



## Experimental comparison of hydrothermal and vapothermal carbonization

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### ABSTRACT

The difference between hydrothermal carbonization and vapothermal carbonization for the densification of the energy content of biomass has been investigated systematically for the first time. Vapothermal carbonization allows for higher solid content (solid biomass mass (dry basis) per total mass of feedstock) in the reactor because the biomass is subject to saturated steam instead of liquid water. Results from the experiments show that the process efficiency can be increased due to two reasons: the carbon losses in the liquid phase are decreased and less water needs to be heated up during carbonization. It was also observed that the carbon content of the solid product is significantly lower than that of hydrothermal carbonization at the same process conditions. As it is even lower for dry torrefaction, it is concluded that liquid water facilitates the carbonization process. Calculations based on these experimental results reveal that a mechanical dewatering of wet biomass increases the process efficiency of hydrothermal processes and should be considered in practice. Due to the low efficiency of state of the art drying, torrefaction is less efficient than vapothermal carbonization.

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### 1. Introduction

The need for utilizing biomass energy put a noticeable pressure on the available feedstock leading to the 'food vs. fuel' controversy [1]. This controversy can be avoided by using biomass waste streams which cannot be turned into food, including the organic fraction of municipal solid waste or sewage sludge. As an example, it has been estimated that about 10 million tons (db) of sewage sludge per year is produced in the EU [2,3] and approximately 8 million tons (db) in the U.S. [4]. Many of these waste streams have a high moisture content which prevents an efficient energetic utilization. Therefore hydrothermal methods are being discussed which by principle do not require drying of the feed [5–7]. Amongst these, hydrothermal carbonization (HTC) for the production of a solid fuel termed 'hydrochar' has attracted interest for the conversion of a variety of biomass [8–18]. Hydrothermal carbonization is usually performed at around 180–250 °C for several hours under at least saturated pressure [19]. The product obtained has a carbon and energy content similar to lignite and exhibits an enhanced dewatering capability [20–22].

It has been recognized by model calculations that the solid content (defined as solid biomass on a dry basis per total mass added to the reactor, i.e. the solid content of the feedstock suspension) has an impact on the process efficiency [23,24], but it is unknown how

this affects the product composition and distribution. Also, a process termed 'vapothermal carbonization' (VTC) has been patented [25,26] which features the treatment of biomass in saturated vapor instead of being submerged in water as is the case for hydrothermal carbonization. Published systematic investigations on this process compared to hydrothermal carbonization are missing [27]. As VTC allows having very high solid content in the reactor, it might be a possibility to carbonize moist biomass with a higher efficiency. Therefore, the aim of this study is to investigate the characteristics and distribution of the solid product obtained from hydrothermal and vapothermal carbonization.

One previous work indicated that there is no difference in the carbon content (dry, ash-free basis) between biomass submerged in water and biomass above the surface [28]. Other results contradict this observation [29–31]. Neither of these observations have been part of a systematic study to investigate the influence of the presence of the biomass in liquid water or saturated water vapor. This work aims at overcoming this gap by systematically investigating the influence of the solid content and the state of aggregation of water on the mass and energy yield of the produced coal. The experiments were designed to compare four different process conditions. The basis is hydrothermal carbonization where biomass is in direct contact with the liquid phase [19]. Vapothermal carbonization separates the liquid phase from the biomass while keeping saturated conditions [25]. These different states of aggregation of water in contact with the biomass are compared to the reference process dry torrefaction, both open (TorrO) and closed (TorrC, containing the produced gas in the reactor) [32]. Due to the low temperature applied for hydrothermal conditions (230 °C), dry processes will resemble 'torrefaction' rather than the traditional slow pyrolysis to produce char.

Abbreviations: HTC, Hydrothermal carbonization; VTC, Vapothermal carbonization; TorrC, Closed torrefaction; TorrO, Open torrefaction; db, dry basis; daf, dry ash-free; TOC, Total organic carbon; TGA, Thermal gravimetric analysis.

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The focus of this work is on the carbonization of digestate from anaerobic digestion. Especially for larger biogas installations, digestate may represent a waste stream that needs to be treated in order to increase the economic feasibility of the installation [33,34]. Hydrothermal carbonization of digestate is generally possible [35,36]. For the aim of this study, digestate from the anaerobic digestion of corn silage has been chosen as well as wheat straw. The latter represents straw digestate, which has been proven to make little difference in the carbonization process [36].

## 2. Materials and methods

### 2.1. Materials

Two different feedstocks have been used. Wheat straw has been obtained from Dittmannsdorfer Milch GmbH in Kitzscher, Germany. Dried digestate was used as second biomass. It was obtained from an anaerobic digester in Dorf Mecklenburg, Germany. The substrate used for mesophilic (39 °C) anaerobic digestion is 70% corn silage and 30% cow manure. The digestate was dried and stored on site. Due to the storing conditions on site, the dry digestate contains a significant amount of calcium carbonate. Analyses of the feedstock are summarized in Table 1.

### 2.2. Analyses

Elemental analysis (carbon, hydrogen, nitrogen, and sulfur) was conducted with a Vario EL elemental analyzer; each sample was analyzed in triplicate. Dry matter (drying at 105 °C until mass constancy) and ash content (oxidation at 550 °C for 5 h in a muffle type furnace) were determined according to VDLUFA Chap 3.5 and 8.4 [37].

