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Maximizing the value of liquid products and minimizing carbon loss in hydrothermal processing of biomass: an evolution from carbonization to humification

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Abstract

Hydrothermal carbonization (HTC) converts wet biomass into hydrochar and a process liquid, but aromatic compounds in the products have been reported as a roadblock for soil applications as they can inhibit germination, plant growth, and soil microbial activity. Here, we compared HTC and hydrothermal humification (HTH) of cow manure digestate while varying the initial alkaline content by adding KOH. HTH converted 37.5 wt% of the feedstock to artificial humic acids (A-HAs) found in both solid and liquid, twice that of HTC. HTH reduced phenolic and furanic aromatic compounds by over 70% in solids and 90% in liquids. The A-HAs in HTH resemble natural humic acids (N-HA), based on FTIR, UV-vis spectra, and CHN and XRD analysis. The HTH liquid possesses 60% higher total organic carbon (TOC) than HTC. Although one-third of TOC can be precipitated as A-HA, a high TOC concentration remains in the liquid, which is shown to be mainly organic acids. Therefore, we also evaluated the HTC and HTH liquids for anaerobic biomethane production, and found that compared to the original cow manure digestate, the HTH liquids increased methane yield by 110.3 to 158.6%, a significant enhancement relative to the 17.2% increase seen with HTC liquid. The strong reduction in organic acids during biogas production from HTH liquid indicates the potential for converting soluble byproducts into methane, while maintaining high A-HAs levels in the solid product.

Highlights

- Hydrothermal humification of the digestate feedstock created about 37.5 wt% artificial humic acids in both solid and liquid phases.
- Increasing the alkaline content of the reaction media significantly decreased the aromatic content in the process liquid while increasing the concentration of organic acids and sugars.

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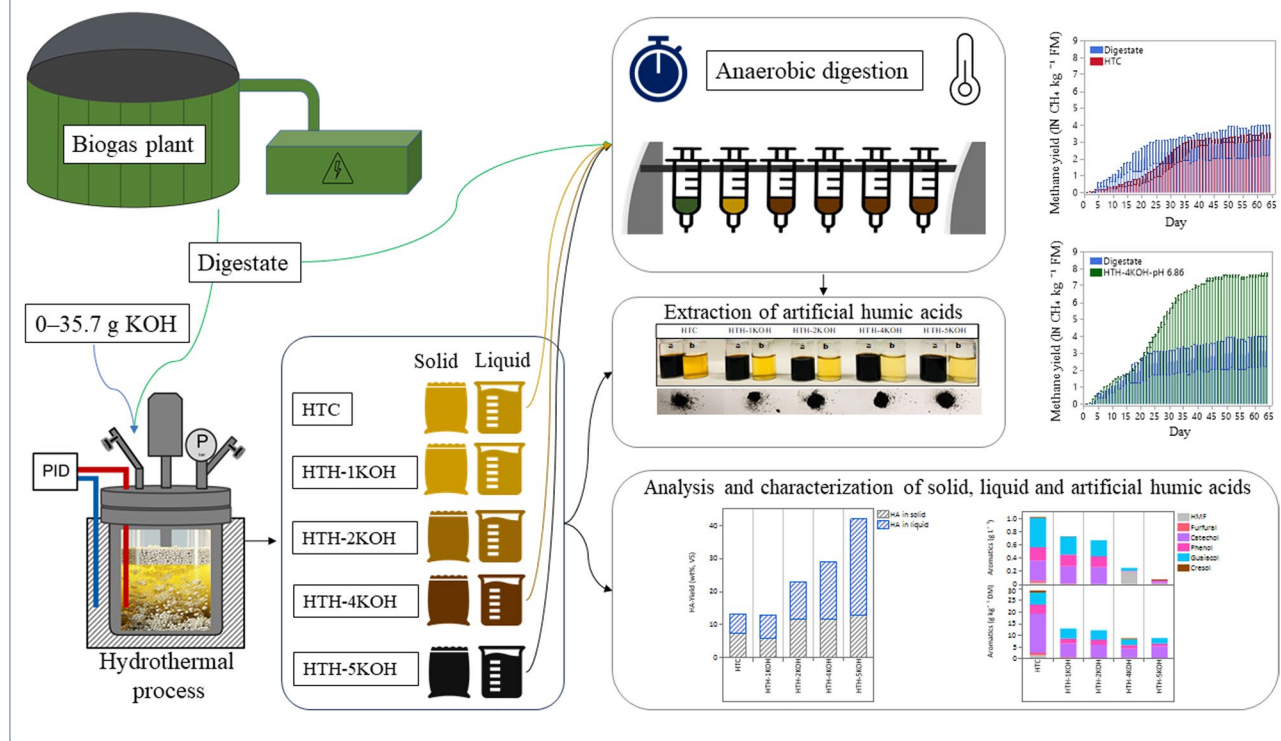


