH

▶ Washing of carbonized rice husk and coal – as SiO_2-enriched feedstocks by: 1) ca. 10-fold excess of HF (concentrated, TU 6-09-3401-88, analytical grade); 2) ca. 10-fold excess of HCl diluted by half); 3) deionized water up to neutral pH – for carbonized rice husk and coal – as SiO_2-enriched feedstocks

▶ Drying at 120 °C up to constant weight

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Experimental setup and conditions

Feedstock composition

CHNS-O composition, moisture, ash, and volatile matter contents of the feedstocks

Feedstock	Moisture W^a, wt. %	Ash content on dry matter A^d, wt. %	Volatile matter V^{daf}, wt. %	CHNS-O-composition, wt. %				
				C daf	H daf	N daf	S daf	O daf
Wheat bran (WB)	8.6	6.9	81.0	49.14	6.66	3.30	0.07	40.83
Rice husk (RH)	5.0	19.5	45.0	51.55	6.83	0.06	0.02	41.54
Peat (P)	9.9	22.8	74.8	52.06	6.31	3.58	0.20	37.85
Coal (C)	14.9	8.3	35.8	77.09	5.43	1.98	0.95	14.55

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Experimental setup and conditions

Feedstock composition

Composition of ash component of the feedstocks in recalculation to oxides of corresponding elements (wt. %) measured by ICP-OES (RH, coal) and XRF (WB, peat)

Oxide	WB	RH	Peat	Coal
SiO_2	1.74	95.8	3.80	54.4
Al_2O_3	26.3	0.11	6.85	23.8
Fe_2O_3	0.41	0.12	8.53	7.07
CaO	0.93	1.06	39.8	5.44
MgO	16.3	0.33	11.1	1.34
Na_2O	28.6	0.30	23.2	0.44
K_2O	17.9	2.17	0.26	1.39
TiO_2	-	-	-	1.10
Mn_2O_3	-	0.08	-	0.07
P_2O_5	7.90	-	6.51	0.95
SO_3	-	-	-	4.00

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Analysis of the products

X-Ray diffraction

Thermo X'tra diffractometer, within the 2θ range from 15° to 75°, with a step of 0.05°, at an acquisition time per point of 4 s, using monochromatic Cu Kα radiation (λ =1.5418 Å)

Nitrogen physisorption

Nitrogen adsorption isotherms were measured by a surface area and pore size analyzer Autosorb 6B (Quantachrome Instruments) at 77 K. Samples were degassed under vacuum to remove adsorbed contaminations and pre-treated at 150 °C for 4 h. Specific surface area was calculated by standard BET method according to IUPAC recommendations, micropore volume was estimated by the αS-plot method using the non-porous carbon Cabot BP 280 as a reference material

SEM

SEM microscope Phenom XL (Thermo Fisher Scientific, USA) was utilized using the beam electrons (beam energy was 10–45 keV)

Raman spectroscopy

Raman spectra were measured using TriVista777 spectrometer (Princeton Instruments). The powder was spread into an even opaque layer onto a glass substrate. Then, the samples were irradiated by solid-state laser at a wavelength of 532.1 nm Using a cylindrical lens, radiation with a power of approximately 7 mW was focused into a line 5 mm long and 0.1 mm thick. The radiation intensity on the samples did not lead to any detectable photoinduced changes in samples. The accumulation time of spectrum for each sample was 20 minutes. The spectra were measured in the range from 700 - 1850 cm 1 with a resolution of 2 cm 1. The baseline was interpolated using a cubic polynomial and subtracted

