



Synthesis and characterization of lignite-like fuels obtained by hydrothermal carbonization of cellulose



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HIGHLIGHTS

- Hydrothermal conversion of cellulose leads to H/C and O/C ratios close to real lignite.
- Leaching of rhenish lignite with acids changes the oxidation temperatures.
- Synthetic lignite was obtained by hydrothermal conversion of cellulose at 48 h at 200°.
- Synthetic lignite has a similar oxidation profile as acid-leached rhenish lignite.
- ATR-IR and NMR spectroscopy are highly useful tools to analyze synthetic and real lignites.

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ABSTRACT

Hydrothermal carbonization of cellulose was used to synthesize a mineral-free lignite-like solid fuel. By varying the reaction time the elemental composition was tuned to fit the composition of real lignite. Minerals were removed from real lignite by HCl and HNO₃ leaching leading to altered oxidation temperatures. After 24 h of hydrothermal treatment a synthetic lignite was obtained exhibiting two peaks in the differential mass loss curve during oxidative thermogravimetric analysis. This oxidation profile was similar to the oxidation profile determined for chemically leached lignite. Attenuated total reflectance infrared and nuclear magnetic resonance spectroscopy revealed comparable chemical structures for both synthetic and real lignite.

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1. Introduction

Lignites vary in composition depending on their origin to a large extent. Among other properties, they differ in water, sulfur and particularly ash content. The amount and composition of the ash has a significant influence on the combustion behavior of the solid [1]. In literature, it is well known that alkali and alkaline metals as well as transition metals can catalyze carbon oxidation [2–6]. Nevertheless, only little is known about the influence of the specific metal compounds on the combustion of carbonaceous materials. To study the particular influence of different metals, the mineral amount has to be varied systematically. Therefore, two possible routes can be pursued: varying selectively the concentration of one mineral based on real lignite by adding or removing [7,8] or starting with a mineral-free carbonaceous material which can be

doped with one defined mineral. For the latter, hydrothermal treatment (HTC) of biomass has gained increasing interest [9–12].

The natural process of coalification, which lasted millions of years, can presumably be imitated by HTC in laboratory scale during a few days [12]. HTC can be used as mild conversion ($T \leq 250$ °C) of saccharides into higher value-added, carbon-rich products [13]. It was already shown that the energy-related properties and structure of biomasses obtained by HTC as well as their chemical and spectroscopical nature are similar to peat or lignite [13,14]. Still, there is a lack of information about the combustion behavior of HTC-derived lignite.

Here, both routes were investigated to clarify the question as to whether the synthetic cellulose-derived lignite has comparable physical and chemical properties compared with the carbon skeleton of real lignite. Thermogravimetric analysis (TGA) in air was used as the most useful and quick technique for evaluating combustion characteristics of solid fuels.

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2. Experimental

3 g of rhenish lignite (RL) from the Garzweiler mine (Table 1) in the sieve fraction of 90–120 μm were suspended in 200 ml 1.5 M aqueous solution of hydrochloric acid or 1 M HNO_3 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. The HCl- and HNO_3 -leached lignite is labeled RL-HCl and RL- HNO_3 , respectively.

Pure cellulose (Sigma Aldrich) was used to produce a mineral-free reference hydrochar. 6 g of α -cellulose were suspended in 30 ml de-ionized water using a 50 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 8–48 h at this temperature. After cooling the reactor to room 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. The hydrochars are labeled HTC \times h depending on the duration of reaction.

TGA was carried out using a magnetic suspension balance (Rubotherm) with a coupled online mass spectrometer (Pfeiffer ThermoStar). All combustion experiments were conducted at atmospheric pressure in the temperature range from room temperature to 850 °C with a linear heating rate of 5 K/min and a total flow of 100 ml/min synthetic air (20% O_2/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 combustion behavior in the TGA experiments.

Proximate analysis was performed using the TGA setup 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 Ca, Fe, and K using a flame spectrometer SpectraAA 220 (Variant).

^{13}C solid-state MAS NMR experiments were performed with a DPX 300 MHz (7 T) spectrometer (Bruker) at room temperature using a 4 mm Zr-Rotor with a MAS spinning rate of $\nu_{\text{MAS}} = 14$ kHz. To enhance carbon sensitivity, proton-to-carbon cross polarized MAS was used with a recycle delay of 3 s and TPPM 15 widerange decoupling. Cross polarization transfers were performed under adiabatic tangential ramps to enhance the signal intensity with respect to other known methods and the CP time was set to 4 ms. The number of scans was 20,000 for all investigated samples. The ^{13}C chemical shifts were calibrated using adamantane ($\delta = 38.48$ ppm).