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- There was little to no gas production observed in the HTH process at higher alkaline contents, indicating carbon preservation in the liquid and solid phases.
- Anaerobic processing of the hydrothermal humification (HTH) process liquid resulted in a 158.6% increase in methane production compared to the primary biomass.
- The organic acid concentrations decreased after the anaerobic fermentation, while the main HTH product, artificial humic acids, remained nearly unchanged.

Keywords Hydrothermal carbonization, Hydrothermal humification, Artificial humic acids, Aromatic compounds, Anaerobic digestion

Graphical Abstract



1 Introduction

Many regions in the world face the simultaneous challenges of decreasing soil fertility and increasing health hazards, environmental pollution, and greenhouse gas emissions from improper animal manure management (Szogi et al. 2015; Ström et al. 2018). Especially in regions with intensive animal production facilities, water-based manure management is producing large amounts of animal slurry manure that is polluting water resources when applied to land, directly or indirectly through runoff (Ström et al. 2018). Sustainable solutions are needed to treat these wet organic residues to reduce their negative impacts, while recycling their valuable carbon and nutrients for agricultural applications (Malomo et al. 2018). A promising strategy for combatting these trends

is to integrate thermochemical conversion processes in the manure management to produce long-lasting soil amendments.

Hydrothermal carbonization (HTC) is a promising technology that converts wet biomass into a stable carbon-rich solid, known as hydrochar, without the need for pre-drying (Libra et al. 2011). The HTC process primarily produces hydrochar, but it also yields a process liquid and a small amount of gas, mostly CO₂ (Alvarez-Murillo et al. 2022). Hydrochar has a variety of applications, including agricultural (Reza et al. 2014a), environmental (Han et al. 2016, 2017), biofuel, and energy production (Berge et al. 2015; Saba et al. 2017; Śliz and Wilk 2020; Brown et al. 2022). The HTC process liquid often contains high concentrations of organic acids that make it

suitable for energy recovery through anaerobic digestion (Wirth et al. 2015; Ipiales et al. 2021). However, the presence of aromatic compounds such as phenols and furans in the hydrochar (Lucian et al. 2018) and process liquid (Reza et al. 2014b; Köchermann et al. 2018; Marzban et al. 2023) may limit their direct use for agricultural purposes, such as soil application (Bargmann et al. 2013) or in un-adapted biogas plants (Ipiales et al. 2021). Seed germination and plant development, especially root growth, are influenced by organic acids and phenolic compounds such as guaiacol and catechol (Bargmann et al. 2013). In order to reduce the amounts of carbonaceous and phytotoxic compounds that can dissolve in water and impede the direct use of HTC products in soil applications, various treatment methods for the hydrochars have been suggested. These methods include approaches like storage and washing (Bargmann et al. 2013) as well as chemical treatment methods (Fornes and Belda 2017). But these, in turn, produce waste streams requiring further processing steps.

An alternative is to modify the hydrothermal processes to avoid the production of furans and phenols. Hydrothermal humification (HTH) and most recently hydrothermal fulvification (HTF) were reported as promising methods that can reduce phenolic and furanic compounds in both solid and liquid products while producing macromolecules that can be classified as artificial humic and fulvic acids (A-HA, A-FA), respectively (Tkachenko et al. 2023). These acids are a large class of complex polymers, which in turn are part of the larger group of complex heterogeneous mixtures of polydispersed materials called humic substances (Lee et al. 2019). They contain acidic carboxyl and phenolate functional side structures that determine their properties in soil and water (Yang et al. 2019a; Sarlaki et al. 2023a), and are classically differentiated according to their pH-solubility (Lee et al. 2019). Their structure, shape and particle size are dynamic and influenced by the type of starting biomass, water content and soil structure, and environmental conditions (e.g., concentration, pH, ionic strength, or redox potential etc.) (Klučáková 2018). Soil amendments incorporating artificial humic substances are becoming increasingly recognized for their environmentally beneficial properties as biostimulants and soil conditioners (Pukalchik et al. 2019; Lee et al. 2019; Sarlaki et al. 2023b). The application of artificial humic substances to soil has been shown to improve plant growth, but the extent is inconsistent and depends on a number of factors such as the source of the humic substances, the environmental growing conditions, the type of plant being treated, and the manner of application (Rose et al. 2014). The mechanisms are highly complex and can occur directly through interaction of humic substances with the plant root or indirectly