Ash content

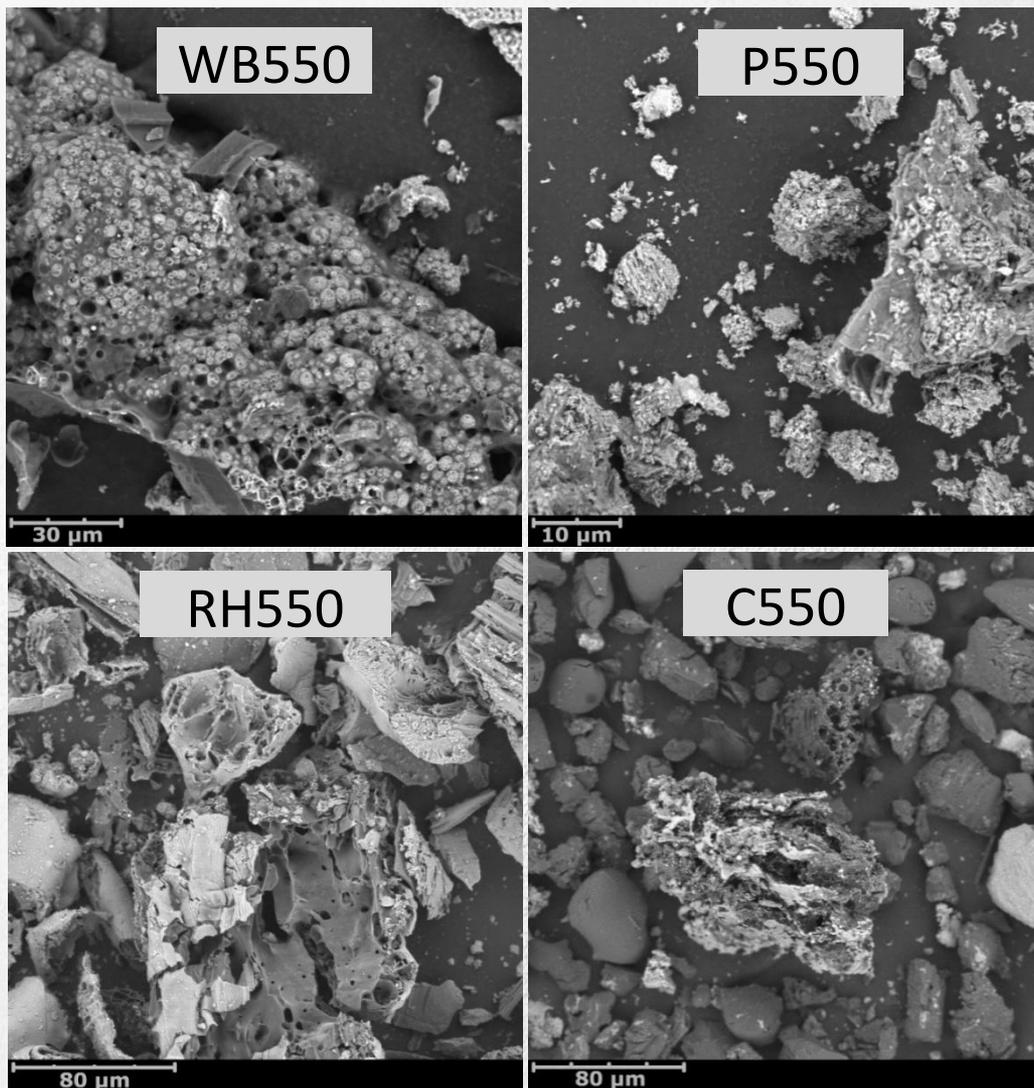Ashing of the samples was carried out in a muffle furnace in air flow at 800 °C for 2 h

Properties of chars – texture characteristics

Texture characteristics, ash content and yield of chars obtained via carbonization in FCB reactor at 465 – 600 °C

Sample	A_{BET}, m^2·g^{-1}	V_Σ, cm^3·g^{-1}	V_μ, cm^3·g^{-1}	$<d_{pore}>$, nm	Ash content, wt.%	Yield, wt. %
Wheat bran						
WB465	43	0.04	0.01	3.7	49.5	13.9
WB550	91	0.05	0.02	2.2	51.4	13.4
WB600	68	0.04	0.01	2.3	57.0	12.1
Rice husk						
RH465	87	0.13	0	6.0	55.7	35.0
RH550	117	0.17	0.01	5.8	66.2	29.5
RH600	99	0.18	0.01	7.4	78.6	24.8
Peat						
P465	11	0.05	0	19.5	57.3	40.0
P550	9	0.06	0	28.5	72.4	31.5
P600	7	0.05	0	32.7	78.5	29.0
Coal						
C465	133	0.07	0.03	2.1	16.1	51.6
C550	126	0.07	0.02	2.1	17.9	46.4
C600	172	0.09	0.03	2.1	19.7	42.1

- All the obtained chars have a developed porosity

- The optimal temperature of carbonization is 550 °C – when porosity is developed at a relatively high char yield

