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Impact of HTC reaction conditions on the hydrochar properties and CO_2 gasification properties of spent grains

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ABSTRACT

The impact of residence time and temperature during hydrothermal carbonization (HTC) on hydrochar properties and CO_2 gasification properties has been studied for brewers' spent grain (BSG), treated at temperatures from 180 °C to 280 °C and residence times from 0.5 to 12 hours. Lower heating values (LHV) of the hydrochars are found to increase to values of bituminous coal and anthracite as reaction severity increases. Temperature is found to have a greater influence on the LHV of the hydrochar than residence time. Mass and energy yields decrease with increasing reaction severity. With higher reaction severity decreased molar O/C and H/C ratios as well as decreased volatile contents and increased fixed carbon contents are observed. The influence of residence time is more pronounced for the formation of fixed carbon, main carbonization reactions occur for a reaction severity greater than 180 °C and 0.5 hours. Char reactivity is found to decrease with increasing carbonization reaction severity with a strong influence of both residence time and temperature due to the formation of fixed carbon in the hydrochar. Activation energies are decreased with increased carbonization temperature but only mildly affected by residence time. Hereby the catalytic influence of ash compounds has to be further determined.

1. Introduction

As part of the ongoing transition to renewable energy, the German government set its goals to provide 35% of the gross electricity consumption from renewable energy sources by 2020 [1]. In 2014, 27.4% of the energy was produced from renewable sources, of which 8.5% originated from biomass [1,2]. However, due to the large diversity of biomass and unfavorable fuel properties, a significant amount of the available bioenergy potential, especially the potential of biomasses with high moisture contents, remains unused. The biggest hurdles regarding thermal usage have proven to be high moisture contents, high corrosion potential because of high chlorine and alkali contents and extensive fouling and slagging due to low ash fusion temperatures [3]. Moreover, degradation during storage and low energy density strongly limit the economic feasibility of using these biomasses for thermochemical conversion processes. In this context, biomass upgrading technologies such as hydrothermal carbonization (HTC) or torrefaction (TF) have gained renewed interest in recent years.

Hydrothermal carbonization was discovered by Friedrich Bergius in 1913 as a method to recreate natural coalification in a hydrothermal environment under typical process conditions of 180 °C–250 °C and residence times from 1 h to 12 h [4–7]. Under these conditions, the liquid high pressure water changes its chemical properties and a complex reaction network of decomposition and polymerization of the hemicellulose and cellulose, and degradation of the lignin transform the biomass into a solid product, often referred to as hydrochar, which is found to exhibit improved fuel properties [6,8,9]. Hydrochars generally show higher heating values, higher ash fusion temperatures and in some cases reduced sulfur and nitrogen contents compared to the raw biomass [8,10]. Also the hydrophobicity of the hydrochars is increased, facilitating the drying process and strongly increasing the storage stability [11]. Compared to TF, the efficiency of HTC, due to the necessary immersion in water, favors the use of wet biomass and therefore presents a possibility of a profitable usage of wet biomass residues in energetic processes.

A promising biomass in this context is brewers' spent grains (BSG) with an annual production of 2 Mt in Germany in 2010 [12]. Currently BSG is mainly used as feed for cattle but a decreasing number of lifestock and the possibility of energy generation for the brewing process open an attractive pathway for energetic use of this biomass [13]. The HTC process itself and its impact on the solid product have been examined by various studies for many different types of biomass and a

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wide range of parameters [7,14-17]. The use of BSG in HTC processes was first examined by Heilmann et al. as an alternative route to drying and combustion, yielding hydrochars with high energy contents at relatively mild conditions [18]. Further investigations in HTC of BSG were performed by Poerschmann et al. and Baskyr et al., giving a detailed picture on the chemistry of the process and proposing a way to treat the process water [19,20]. The first part of this study extends the findings of the previous studies to wider range of process parameters and gives a detailed picture of the impact of reaction conditions on fuel properties, which are important for thermochemical conversion processes.

A new approach to thermochemical conversion of biomass is entrained flow gasification, which has the advantage of high and fast conversion, a high efficiency and low tar generation [21]. The resulting product gas then can be subject to either cogeneration (CHP), conversion to synthetic natural gas or provision of syngas. For this type of gasification an easily grindable, high grade fuel is required, all of which are features reported from hydrochars. Tremel et al. reported a potential conversion of hydrochars made from beech wood in an entrained flow gasifier with conversions of 84%–88 % at temperatures from 1000 °C to 1400 °C [21]. Gunarathne et al. reported a general feasible conversion in a lab-scale gasification setup [22]. However, a link between HTC reaction conditions and the gasification behavior of the resulting hydrochars is still missing. For this reason the second part of this study focuses on the effect of process conditions on the CO_2 gasification reactivity of chars, obtained from pyrolysis of the hydrochars.

2. Experimental method

HTC experiments are carried out in a stirred mini batch reactor with a volume of 600 mL designed for a temperature range of up to 350 °C and a pressure range of up to 200 bar. Temperature is controlled with three heating sleeves with a power of 700 W each. The system is pressurized with argon (4.6 purity) and the pressure is kept constant throughout the process with a backpressure regulator. The biomass used for the experiments is BSG provided by a local brewery. Proximate and ultimate analysis for the biomass is shown in Table 1.