through pH buffering, increased soil water retention, mobilization of nutrients, and interactions with soil autotrophic bacteria (Vallini et al. 1997; Pukalchik et al. 2019). Wider positive environmental and climatic effects have also been found. For instance, Jin et al. (2023) found that utilizing A-HA derived from eucalyptus leaves as novel fertilizer improved the nitrogen utilization efficiency, and reported it can be utilized to mitigate nitrogen pollution from the agricultural sector (Jin et al. 2023). The joint application of phosphate fertilizer and A-HA showed positive impacts on soil microbiome and phosphorus uptake when used for maize growth in black soil (Yuan et al. 2022), and can help prevent phosphate leaching into groundwater (Yang et al. 2019b). A study by Ai et al. (2023) explored the potential of A-HAs for soil carbon sequestration. They reported that the application of A-HA enhanced total and dissolved organic carbon in soil, promoting macroaggregate formation and microbial interactions, thus promoting restoration of soil fertility (Ai et al. 2023). Similarly, Tang and co-authors in 2022 found that the combination of artificial humic acid (A-HA) with freezing–thawing events enhanced carbon sequestration in the soil (Tang et al. 2022). Yang et al. (2023) reported that A-HA can be part of a strategy for mitigating saline toxicity because of its mitigating effect on alkali damage in the root systems (Yang et al. 2023). They demonstrated that maize seed germination and seedling growth were improved under alkali stress by applying A-HA derived from corn straw.

Research on the hydrothermal production of A-HA is being pushed by the growing market for such products in agriculture and the limited supply of natural coal-related resources such as lignite and Leonardite currently used for bulk extraction of humic substances (Lee et al. 2019). In contrast to HTC, HTH is carried out at a higher pH in the reaction medium, in which the initial alkaline content is adjusted according to the carbohydrate content of the feedstock (Tkachenko et al. 2023). HTH results in a decreased production of unwanted by-products, such as phenolic and furanic compounds. In a study combining an acid and alkaline hydrothermal process step, Shao et al. (2022) found that acidic hydrothermal conditions favored the formation of precursors required for production of A-HA, while alkaline conditions were suitable for conversion of these precursors to A-HA (Shao et al. 2022). Various alkaline agents, including potassium hydroxide (KOH) (Volikov et al. 2024), hydrated lime (Ghaslani et al. 2024), or combustion ashes (Zhang et al. 2020), have been used in the hydrothermal humification process.

These advantages make HTH a suitable choice for transforming process liquid into an agricultural soil enhancer (Ghaslani et al. 2024). While the first variants

of hydrothermal humification have highlighted the large potential of this process (Yang and Antonietti 2020a), further exploration and optimization of this process is necessary, particularly when applied to various types of biomasses. Furthermore, although HTH can reduce aromatic compounds (phenols and furans) (Tkachenko et al. 2023), it has been observed to increase organic acid levels in the liquid product (Tkachenko et al. 2023; Ghaslani et al. 2024), which then requires further treatment. Hence, utilizing anaerobic processing for HTH liquid could be a practical solution to recovering biomethane, considering the extensive research already conducted on HTC liquid in anaerobic processes (Ipiates et al. 2021).

The goal of this study was to compare hydrothermal carbonization (HTC) and hydrothermal humification (HTH) of cow manure digestate in terms of the generation of organic compounds, especially aromatics (phenols and furans) and A-HA, as well as carbon distribution among the solid, liquid, and gas phases. This was done throughout by varying the initial alkaline content in the reaction medium through KOH addition. For HTC, no KOH was added, while in the HTH runs, the initial KOH content was varied by a factor of five. We investigated the quantity of A-HA produced in both the solid and liquid phases. Furthermore, to study the effect of soluble organic compounds in the liquid phase on biogas and methane production through anaerobic digestion, we assessed the impact of HTC and HTH process liquids while monitoring the humic acid content in the residues from biogas production. This work introduces a novel approach for the valorization of cow manure digestate into A-HA-rich fertilizer, along with the enhancement of methane production as a value-added product, through the detailed examination and comparison of HTC and HTH processes.