- Coal-derived chars are microporous and characterized by the highest yields due to the highest degree of maturation of carbon-containing phase causing its high stability to oxidation
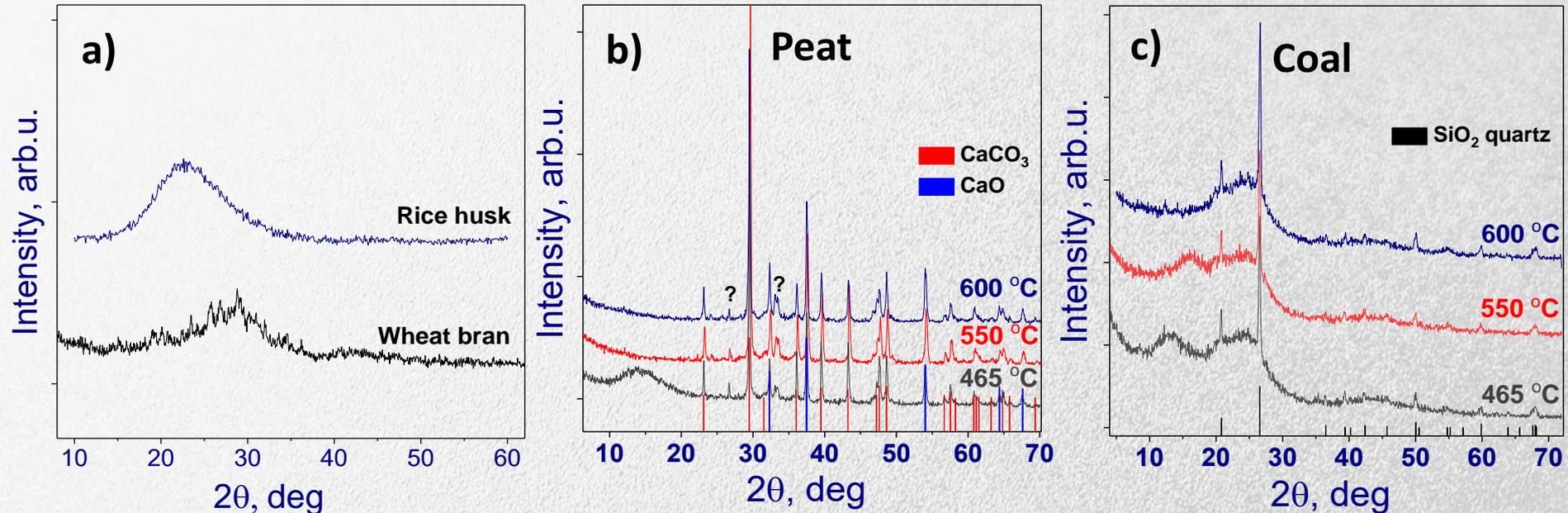
Properties of chars - SEM

WB550

P550

RH550

C550

30 μm

10 μm

80 μm

80 μm

SEM images of chars obtained at 550 °C

- Size and shape of the particles remained close to those of an initial feedstock
- They are enriched with mineral phase that seems to be distributed rather homogeneously for WB and RH

Properties of chars – XRD

XRD patterns of a) RH and WB carbonized at 600 °C; b) peat and c) coal – both at 465 – 600 °C

▸ In biochars mineral phase is amorphous, while peat is enriched with $CaCO_3$ and CaO, and coal – with quartz

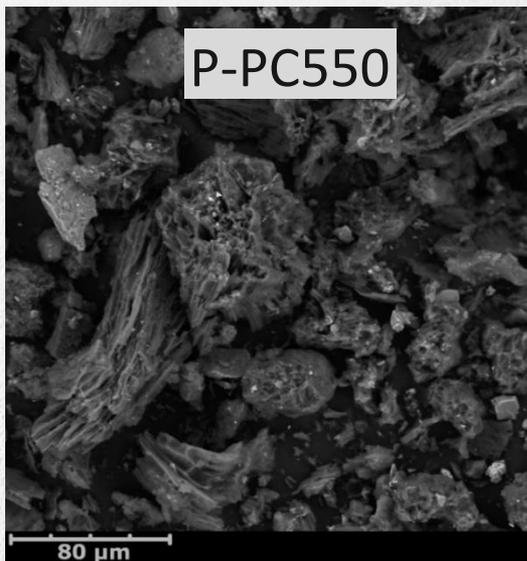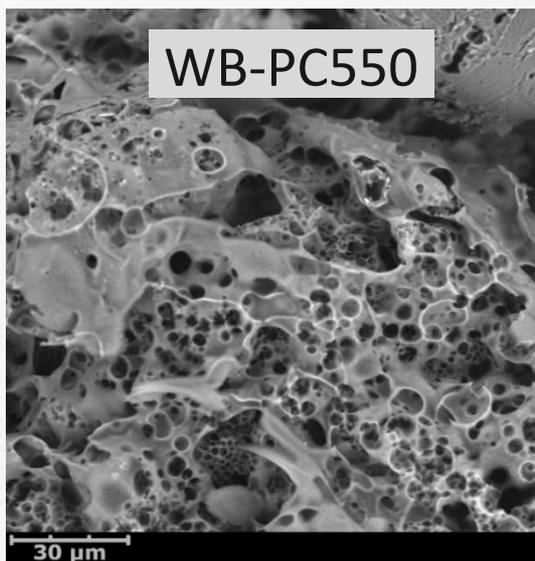# Properties of porous carbons – texture characteristics

