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Hydrothermal carbonization of agricultural residues

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HIGHLIGHTS

- HTC converts organic residues into a solid fuel comparable to brown coal.
- Most of the tested agricultural residues are suitable for the HTC process.
- Blending of different agricultural residues ensures a successful carbonization.
- Dewatering and drying properties of most HTC-Biochars are very good.
- HTC-process water can be used in biogas plants increasing process energy efficiency.

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ABSTRACT

The work presented in this article addresses the application of hydrothermal carbonization (HTC) to produce a solid fuel named HTC-Biochar, whose characteristics are comparable to brown coal. Several batch HTC experiments were performed using agricultural residues (AR) as substrates, commonly treated in farm-based biogas plants in Germany. Different AR were used in different combinations with other biomass residues. The biogas potential from the resulting process water was also determined.

The combination of different AR lead to the production of different qualities of HTC-Biochars as well as different mass and energy yields. Using more lignocellulosic residues lead to higher mass and energy yields for the HTC-Biochar produced. Whilst residues rich in carbohydrates of lower molecular weight such as corn silage and dough residues lead to the production of a HTC-Biochar of better quality and more similar to brown coal. Process water achieved a maximum of 16.3 L CH_4/kg FM (fresh matter).

1. Introduction

Over the years, fossil fuels have been the cheapest source for the petroleum and petrochemical industries, which led to the development of millions of petroleum based products. However, fuel prices demand have reached record heights in recent years triggered by factors like the depletion of easily accessible deposits and also increasing demand by emerging economies. Biomass was once the global energy source before the arrival and the unbridled expansion of fossil fuels during the Industrial Revolution in the 1800–1900s.

Germany's decision to shut down all the nuclear reactors by 2022 increases the country's demand for other sorts of energy like: coal fired plants, natural gas imports and renewable energy production (Spiegel, 2011; Euractiv, 2011). Therefore, the adoption of decentralized systems like many small interconnected units harvesting wind, solar, hydroelectric and biomass power is expected in the near future.

Hydrothermal Carbonization (HTC) was discovered by Bergius in 1913, and has been re-discovered and further developed under the direction of Professor Antonietti, director of the Department of Colloid Chemistry at the Max-Planck Institute of Colloids and Interfaces in Golm/Potsdam (MPI). HTC is now being mentioned as a promising technology to convert biomass into multiple bio-products: a solid fuel compared to brown coal (Parshetti et al., 2013; Funke and Ziegler, 2010; Kleinert et al., 2009; Ramke et al., 2009; Titirici et al., 2007); liquid fuel or bio-oil (Akhtar and Amin, 2011; Heilmann et al., 2010, 2011a,b; Hoekman et al., 2011; Titirici et al., 2007; Xiao et al., 2012) as a soil amendment to increase soil fertility and crop yields (Du et al., 2012; Kleinert et al., 2009; Libra et al., 2011; Rillig et al., 2010); carbon material that could be either activated to work as an adsorbent for water purification systems or CO_2 sorption (Libra et al., 2011) and as a low cost adsorbent or permeable reactive barrier for Uranium(VI), Copper and cadmium-contaminated waters (Kumar et al., 2011; Regmi et al., 2012); nanostructure carbon material (Cui et al., 2006; Inagaki et al.,

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2010; Libra et al., 2011); carbon catalyst, which could be used in the production of fine chemicals (Xiao et al., 2012); and lastly a carbon material that could increase a fuel cells efficiency (Libra et al., 2011).

The objective of this research work was to give more data about the use of HTC in the production of a solid fuel similar to brown coal (HTC-Biochar) using different agricultural residues. Agricultural residues[1] (AR) are a type of biomass that could present considerable heterogeneity depending on the country and region. We considered AR as energy crops (corn and grass silage), livestock manures from poultry, cattle, and piggery farms, bedding material used in barn stalls and digestate (or Biogas Slurry) from biogas plants all present in the region of Höxter, Germany.

In Germany this type of AR are being treated through farm-based biogas plants which produce a renewable fuel (biogas) used to generate heat and power, and a digestate (solid and liquid) used as fertilizer. However, several problems have been reported related to the use of energy crops. Due to its lignocellulosic structure these substrates are not fully hydrolyzed. Hydrolysis of lignocellulosic material has been referred to for years as the rate limiting step in anaerobic digestion of lignocellulosic biomass (Alvarez et al., 2000; Chynoweth and Isaacson, 1987; Hendriks and Zeeman, 2010; Lindorfer et al., 2007; Prochnow et al., 2009; Ward et al., 2008). As a result, the material tends to float upon the fluid surface in the digester, leading to increased stirring expenses. For instance wrapping of longer grass particles around moving devices can cause failures in operating the biogas plant (Prochnow et al., 2009). Therefore, long retention times (30–80 days) are utilised increasing the operating volumes and digestate storage costs (Lindorfer et al., 2007; Prochnow et al., 2009). However, these technical problems arising from energy crops utilization for anaerobic digestion have not been the subject of systematic scientific investigation thus far.