2 Material and methods

2.1 HTC and HTH experiments

The carbonization procedure was performed with digested cow manure slurry obtained from a local biogas plant operating on a cattle farm. The composition of the feedstock, i.e. organic compounds, N, P, K, Ash%, COD, TS%, oTS%, and pH is summarized in Additional file 1: Table S1. The fiber content of the feedstock was determined according to VLUDEFA method (VDLUFA 2012) using an FIBRETherm FT12 Automated Fiber Analyzer from C. Gerhardt GmbH & Co. KG, Königswinter, Germany, and is summarized in Additional file 1: Table S2. The details on sample preparation, methods and instruments for all analyses can be found in supplementary information (method section). To determine the required KOH content, the measured carbohydrate content (wt%) of the feedstock, which includes cellulose (40.89%) and

hemicellulose (9.89%), was used as a basis. A molar equivalent (mole eq.) of KOH to carbohydrate content of over 0.5 is needed in the reaction medium to shift the process from HTC to HTH, a trend that becomes particularly evident beyond an eq. of 1, as described by Tkachenko et al. (2023). For the HTC experiment, no KOH was added, so the eq. of KOH to carbohydrate content was 0. For the HTH experiments, it was adjusted to 0.87 eq. (7.58 g), 1.75 eq. (15.16 g), 3.5 eq. (30.32 g), and 4.5 eq. (37.90 g). For all hydrothermal reactions, 600 g of the feedstock slurry with a solids content of 8.3% (wt-db) and the required amounts (0, 7.58, 15.16, 30.32 and 37.90 g) of KOH were placed in a 1-L high-pressure reactor from Parr Instrument (series 4520, Moline, Illinois 61265-1770 USA). The reactor was sealed and heated to 240 °C at a rate of 2 K min⁻¹, and held for 4 h at 240 °C. In total, five hydrothermal experiments were performed and labeled as HTC, HTH-1KOH, HTH-2KOH, HTH-5KOH, and one run was performed for 6 h at 240 °C and was labeled as HTH-4KOH. At the end of the reaction period, the heater was turned off, and the reactor was cooled down to room temperature. The solid–liquid slurry was filtered using flat filter paper (ROTH Type 113A-110, 5–8 µm). The solid product (referred to as HT-solids to include HTC and HTH solids) was placed into a vacuumed plastic bag, and the liquid was stored in a closed bottle and stored at -18 °C, and analyzed within 24 h. For the runs that produced gas, the gas phase was collected in a gas bag and let to cool down to room temperature. Then the composition of gas was analyzed using Geotech BIOGAS 5000, and the volume was measured using Drum-type gas meters, Ritter, Germany. The experimental conditions are summarized in Additional file 1: Table S3.

The solid yield (SY) describes the percentage of input mass recovered as solid product and is calculated as the ratio of carbonized product in dry weight (M_C (g)) to raw feedstock dry weight (M_b (g)).

$$SY = \frac{M_C}{M_b} \times 100 [\%] \quad (1)$$

2.2 Humic acid extraction

The extraction of A-HA from solid and liquid products, as well as from anaerobically digested materials, was conducted in duplicate in accordance with the procedures outlined in ISO 19822 with modifications. Prior to acidification 10 g of process liquid was weighed and placed into a 50 ml centrifuge tube. A-HAs were then separated from the process liquids by acidification with HCl (32%) to pH ≈ 1. After acidification, the solution was left to stand for 1 h, and then centrifuged for 10 min at 5000 rpm. The supernatants were separated and

subjected to further analysis. The precipitate was dried in the oven at 60 °C for 48 h and weighed. The precipitates were also subjected to further analysis (Additional file 1: Fig. S1). The A-HA was separated from the HT-solids by dissolving 0.3 g solid (dried at 60 °C for 48 h) into 30 ml, 1 M KOH solution. After mixing for 1 h at mixing speed of 150 rpm, the samples were centrifuged and separated, and the supernatant was treated following the method for the process liquid: acidified to pH=1 and separated. The A-HA from solid and liquid products was dried at 60 °C, for 48 h and submitted to the analysis (Additional file 1: Figs. S1 and S2).

To monitor the content of A-HA in the biogas digestate after anaerobic treatment (which is described in the following section), the digestate (including bacteria, remaining inoculum solids and the liquid) was centrifuged (for 10 min at 500 rpm) to remove the solid residues coming from inoculum. Then the supernatant was acidified by HCl (32%), centrifuged, and the A-HA was dried following the method for the process liquid. The amount of humic acid after biogas production was calculated as:

$$\text{HA after biogas production (g)} = \text{HA in inoculum and process liquid (g)} - \text{HA in control inoculum (g)} \quad (2)$$

where HA is used to refer to the artificial humic acid for clarity.

