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Integration of pyrolysis and anaerobic digestion – Use of aqueous liquor from digestate pyrolysis for biogas production

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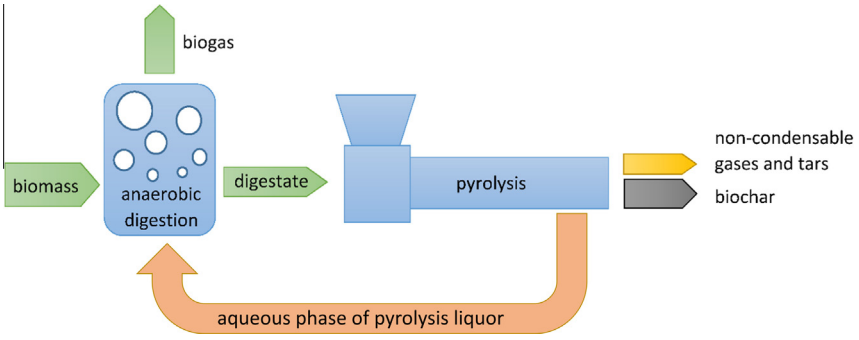
HIGHLIGHTS

- Aqueous pyrolysis liquor can be digested by an un-adapted inoculum without additives.
- Up to 63.4% of COD was removed.
- Pyrolysis temperature has strong impact on degradability of pyrolysis liquor.
- Methanogenic microflora showed high adaption potential.
- VOCs were removed by large extent.

GRAPHICAL ABSTRACT



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ABSTRACT

Anaerobic digestion of aqueous pyrolysis liquor derived from pyrolysis of solid digestate was tested in batch mode using an un-adapted inoculum. Three pyrolysis liquors produced at 330 °C, 430 °C and 530 °C in four COD-based concentrations of 3, 6, 12 and 30 g L^{-1} were investigated. The three lower concentrations showed considerable biogas production, whereas the 30 g L^{-1} dosage caused process inhibition. The highest methane yield of 199.1 ± 18.5 mL g_{COD}^{-1} (COD removal: 56.9 ± 5.3%) was observed for the 330 °C pyrolysis liquor, followed by the 430 °C sample with only slightly lower values. The 530 °C sample dropped to a yield of 129.3 ± 19.7 mL g_{COD}^{-1} (COD removal: 36.9 ± 5.6%). Most VOCs contained in the pyrolysis liquor (i.e. furfural, phenol, catechol, guaiacol, and levoglucosan) were reduced below detection limit (cresol by 10–60%). Consequently, integrated pyrolysis and anaerobic digestion in addition to thermochemical conversion of digestate also promises bioconversion of pyrolysis liquors.

1. Introduction

The use of biomass as a renewable resource for energy and various biomaterials gains more and more attention. A currently vividly discussed use of biomass is the production of biochar, which is among other applications considered as soil amender and for carbon sequestration. Biochar is a charcoal-like material usually produced by pyrolysis of biomass, where organic material is transformed into a carbon-rich material under the influence of high temperatures and limited oxygen supply (Lehmann and Joseph, 2009). Using charcoal for improving soil fertility is an old technique that was already used by indigenous civilizations living in the amazon basin centuries ago (Woods and McCann, 1999). In this region archaeologists found untypical black soils that contained very high amounts of stable organic matter and high amounts of nutrients compared to the typically infertile clay soils

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of the tropics. This so called 'terra preta' was discovered to be of anthropogenic origin which was created by mixing soil with charcoal and residues of burned biomass (Glaser et al., 2001). Presumably the indigenous people of the amazon basin already knew how to produce charcoal by pyrolysis of organic material in clay furnaces (Basu, 2013). Today, this knowledge about the soil amending properties of highly carbonaceous materials is successively recovered.

Despite its ancient history, pyrolysis as a process and technology is still a subject of ongoing research and development. The goals are to improve the material properties of chars for use as soil amender or other material uses, to enable the use of complex feedstocks, to improve the energetic and economic efficiency, and to reduce the production and release of unwanted by-products (Manyà, 2012). One group of by-products with no direct use besides burning is the condensable fraction of the pyrolysis gas known as pyrolysis oil, biocrude or bio-oil. It is a dark-brown, free-flowing liquor with a distinctive odor that consists of a complex mixture of up to 400 organic compounds (Evans and Milne, 1987; Huber et al., 2006). It is a potential feedstock for the production of energy, bio-fuels and chemicals. However, because of the wide range of components and its pronounced toxicity, thermal or catalytic upgrading is necessary to meet the high requirements for fuel and chemical production (Mohan et al., 2006; Cordella et al., 2012). Common treatment methods for bio-oil that are proposed in the literature focus on solvent separation to obtain fractions with similar polarities and to concentrate the undistillable fraction (Mohan et al., 2006). However, these procedures require high amounts of organic solvents and increase the cost of the process.

