

Research article

Oxidation characteristics of a cellulose-derived hydrochar in thermogravimetric and laminar flow burner experiments



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ABSTRACT

Synthetic lignite was prepared by hydrothermal carbonization, in which minerals typical for coal ashes were incorporated during hydrothermal carbonization allowing us to study the catalytic effect of ash components on the oxidation rate of the fuel. Chemically leached lignite using hydrochloric acid was applied as reference material. Combustion experiments were performed by thermogravimetric analysis under chemically controlled conditions and in a laminar flow reactor under pore-diffusion limitation. The investigation of the hydrochar in the laminar flow reactor provided gas temperatures and heating rates typical for pulverized coal combustion. The combustion rate of the chemically leached lignite was found to be comparable to the hydrochar. Furthermore, the catalytic effect of incorporated iron oxide was detected in both combustion experiments.

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1. Introduction

Lignites vary in composition to a large extent depending on their origin. In addition to the water and sulfur content, they differ particularly in ash content and composition. These differences influence the combustion behavior of the solid [1]. Alkali and alkaline earth metals as well as transition metals are well known to catalyze carbon oxidation [2–5]. Commonly, investigations consider the catalytic influence of the specific metal compounds by increasing the concentration of a defined mineral or by decreasing the total mineral content by chemical leaching [6,7]. According to this procedure it is difficult to distinguish the specific influence of each mineral on the combustion. Most of these results were obtained by thermogravimetric analysis (TGA) characterized by low heating rates [2–6], whereas typical industrial applications for pulverized-coal combustion proceed at heating rates in the order of 10^4 – 10^5 °C/s [8]. The amount of volatiles as well as the surface structure of the obtained chars depend strongly on the temperature history of the particle and, therefore, on the heating rate [9]. At low heating rates, combustion is mainly under kinetic control (Zone I), whereas at high heating rates combustion is diffusion-controlled (Zone II + III) [10–12]. Therefore, the description of combustion behavior requires different apparent kinetic models resulting in different apparent kinetic parameters for different regimes [13].

To study the influence of different oxides, a mineral-free carbonaceous solid fuel obtained by hydrothermal carbonization (HTC) was doped systematically with minerals. To mimic the natural coalification process, minerals were included in the hydrothermal carbonization yielding a lignite-like solid fuel as presented in Ref. [14]. Thereby, it is possible to vary the concentration as well as the chemical nature of the mineral.

Herein, we investigate the influence of minerals on the oxidation behavior of the hydrochar in TGA and the application of the mineral-doped hydrochars under more realistic conditions using a laminar flow reactor, which provided typical heating rates for pulverized-coal combustion excluding particle-particle interactions [15–18]. Thus, the combustion behavior of single hydrochar and mineral-doped hydrochar particles was investigated.

2. Material and methods

Pure α -cellulose (Sigma Aldrich) was used to synthesize a reference hydrochar. Mineral doping was carried out by pre-mixing of cellulose and SiO_2 (Riedel-de Haën) in the sieve fraction of 40–63 μm and Fe_2O_3 (Sigma Aldrich) in the sieve fraction of <5 μm , respectively, on a dry basis. The mixture of 60 g cellulose and 1.5 g mineral was suspended in 300 ml de-ionized water using a 500 ml stainless-steel autoclave with PTFE inliner. The reactor was heated in an oven equipped with hot air ventilation to 200 °C resulting in a H_2O pressure of 16 bar and held for 24 h at this temperature. After cooling the reactor to room

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Table 1

Ash analysis of the investigated rhenish lignite after oxidation at 815 °C.

Compound	Amount (wt.%)
CaO	37.1
MgO	19.5
SO ₃	14.4
Fe ₂ O ₃	11.5
SiO ₂	5.7
Na ₂ O	5.5
Al ₂ O ₃	4.0
K ₂ O	1.2
TiO ₂	0.3
BaO	0.3
SrO	0.3
MnO	0.1
P ₂ O ₅	0.1

temperature, the solid residue was washed with de-ionized water until the pH was neutral. The hydrochar was obtained after drying the washed residue over night at 105 °C and labeled HTC and X/HTC with X: Fe or Si.

For chemical leaching, 30 g of rhenish lignite (RL, delivered from the Frimmersdorf bed at the Hambach mine, Table 1) in the sieve fraction of 63–90 µm were suspended in 200 ml of a 1.5 M aqueous solution of hydrochloric acid and stirred for 72 h at room temperature. Thereafter, the suspension was filtered and the residue was washed until the pH was neutral. The obtained solid was dried over night in an oven equipped with hot air circulation at 105 °C and labeled RL-HCl.

TGA was carried out using a magnetic suspension balance (Rubotherm) with a coupled online mass spectrometer (Pfeiffer ThermoStar). All oxidation experiments were conducted at atmospheric pressure in the temperature range from room temperature to 850 °C with a linear heating rate of 5 °C/min and a total flow rate of 100 ml/min synthetic air (20% O₂ in He). Helium was used as diluent instead of nitrogen due to the application of mass spectrometry. Approximately 30 mg of the sample were used to investigate the oxidation behavior in the TGA experiments.