The difference between HA before and after biogas production was calculated as:

$$\% \text{HA changes} = \frac{\text{HA after biogas production (g)} - \text{HA in process liquid (g)}}{\text{HA in process liquid (g)}} \times 100 \quad (3)$$

The HA yield describes the percentage of input dry mass recovered as A-HA (in liquid or solid in g) and is calculated as the ratio of extracted product in dry weight (M_{HA}) to dry feedstock weight (M_b).

$$\text{HY} = \frac{M_{\text{HA}}}{M_b} \times 100 [\%] \quad (4)$$

2.3 Analysis and characterization

Several techniques, FTIR, SEM-EDX, XRD, HPLC, GC, ICP-OES, IC, N- Kjeldahl, and elemental analysis, were used to quantitatively and qualitatively analyze the feedstock cow manure digestate, HT-solids, process liquids, and A-HAs (see Additional file 1: Table S3 for details on methods used for each stream). The parameters measured in the solid and liquid streams include: total solids, ash content, artificial humic acids (A-HAs), aromatic compounds (HME, furfural, phenol, catechol, guaiacol,

and cresol), organic acids (formic, acetic, lactic, caproic, valeric, butyric, and propionic acids), sugars (glucose, sucrose, fructose, xylose, and arabinose), alcohols (methanol, ethanol, propanol, and butanol) as well as several inorganic compounds. The details for sample preparation and instruments can be found in supplementary information (method section). The quantitative analyses were conducted at least twice, and the average values were reported (Additional file 1: Table S8). All chemicals utilized in this study were purchased from Carl ROTH, Germany, except the standard humic acid which was purchased from Sigma Aldrich.

2.4 Anaerobic digestion experiments

Anaerobic digestion experiments were conducted to evaluate the biogas production potential of the process liquids from three hydrothermal runs and the original feedstock, cow manure digestate. A selected amount of the feedstock digestate and the process liquids as produced in the HTC and HTH-5KOH (with an adjusted pH to 8 using HCl) runs were added to a 100 ml glass syringe with an inoculum. The inoculum (with pH of 8) was taken

from our biogas laboratory, ATB, Potsdam. In order to estimate the effect of reduced pH and cation concentrations on biogas production, three more experiments were made with pre-treated process liquid from HTH-4KOH,

in which the pH was reduced by HCl addition and cation exchange resins to 8 and 6.86. Thus, we had two types of comparisons, each with three liquids: (1) using HCl to lower the pH of HTH liquids to 8, matching the inoculum pH and close to pH of HTC process liquid, comparing HTC, HTH-5KOH, and HTH-4KOH-HCl; and (2) analyzing the effect of reduced ion concentrations, from no reduction in HTH-4KOH-HCl to HTH-4KOH-pH 6.86, and HTH-4KOH-pH 8. The amount of sample added to the syringe was based on its measured TS%, VS%, and total fatty acids content in order to adjust the ratio of inoculum to substrate on VS basis to 2. Details are summarized in Additional file 1: Table S4. The experiments were based on the methodology described in detail in a previous study (Helfrich and Oechsner 2003), and according to VDI standard procedure (VDI 2006). Briefly, the syringes were weighed and sealed with a piston, ensuring anaerobic conditions by removing the air until the solid substrate reached the outlet, and a gas-tight seal

was provided with silicone paste. The samples were incubated for 64 days at a constant temperature of 37 °C in an incubator, with three replicate determinations for each process liquid. Residual gas production of the inoculum was measured individually in triplicate, and gas production of the test syringes with substrate and inoculum was corrected by gas production from the inoculum. The volume of gas produced was measured by recording the displacement of the plunger at least five times per week, which was then converted to standard temperature and pressure conditions (dry gas, 0 °C, 1013 hPa) and divided by the mass of volatile solids (VS) of the substrate. The composition of produced gas was measured using an infrared gas analyzer system for CH₄ and CO₂ (Sensors Europe GmbH, Erkrath, Germany; Pronova Analysetechnik GmbH & Co. KG, Berlin, Germany). Gas analysis was performed at around 30 ml of gas production, and chemical analyses of the supernatant were conducted to verify composition changes after anaerobic digestion. Methane production was expressed as L_NCH₄ per kg of FM (L_Nkg⁻¹FM). After anaerobic experiments, the humic acid was extracted from a sub-sample of the supernatant, as shown in Additional file 1: Fig. S1 and explained above.

2.5 Cation exchange

High concentrations of K may inhibit biogas production (Chen et al. 2008), but this can be mitigated through the use of cation exchange resin (Geng et al. 2022). Therefore, to investigate the impact of reduced cations content (e.g., K and ammonium) and pH levels in the HTH liquid on the biogas and methane yield, a cation exchange resin (RELITE EXCO8, RESINDION S.r.l., Italy) was used to pre-treat two samples of the HTH-4KOH process liquid.