For the HTC experiments, the biomass is immersed in deionized water with a concentration of 10 g dry substance per 100 mL and poured into the reactor. The system is then pressurized, brought to reaction temperature at a heating rate of 7 K min $^{-1}$ and held at the specified residence time. The reactor is cooled down after the reaction and the slurry is filtered and dried to isolate the solid product. Proximate analysis is done according to industrial standard methods DIN 51718, DIN 51719 and DIN 51720, ultimate analysis is done according to industrial standard methods DIN 51900-1 and DIN 51732.

Table 1
Fuel properties of brewers' spent grains.

Proximate analysis (wt.%)	
Ash content (dry)	3.8
Volatile matter content (dry)	83.9
Moisture content (as received)	80.0
Fixed Carbon (dry)	12.3
Ultimate analysis (wt.%, dry)	
C	50.4
H	6.4
N	4.1
S	0.7
O	34.6
Cl[1]	0.03
Caloric Properties (MJ kg $^{-1}$, dry)	
LHV	21.5
HHV	23.3

[1] Not included in CHNSO balance

Gasification properties are analyzed in an atmospheric thermogravimetric analyzer (TGA). To ensure uniform pyrolysis and high heating rates, sample pyrolysis is done at 1100 °C for 7 min in a preheated muffle furnace under inert atmosphere. The pyrolysis method is based on DIN 51719 with the high temperature chosen to avoid pyrolysis during gasification experiments. 20 mg of the resulting char sample is then distributed evenly on the sample holder of the TGA with no particles lying on top of each other to minimize mass transport limitation effects. Subsequently, the TGA is heated to the specified temperature with a heating rate of 20 K min $^{-1}$ under nitrogen atmosphere and a volume flow of 200 cm^3 min $^{-1}$ and held constant for at least 30 min to avoid ongoing pyrolysis during gasification. When the mass signal remained constant during holding period, the nitrogen flow is switched to 200 cm^3 min $^{-1}$ CO_2 and the mass signal is recorded. If pyrolysis from the char is detected during the holding period, the sample is discarded. When necessary the mass signal is smoothed using the Gaussian method as proposed by *Chen et al.* [23].

The temperature range for the measurement of the reactivity and the activation energy is determined by heating the samples from room temperature to 1100 °C with a heating rate of 20 K min $^{-1}$ with 200 cm^3 min $^{-1}$ CO_2 volume flow until the sample weight remains constant. After adjustment of the weight loss curve with the temperature related buoyancy effects the start of the CO_2 reaction can be determined. Based on this temperature the starting temperature for the activation energy measurement is selected. The reactivity of the char samples is measured isothermally at 20% char conversion. Linear regression of the mass loss curve from 15% to 20% conversion proves to be the best method to determine the mass loss rate, since the mass loss rate is constant in this range. The mass loss signal received from the thermogravimetric analyzer (TGA) is averaged from 15% conversion to 25% conversion to get the reaction rate at 20% conversion. In this conversion range the mass signal decreases linearly (R^2 > 0.999, error of the slope < 0.01 %), so that the conversion rate at 20 % can be obtained with a high precision of appr. 0.5% for two char samples with the same HTC-reaction conditions. After the starting temperature of the CO_2 reaction is found to be appr. 850 °C for all samples, the reactivity is measured at 850 °C, 950 °C and 1050 °C. The observed reaction rate r_{obs} is determined with the derivative of the weight loss curve as shown in Eq. (1) with m as the recorded mass of the sample in mg and X the char conversion.

$$r_{obs} = \frac{1}{m}\cdot\frac{dm}{dt} = \frac{1}{1-X}\cdot\frac{dX}{dt} \tag{1}$$

The activation energies E_A of the CO_2 reaction were modeled based on the Arrhenius equation as suggested by *Irfan et. al.* [24]. In this simplified modeling approach the reaction order is assumed to be 1 and the activation energy $E_{A,obs}$ in kJ kg $^{-1}$ is modeled as an observed activation energy from linear regression of $\ln(r_{obs})$ measured at 850 °C, 950 °C and 1050 °C, the universal gas constant R and temperature T in K according to Eq. (2).

$$E_{A,obs} = -R\cdot\frac{\sum_{i=1}^{N}\left\{\left(\frac{1}{T_i}-\frac{1}{\overline{T}}\right)\cdot\left(\ln r_{obs,i}-\overline{\ln r_{obs}}\right)\right\}}{\sum_{i=1}^{N}\left\{\frac{1}{T_i}-\frac{1}{\overline{T}}\right\}^2} \tag{2}$$

The determination of the activation energy proved to be reproducible with a deviation of 1.5% for two different samples with the same HTC-reaction conditions. However, the reproducibility test could not be done for all samples due to the long experimental procedure of hydrothermal carbonization followed by pyrolysis and gasification experiments so an error of 1.5% is assumed for all activation energies. The reactivity of the most reactive char samples is additionally determined at 650 °C and the Arrhenius plot of the respective samples is checked for linearity to ensure the absence of mass transport limitations.