Proximate analysis was performed using the TGA set-up according to the ASTM standard. The C, H, and O elemental analysis was conducted by chromatographic analysis using a Vario EL (Elementar Hanau). Atomic absorption spectroscopy (AAS) was performed to detect the specific amounts of Si, Ca, Fe, and K using a flame spectrometer SpectraAA 220 (Variant). X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–80° using a step width of 0.030° with a Panalytical MPD diffractometer applying CuK_α radiation, 0.5° divergent and antiscatter slits, a 0.2 mm high receiving slit, incident and diffracted beam 0.04 rad Soller slits, and a secondary graphite monochromator. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy were performed using a FEI eSEM Dual Beam Quanta 3D FEG. The samples were positioned on a sample holder covered with an adhesive carbon film.

Pyrometric measurements of char burnout were carried out in a combustion-driven laminar flow reactor (Hencken burner). CH₄ was passed separately from the oxidizing mixture consisting of O₂ and CO₂

Table 2

Proximate and ultimate elemental analysis of the investigated samples.

Sample	Volatiles (wt.%)	Fixed carbon (wt.%)	Ash (wt.%)	C (wt.%)	H (wt.%)	O ^a (wt.%)
RL	52	45	3	59.9	4.9	32.2
RL-HCl	53	46	1	63.0	5.1	30.9
HTC	53	47	0	65.0	4.2	30.4
Si/HTC	52	44	4	64.6	3.8	27.6
Fe/HTC	50	46	4	63.0	4.3	28.8

^a The amount of oxygen was calculated according to $O(\text{wt.}\%) = 100 - C(\text{wt.}\%) - H(\text{wt.}\%) - \text{ash}(\text{wt.}\%)$.

Table 3

Mineral analysis of the investigated samples detected by AAS. Results represent the mineral content with respect to the total mass of the sample.

Sample	SiO ₂ (wt.%)	Fe ₂ O ₃ (wt.%)	CaO (wt.%)	K ₂ O (wt.%)	Na ₂ O (wt.%)
RL	<1.3	0.33	1.96	0.08	0.49
RL-HCl	<1.3	0.40	1.16	0.02	0.11
HTC	n.d.	n.d.	n.d.	n.d.	n.d.
Si/HTC	3.96	n.d.	n.d.	n.d.	n.d.
Fe/HTC	n.d.	3.59	n.d.	n.d.	n.d.

n.d.: not detectable.

through a ceramic honeycomb body. A matrix of homogeneously distributed small diffusion flames at the bottom of the reactor produced a hot-gas atmosphere containing 30% O₂, 52.2% CO₂ and 17.8% H₂O, typical for O₂ mixed with recirculated wet oxy-fuel flue gas. The average gas temperature in the particle reaction zone was 1250 °C. Single fuel particles were injected at the centerline of the burner. The small fuel dosing of 0.5 g/h avoided particle-particle interactions and kept the gas composition of the reaction atmosphere constant. The camera-based pyrometer system SCOT (Stereoscopic Camera system for Optical Thermography) was used to measure single particle surface temperatures and diameters for statistically meaningful numbers of particles. The optical set-up of the system consisted of 4 intensified CCD cameras working on the principle of two-color pyrometry. The particle streak was measured at different reactor heights covering the particle history from ignition to a significant char burnout. At every distance, at least 500 particles were recorded. In addition to temperature and diameter, particle velocities measured by long-term exposure were used to calculate the residence time of the burning particles. Both temperature/diameter and velocity determination required image processing. In brief, particles were clearly identified by their radiation exceeding the background noise by several orders of magnitude. Diameter determination was carried out at 50% of a particle's maximum intensity. For temperature determination, the total light intensity in both color bands of the pyrometer (650 nm and 785 nm) exceeding the background noise was integrated. Subsequently, the ratio was compared to a calibration curve. A detailed description and sensitivity analysis of the SCOT set-up can be found in Ref. [18].

3. Results and discussion

As revealed by AAS and proximate analysis, the minerals were still present after the hydrothermal carbonization for all doped hydrochars (Tables 2, 3). The amount of metal oxide was slightly lower than the desired 5 wt.%. However, the oxidation profiles of the obtained hydrochars

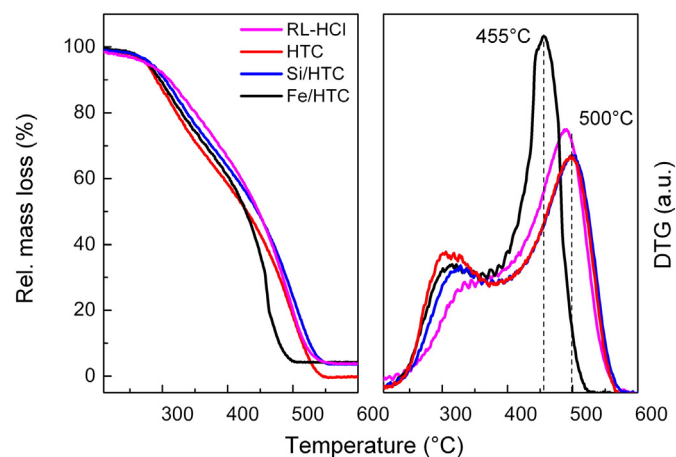


Fig. 1. Relative mass loss (left) and DTG curve (right) of chemically leached rhenish lignite, pure hydrochar, and hydrochars obtained in the presence of Fe₂O₃ and SiO₂ during the HTC heating in 20% O₂ in He with a heating rate of 5 °C/min.

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