First, experiments on the effect of contact time (30 min to 24 h) on pH and K removal were carried out with the resin and HTH-4KOH process liquid (Additional file 1: Fig. S3). The HTH-4KOH liquid was chosen because of its lower K concentration compared to HTH-5KOH. The experiments were conducted in duplicate. Two contact times were chosen for pH adjustment to 8 (based on the reference pH detailed in Sect. 2.4) and to 6.86 (selected after 30 min, since no significant pH reduction was noted with extended treatment), resulting in the samples being labeled HTH-4KOH-pH8 and HTH-4KOH-pH6.86.

3 Results and discussions

3.1 Solid yield, and carbon distribution

The amount of initial HT-solids decreased as pH increased (Fig. 1a). The range of solid yield values found for the HTC and HTH experiments (43–56%) is common for the relatively high process temperature of 240 °C. It can be seen in Fig. 1b that little to no gas was produced in the runs with KOH addition, while the amount of organic compounds in the process liquid increased with increasing amounts of KOH. Although approximately one third of the organic carbon could be recovered from the liquid as humic acid (A-HA,l), a high concentration of TOC remained in the process liquid (Fig. 2b). The majority was made up of organic acids, even though the concentration of the aromatic compounds decreased significantly.

The cow manure digestate contained a large amount of inorganic compounds as seen by the high ash content (Additional file 1: Table S1). As the KOH addition and initial pH were increased, the proportion of ash in the solid products increased, while the organic compounds

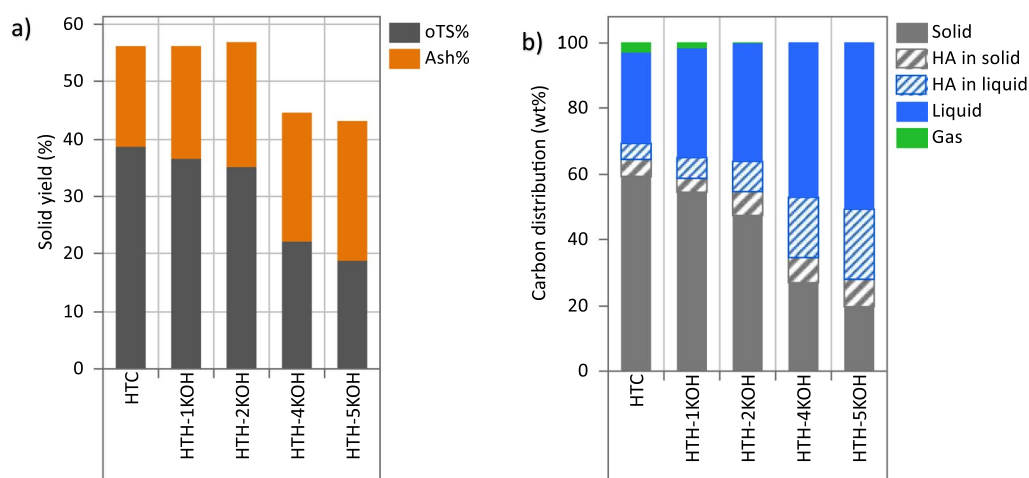


Fig. 1 Comparison of **a** total solid yield for each experiment, composed of ash content and volatile solids, and **b** comparison of the distribution of carbon (wt%) between the three phases, including the carbon in HA recovered from the HT-solids and liquids

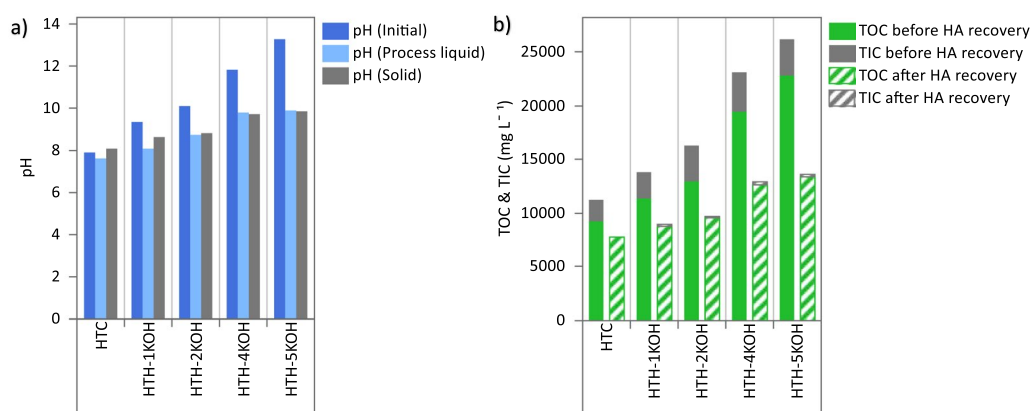


Fig. 2 Changes in: **a** Initial pH and pH of solid and liquid products, **b** total organic carbon (TOC) and total inorganic carbon (TIC) of process liquids