HTC is an exothermic process that lowers both the oxygen and hydrogen content of the feed (described by the molecular O/C and H/C ratio) by 5 main reaction mechanisms which include hydrolysis, dehydration, decarboxylation, polymerization and aromatization (Funke and Ziegler, 2010; Hoekman et al., 2011). This is achieved by applying temperatures of 180–220 °C to a suspension of biomass and water at saturated pressure for a couple hours. At the end of the process the solid phase, denominated as "HTC-Biochar", can be easily separated from the water. Approximately 75–80% of the carbon input is found in the solid phase (HTC-Biochar); about 15–20% is dissolved in the liquid phase (process water); and the remaining 5% are converted to gas (mainly carbon dioxide). The liquid phase is highly loaded with organic components, which for example could be easily degradable through anaerobic digestion (Ramke et al., 2009).

Carbonization of Biomass has a number of advantages when compared with common biological treatment. It generally takes only hours, instead of the days or months required for biological processes, permitting more compact reactor design. When compared to fermentation and anaerobic digestion, HTC is referred to as the most exothermic and efficient process for carbon fixation (Titirici et al., 2007). Therefore, HTC is now seen as a promising technology also for CO_2 sequestration. In addition, some feedstocks are toxic and cannot be converted biochemically. The high process temperatures can destroy pathogens and potential organic contaminants, such as pharmaceutically active compounds that could be present for example in AR (Libra et al., 2011). It is therefore important to study the quality[2] of the "HTC-Biochar" produced through carbonization of AR, envisioning its application as a solid fuel. Recently, a first study has been reported using digestate produced from maize silage previously treated at 55 °C in a two-stage solid-state reactor system (Mumme et al., 2011), however with different experimental conditions from the work presented here.

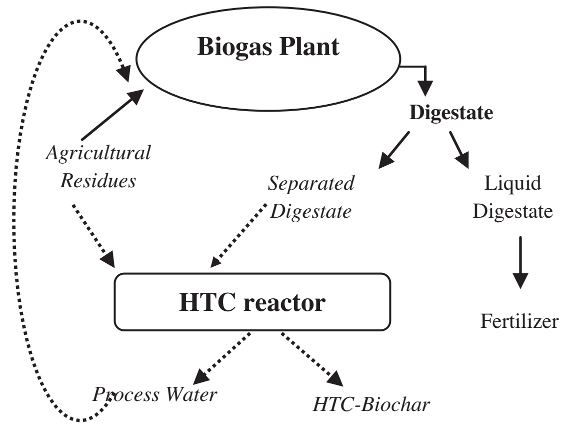

Fig. 1. Presumed combination of anaerobic digestion and hydro-thermal carbonization of agricultural residues.

The present work was performed considering a hypothetical situation (Fig. 1) where an HTC reactor could be used to improve the efficiency of an existing farm-based biogas plant. In this case, AR and separated digestate are used as input material for the HTC reactor to produce a high quality solid fuel (HTC-Biochar) compared to brown coal, while process water (liquid phase) is treated by anaerobic digestion.

This preliminary work has the objective to present the first results about the HTC of AR and the quality of the HTC-Biochar produced (Trial I). Additionally, carbonization tests with different combinations of AR and some industrial organic wastes and silvicultural residues were also performed (Trial II). The results of biogas and biomethane potential determination of the liquid phase are also given.

2. Methods

2.1. Substrates

Several biomass substrates were used in this work: Agricultural Residues, Industrial Organic Waste (IOW) and Silvicultural Residues (SR). The AR used in this work were collected from a farm-based biogas plant located in the town of Marienmünster in Höxter district. The AR used were: corn silage (CS), poultry manure (PM), separated (solid) digestate (SD), bedding material (BM; a heterogeneous mixture mainly composed by hay, straw and manure), and also dry straw (DS). The IOW used was collected from different local small industries. Those substrates were: cabbage (CR) and dough (DR).

The SR were collected from the main biomass supply platform in the region of Höxter located in the city of Borlinghausen. The following SR were chosen: forest (FWC) and landscape (LWC) wood chips with low market value, and forest wood chips with high market value (FWCH). Every substrate was representatively sampled and transported in closed barrels of 200 L. Table 1 shows the characterization of each substrate used. AR and IOW were only stored for a short period of time before being used in the HTC experiment due to their susceptibility to degradation. To avoid any losses of material (organic and water) the IOW were only stored for 3 days while AR such as CS and SD were stored for a period no longer than two weeks.

[1] The term AR was adopted to combine different streams of Biomass in the Agricultural sector.

[2] Quality of HTC-Biochar is used in the manuscript to avoid describing elemental composition (C/H/N/O) or molar ratios as well Higher Heating Value. The quality of HTC-Biochar is then compared to Lausitz brown coal.