An approach to utilize the aqueous phase of pyrolysis oil is to convert it into a fuel by anaerobic digestion. The principal suitability of an anaerobic treatment has been reported previously for bio-oils from pyrolysis of wood (Andreoni et al., 1990), for the aqueous phase from pyrolysis of corn stalks (Torri and Fabbri, 2014) as well as for bio-oil from flash pyrolysis of wood (Willner et al., 2004). Similar materials that are susceptible to anaerobic digestion are process liquors from coal gasification (Cross et al., 1982) and hydrothermal carbonization of maize silage (Wirth and Mumme, 2013). Treating these process liquors by anaerobic digestion was generally found to reduce large parts of their organic fractions including hazardous compounds such as phenol.

Integration of anaerobic digestion and pyrolysis offers further potentially synergistic combinations including use of digestate as feedstock for pyrolysis (Inyang et al., 2010), biomethanation of syngas (Guiot et al., 2011) or use of biochars as additive in anaerobic digestion to overcome inhibition problems (Mumme et al., 2014; Torri and Fabbri, 2014).

With the intention to further investigate the concept of integrated anaerobic digestion and pyrolysis, the overall aim of this study was to determine to which extent aqueous liquors from pyrolysis of digestate can be used as feedstock for biogas production. Further objectives were to characterize potential inhibitory effects on anaerobic digestion, to determine the efficiency with respect to COD reduction and methane production, to describe the impact of pyrolysis temperature on the degradability of the aqueous liquor, and to determine the removal rates for selected organic compounds.

2. Methods

2.1. Origin and properties of pyrolysis liquor and anaerobic inoculum

The digestates used as feedstock for pyrolysis and as inoculum for anaerobic digestion were both obtained from an on-farm biogas plant (Hof Karp, Rastow, Germany). The biogas plant operates at mesophilic temperature at an organic load rate (volatile solids basis) of 5.72 kg m^{-3} d^{-1} feeding cow manure and maize at a ratio of 4:3. For pyrolysis, the raw digestate was dewatered on site by a press screw separator and belt dryer (70 °C, 8 h). A batch of 20 kg of this solid digestate was retrieved and stored in a sealed 80 L barrel. Before being pyrolyzed the digestate samples were again dried for 24 h at 105 °C and then grinded to a particle size below 1 mm. For use as inoculum, the liquid phase from mechanical dewatering was filtered by a food mill (mesh size: 5 mm) and sieve (mesh size 1.5 mm). Before the anaerobic digestion experiments started, it was stored for 2 weeks at mesophilic temperatures.

The pyrolysis liquors were produced in multiple runs using 500 g of ground solid digestate per each run. Pyrolysis was conducted in a 150 mm × 1500 mm rotary kiln (HTM Reetz, Berlin, Germany) at a solids retention time of 45 ± 15 min and set temperatures of 300 °C, 400 °C, and 500 °C. Because of exothermic reactions, the mean and peak pyrolysis temperatures were on average 18–29 K and 32–41 K higher than the set temperatures (Table 1). Based on the measurement data, it was assumed that pyrolysis conditions were described accurately by adding 30 K to each set temperature resulting in effective temperature steps of 330 °C, 430 °C, and 530 °C. The kiln was continuously purged with nitrogen gas at a flow rate of 120 L h^{-1}. Pyrolysis gases were led through a gas-washing bottle filled with 700 mL of tap water. The bottle was placed in a 4 °C cold-water bath, which kept the washing water at a mean temperature of 12 °C or below. Tarry fractions were observed to condense already in the tubing between kiln and washing bottle. Minor amounts of tar that reached the washing bottle were removed from the water-diluted pyrolysis liquor through filtration using a paper filter. Afterwards the aqueous fraction of the pyrolysis liquor was stored in 250 mL glass bottles at 4 °C for later anaerobic digestion and chemical analysis.

The main chemical properties of all materials are shown in Table 2 (see Table S1 for further properties).

2.2. Anaerobic digestion test system and design of experiment

Anaerobic digestion was carried out at 40.5 ± 1.0 °C based on the well-established biochemical methane potential (BMP) procedure, as described in the guideline VDI 4630 (VDI, 2006). Detailed information can be obtained from Mumme et al. (2014).

Two BMP runs were conducted using pyrolysis liquor from two different pyrolysis runs for each temperature step of 330 °C, 430 °C, and 530 °C (Table 1). In the first run, initial substrate COD (COD_s) concentrations were about 12 and 30 g L^{-1} and in the second run 3 and 6 g L^{-1}. Because the first calculations were based on COD_s to COD_i (inoculum COD) ratios, the dosages of COD_s differ slightly from this set values (Table 3). Each sample was incubated with 20 mL of inoculum. To allow statistical analysis each fermentation was done in triplicates. As reference, each run included a triplicate of inoculum-only fermentation (control).

The duration of the experiment was 69 days (first run) and 49 days (second run). Gas production was measured daily during the first week of the experiments, afterwards two or three times a week. The methane content of the produced gas phase was measured at 5 times during the first experiment and at 3 times during the second experiment. After each experiment, the content of the three replicate syringes were merged and frozen (−4 °C) for later chemical analyses. Concentrations of selected organic substances contained in the pyrolysis liquor (volatile fatty acids VFA, lactic acid, 5-HMF, furfural, levoglucosan, phenol, cresol, catechol, and guaiacol) were analyzed before and after the experiment.

2.3. Analytical methods

Contents of total solids (TS) and volatile solids (VS) were determined gravimetrically by drying the samples at 105 °C for 24 h and