measured as % volatile solids (VS%) decreased. The carbon balance in Fig. 1b shows that more carbon was found in the liquid for HTH runs, and it increased with KOH addition. The amount of carbon recovered from the solids and liquid as A-HA also increased with KOH addition. Results from the five hydrothermal experiments, detailing mass recovery, yields, and volatile solids for solids and humic acids, are summarized in Additional file 1: Table S5.

In HTC, a small amount of gas was produced by the hydrothermal reactions and was transferred to the gas phase, increasing the reactor pressure (Additional file 1: Table S6). It was captured and measured after the reactor cooled down. The main gas was CO₂, with some amounts of H₂S and CH₄ produced. In contrast, no gas could be measured in the HTH process. The higher pH of the process liquid (Fig. 2a) could potentially increase the amount of CO₂ dissolved in the liquid. The higher TIC values in Fig. 4b may be indicative of this.

The organic concentration, measured as total organic carbon (TOC), in the HTH process liquid was up to 60% higher than in HTC at the highest KOH addition (as shown in Fig. 2b and can be found in Additional file 1: Table S7). Alkaline hydrolysis of complex organic compounds and solids to produce lower molecular biodegradable organic compounds is a well-known treatment process. Even after the precipitation of the A-HAs from the process liquid from the three highest pHs, the TOC remained between 35% and 45% higher than the HTC process liquid.

3.2 Overview of total HA recovery on a mass basis

The total yield of A-HAs (37.5 wt%) recovered from both the solid and liquid phases, with the highest KOH addition (HTH-5KOH) was more than twice that found in the HTC run. The majority was recovered from the process liquid (Fig. 3a, and b). The ash content of the A-HAs

recovered from the solids was slightly higher than in the reference HA purchased from Sigma Aldrich (28%) (Fig. 3d). We assume that a feedstock with a lower ash content would result in a higher organic content in the HA. In contrast, the HA from the process liquids had a much higher organic content $\geq 95\%$ (Fig. 3c). The yield of A-HA achieved in this study was 9.2% higher compared to the 28.28% yield reported for the acidic-alkaline hydrothermal treatment of corn stalk (Shao et al. 2022).

3.3 Elemental composition of the solids and humic acids

The difference between the composition of the artificial humic acids recovered from the solids (A-HA,s) and liquids (A-HA,l) from the five experiments can be clearly seen in the Van Krevelen diagram (Fig. 4). The A-HA,s from the solids fall below the envelope containing most of the natural HA with higher O/C ratios, while the opposite is seen for A-HA,l from the liquids. They have higher H/C ratios, similar to the commercial reference HA from Sigma Aldrich Chemicals, and two A-HA recovered from hydrothermal processes (Fig. 4b). One such A-HA, designated A-HA,Y, was obtained from HTH of dried fruit stands from a tulip tree (Yang et al. 2019a), while the other, termed A-HA,dS, was isolated following the HTC of sugarcane by-products at 230 °C (dos Santos et al. 2020).

In all cases, the composition of the synthesized A-HA is remarkably different when isolated from the solid and the liquid phase. The A-HA from the solids is rather oxygen-rich and characterized on average by H/C ≈ 1 and O/C ≈ 1 , a rather unusual place in the Van Krevelen diagram. We speculatively attribute that to a high mineral binding carboxylate content. The non-adsorbed, liquid-phase A-HA has on average H/C ≈ 1.5 and O/C ≈ 0.5 , that is a rather hydrocarbon and lignin-rich material. The N-HA and previously reported A-HA analyses (not separating in two solubility or adsorption fractions) are in between and a nice mix of the two.