Attenuated total reflectance infrared (ATR-IR) spectroscopy was used to obtain information on the moieties present in the investigated samples. The spectra were obtained with a Fourier transform spectrometer Nicolet 6700 FTIR (Thermo Scientific) using a diamond ATR accessory DuraSamplIR II (Smiths Detection) with a resolution of 2 cm^{-1} from 4000 to 500 cm^{-1} over 100 scans.

Table 1
Ultimate ash analysis of the investigated rhenish lignite after oxidation at 815 °C.

Metal oxide	Amount (wt%)
SiO_2	67.4
CaO	13.9
Fe_2O_3	4.7
MgO	3.8
Al_2O_3	1.3
Na_2O	0.8
K_2O	0.3
TiO_2	<0.3

3. Results and discussion

In Fig. 1 the TG/DTG profiles of raw rhenish lignite and chemically-leached lignite during temperature-programmed oxidation (TPO) experiments are shown. For the raw lignite only one major mass loss at temperatures between 300 and 420 °C was observed. The chemically leached lignites exhibited two peaks in the TGA. The first peak occurred at 340 °C and can be assigned to pyrolysis, whereas the second one at 490 °C originates from char oxidation. According to proximate analysis, the chemical leaching led to partial removing of mineral matter from the raw lignite. The amount of ash was determined to decrease from 19% for the raw lignite to 8% for RL-HCl and 2% for RL- HNO_3 (Table 2). The remaining solid can most likely be assigned to SiO_2 . Due to partial carbothermal reduction, the relative mass loss at 600 °C is comparable for RL-HCl and RL- HNO_3 . With increasing oxidation temperature up to 800 °C, a mass increase was observed originating from reoxidation of the remaining metal compounds ending up with the ash contents determined by proximate analysis.

The HNO_3 treatment led to a higher degree of demineralization compared with the HCl leaching, which did not contribute to a significant change in the oxidation profile. The TG/DTG curves of RL- HNO_3 show a higher mass loss at low temperatures indicating a higher amount of highly reactive functional groups. These additional functional groups originate from the exposure to HNO_3 acting as oxidant as indicated by the higher oxygen amount detected by proximate analysis (Table 2).

The composition of the potentially catalytically active minerals in the natural lignites determined by AAS decreased in the order calcium, iron, sodium and potassium (Table 3). After chemical leaching the concentrations decreased from 0.39 wt% for Fe, 1.21 wt% for Ca and 0.04 wt% for K close to 0 wt% for each element. The concentration of sodium decreased as well from 0.20 wt% to 0.09 wt%, but its final concentration was higher compared with the other metals (Table 3). RL-HCl and RL- HNO_3 showed similar composition, which is in line with the comparable oxidation profiles detected by TGA.

The ATR-IR spectra of raw and chemically leached lignite resemble each other (Fig. 2) showing strong aliphatic C–H vibrations at 2920 and 2848 cm^{-1} [15], and additional aromatic C=C vibrations at 1602 cm^{-1} as well as aromatic out of plane vibrations from 900 to 700 cm^{-1} . The band at 1510 cm^{-1} originates from the aromatic skeletal C=C vibration of benzene, which is characteristic for lignin [16,17]. Furthermore, several C–O bands were identified: first of all, the C=O vibrations at 1702 cm^{-1} [18,19], asymmetric

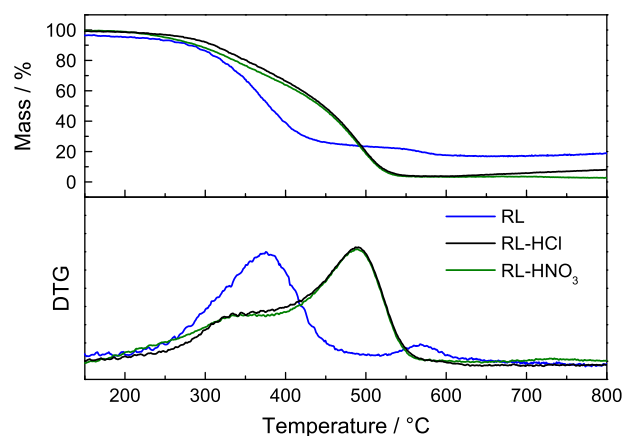


Fig. 1. Relative mass losses and resulting DTG curves of rhenish lignite and chemically leached lignites during the TPO experiment in synthetic air using a heating rate of 5 K/min.

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