Texture characteristics, ash content and yield of porous carbons obtained via acid leaching of the carbonized feedstocks

| Sample	A_{BET}, $m^2 \cdot g^{-1}$	V_Σ, $cm^3 \cdot g^{-1}$	V_μ, $cm^3 \cdot g^{-1}$	$<d_{pore}>$, nm	Ash content, wt.%	Yield, wt^*. %
Wheat bran						
WB-PC465	175	0.16	0.05	3.6	9.7	7.8
WB-PC550	231	0.18	0.05	3.2	11.7	7.4
WB-PC600	250	0.19	0.04	3.1	9.1	5.7
Rice husk						
RH-PC465	28	0.04	0	5.2	0.4	15.6
RH-PC550	207	0.17	0.05	3.2	2.0	10.2
RH-PC600	369	0.28	0.09	3.0	2.2	5.4
Peat						
P-PC465	10	0.04	0	17.4	3.3	9.3
P-PC550	27	0.11	0	15.7	2.3	2.3
P-PC600	56	0.16	0.01	11.6	4.9	0.7
Coal						
C-PC465	102	0.06	0.02	2.4	1.4	43.9
C-PC550	117	0.06	0.03	2.1	1.0	38.5
C-PC600	189	0.10	0.03	2.1	1.3	34.3

* - relating to initial feedstock

- Biomass-derived porous carbons have the highest porosity due to probably higher dispersity of mineral template phase in the biochars

- Leaching of the mineral template phase from coal-derived chars did not significantly affect specific surface area of the corresponding PCs that can be connected with the large size of mineral phase particles. The same concerns peat-derived PCs

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Properties of chars - SEM

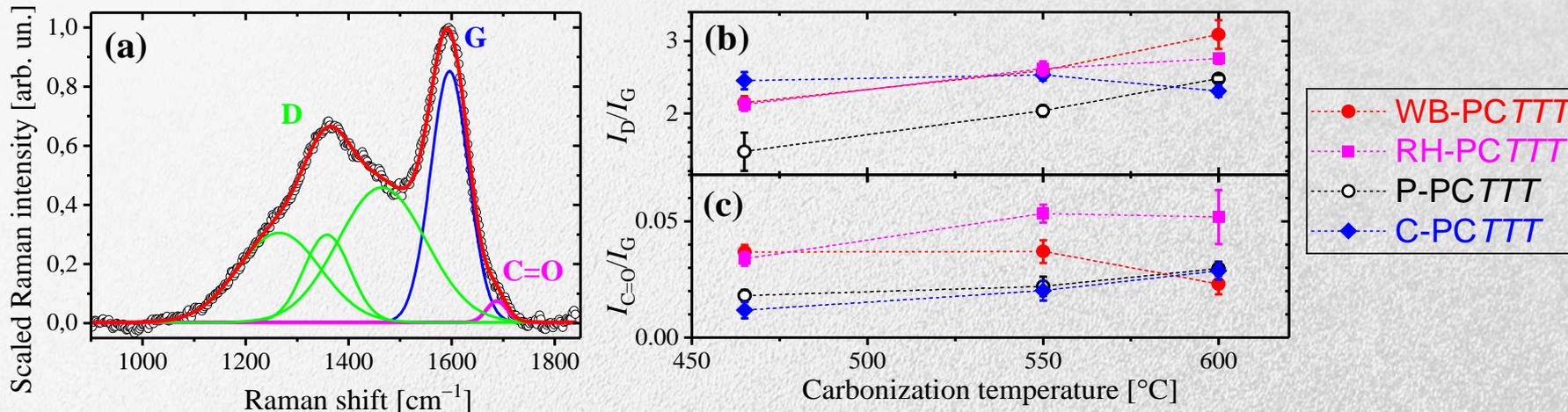Labels on images: WB-PC550, P-PC550, RH-PC550, C-PC550; scale bars: 30 µm, 80 µm, 100 µm, 80 µm