The gas produced was collected in a gas bag after the reactor has cooled down and analyzed for CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>S using an industrial biogas analyzer (SSM6000 from Pronova, Germany). The volumetric gas production was measured simultaneously with a TG05 multi-chamber rotor gas meter (Ritter, Germany).

Total organic carbon (TOC) of the liquid phase was measured using a TOC Analyzer 5050A (Shimadzu Scientific Instruments, Columbia, MD, USA) and the method for measuring the non-purgeable organic carbon. Samples were measured until the standard error was <2%.

Fiber analysis of the biomass has been conducted according to VDLUFA [37] with the acid detergent fiber method. Lignin content has been determined via the acid detergent lignin fraction.

The solid formed during the reactions has been characterized by a field emission scanning electron microscope (FESEM; LEO Corp.), combined with an energy-dispersive X-ray analysis system (EDX; Link Isis 300, Oxford Microanalysis Group). The thermal behavior was measured by a thermogravimetric balance TGA851 by Mettler-Toledo (STARe-Software). The IR measurements were made with the FTIR spectrometer Varian 660-IR in KBr tabs.

**Table 1**  
Properties of the feedstock used.

	C	H	N	S	O <sup>c</sup>	Cellulose	Hemicell.	Lignin	Ash
	[% daf]					[% daf]			[% db]
Digestate <sup>a</sup>	51.0	8.3	3.1	0.6	37.0	33.3 <sup>d</sup>	24.7 <sup>d</sup>	25.0 <sup>d</sup>	24.4
	(3.7)	(1.3)	(0.2)	(0.1)					(5.4)
Wheat	49.5	7.1	0.3	0.1	43.0	49.6 <sup>d</sup>	32.0 <sup>d</sup>	9.2 <sup>d</sup>	4.9
Straw <sup>b</sup>	(0.8)	(0.9)	(0.0)	(0.0)					(0.0)

<sup>a</sup> Number of samples analyzed n = 8.

<sup>b</sup> Number of samples analyzed n = 4.

<sup>c</sup> Determined by difference.

<sup>d</sup> Analysis for one sample n = 1.

### 2.3. Experiments

One part of the experiments has been conducted in an 18.75 L reactor (Parr Instrument Company, T 316 Stainless Steel) with a temperature controller. Inside the reactor, a mesh was installed which formed a cage for the feedstock to ensure a gap of approximately 50 mm to the bottom of the reactor. All constructive materials have been aged with several reactions according to the hydrothermal method in order to decrease possibly existing catalytic effects. The feedstock was weighed in as dry substance (dried at 105 °C for at least 24 h) and put into the cage. The amount of feedstock was around 630 g of digestate and 450 g of wheat straw. It was ensured that no feedstock fell through to the bottom of the reactor prior to the reaction.

Most of the experiments were conducted at 230 °C with a holding time of 6 h (denoted as 'reaction time' in the following) and a heating rate of 2 K min<sup>-1</sup>. The amount and physical condition of the water was changed. For hydrothermal carbonization, distilled water was added to the reactor to achieve a solid content of 5% (denoted as 'HTC' in the following). To achieve vapothermal carbonization, as much water was added to the biomass as it could soak. This amount was tested prior to the experiments and fixed to a solid content of 25% (denoted as 'VTC' in the following). Torrefaction was conducted without the addition of water or inert gas (i.e. some oxidation occurred due to the oxygen in the atmosphere, however, the stoichiometric air ratio was  $\lambda < 0.01$  for all cases). The reactor was kept closed in one case during the whole reaction time allowing for an increase in pressure ('closed torrefaction', denoted as 'TorrC' in the following) and one valve at the head of the reactor kept open in another case ('open torrefaction', denoted as 'TorrO' in the following). It is possible that an exchange between reactor and ambient atmosphere took place after gas developing reactions have finished during open torrefaction.

After reaction, the reactor cooled down uncontrolled which took approximately 1 h from 230 to 130 °C. In the case of the closed experiments, the over pressure was released into a gas sampling bag and the gas analyzed. The solid product was removed and weighed as bulk material for the case of the different torrefaction experiments. For the case of hydrothermal and vapothermal carbonization two fractions of the upper and the lower part of the pile within the cage were taken separately, each from a layer with a thickness of approximately 30–50 mm (the total height was around 200–300 mm). A third fraction was taken from the bottom of the reactor in case some of the feed fell through the mesh during reaction. A fourth fraction consisted of all remaining material, i.e. the material between the upper and the lower layer and other materials which could not be allocated exactly due to handling difficulties. All these fractions were weighed and dried at 105 °C until mass constancy. A sample of the process liquor was taken in case there was enough to do so.

Another part of the experiments was conducted in an autoclave of around 250 mL with a sieve inlet. This autoclave was used because it usually produces HTC of large particle size. It was designed in a way that only liquid intermediates or (by) products could pass the sieve. They react further to carbon particles on the other side where they can be examined separately. The autoclave was heated by heating cartridges integrated into the bottom part of the autoclave and equipped with a thermocouple and pressure sensor at the top measuring inside. The reaction conditions have been 5 h reaction time at 240 °C. The feedstock was an alternative digestate from 80% corn silage, silage of winter barley and grist, different from that reported in the Materials section. About 20 g of dry biomass was placed in the reactor with as much water to achieve a solid content of 10%. The reaction took place in the two phase region of water and the 'coal' investigated was formed at the phase boundary at the sieve.

### 2.4. Calculations

Mass balances were made on the basis of dry mass. In order to estimate the amount of carbon in the liquid phase, the water evaporated

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