- Mineral part was leached practically completely
- Porosity significantly increased due to mineral part removal, especially for biochar-derived PCs
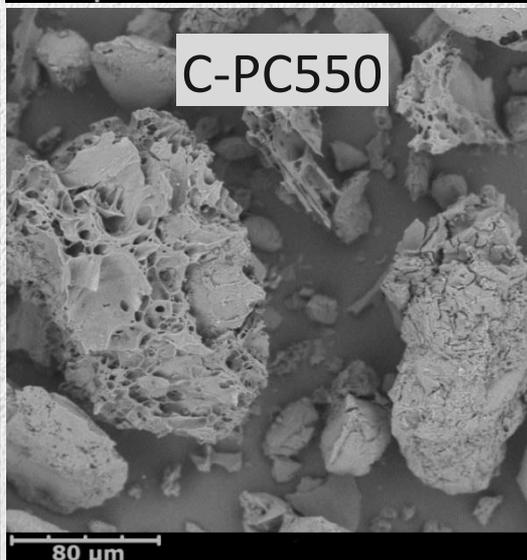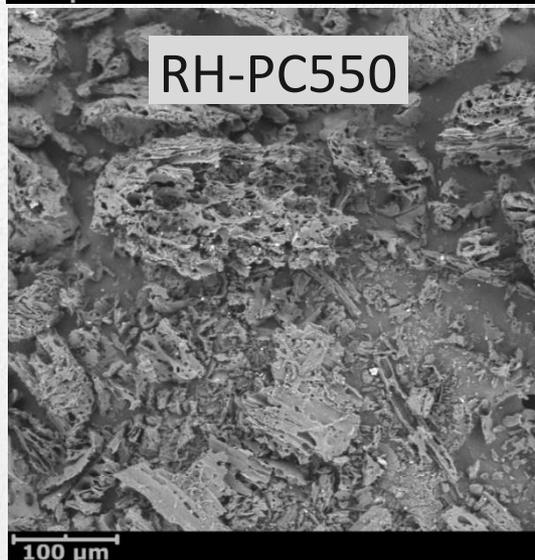
SEM images of PCs produced from chars obtained at 550 °C

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Properties of porous carbons – Raman spectroscopy

Raman study of PCs: (a) spectrum decomposition by the example of WB-PC550; (b) I_D/I_G ratio dependence on the carbonization temperature; (c) $I_{C=O}/I_G$ dependence on the carbonization temperature

▮ Biomass-derived PCs tend to be more disordered than those formed from peat, and have a higher content of carbonyl groups than PCs synthesized from the both sedimentary feedstocks (peat and coal)

Conclusions

- Oxidative carbonization of natural carbon-containing feedstocks in a reactor with fluidized bed of deep oxidation catalyst, at low temperatures (≤ 600 °C), allows for clean and energy-effective production of charcoals representing porous carbon-mineral composites, with ash content and porosity depending on a raw material. In the case of cereal husks (wheat bran and rice husk), their BET specific surface area can achieve ~ 100 $m^2 \cdot g^{-1}$ and pore volume of ~ 0.2 $cm^3 \cdot g^{-1}$ with a high share of mesopores and ash content $\sim 50 - 80$ wt. %. Their mineral phase, formed in the course of rice and wheat growing, is amorphous, for RH – it is mainly SiO_2. For coal, the obtained chars are microporous and have the highest A_{BET} (up to ~ 170 $m^2 \cdot g^{-1}$) and yields (up to 52 wt. %).

- Leaching the mineral template phase significantly developed porosity for biochars – it was possible to synthesize porous carbons with A_{BET} up to ~ 370 $m^2 \cdot g^{-1}$ and pore volume of ~ 0.3 $cm^3 \cdot g^{-1}$ (for RH), while for PCs from peat A_{BET} increased not too significantly, and for coal – remained the same. This can be caused by a low dispersity of the mineral phase that contains well-crystallized CaO and $CaCO_3$ (peat) and quartz (coal).

- The obtained materials can find such applications as cheap adsorbents for soil remediation, wastewater treatment, as a source of SiO_2-based products (in case of RH and coal) etc.

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