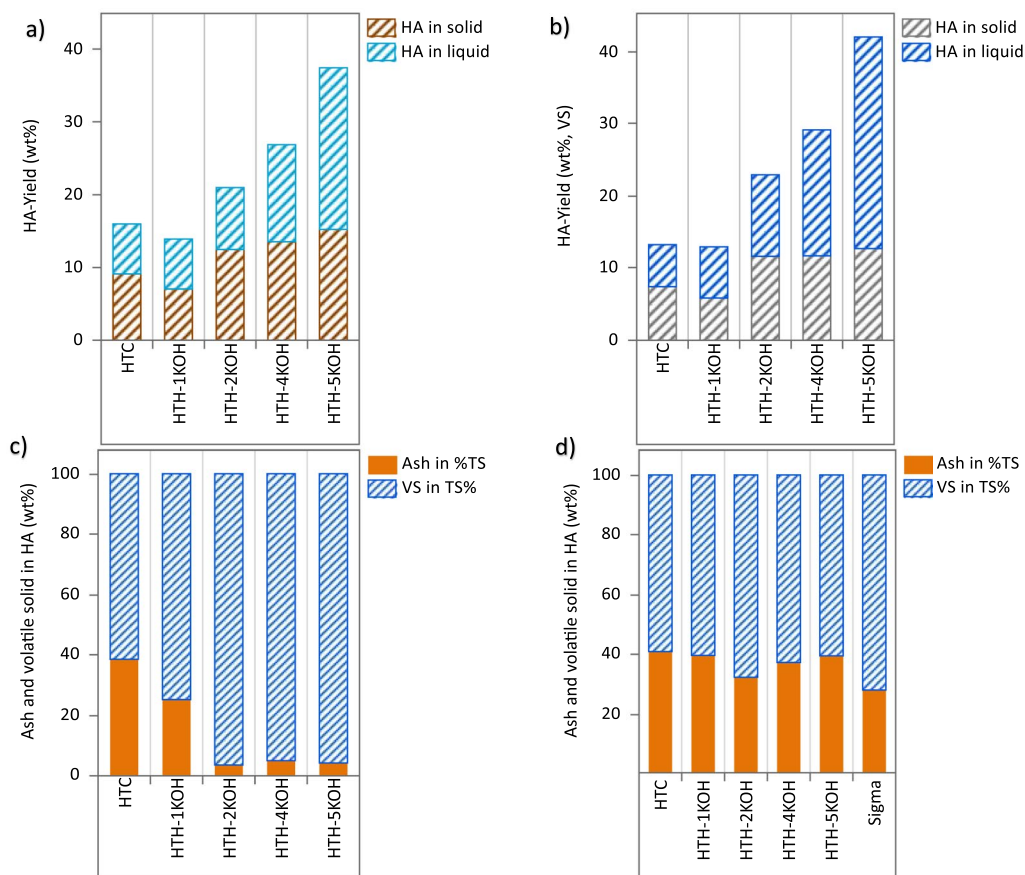


Fig. 3 **a** Yield of HA from solid and liquid phases (% of input mass (DM) recovered as HA), **b** yield of HA as volatile solids from solid and liquid phases (% of input mass recovered as HA, and corrected for %VS), **c** volatile solids and ash content of HA recovered from liquid, and **d** volatile solids and ash content of HA recovered from solid

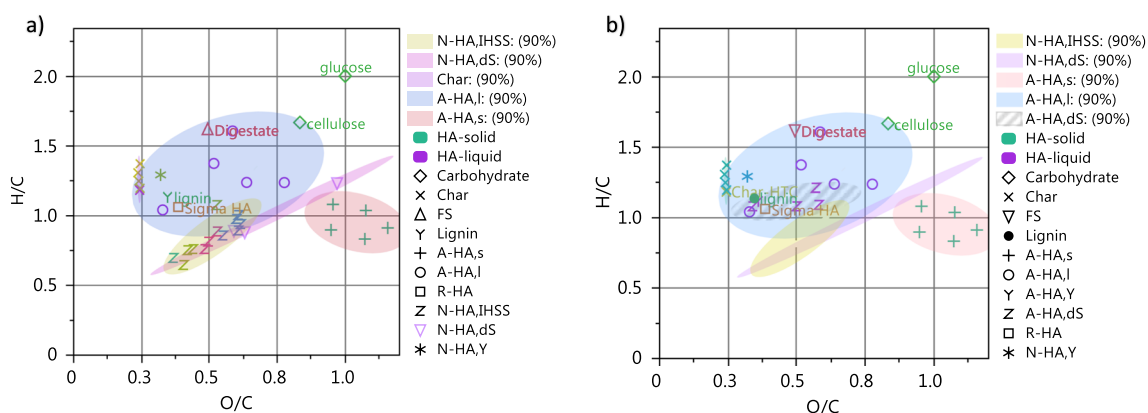


Fig. 4 **a** Comparison of the molar composition of natural HA (N-HA) to the feedstock (cow manure digestate), HT-solids, and the A-HA recovered from the solids (A-HA,s) and process liquids (A-HA,I). **b** Further comparison with literature values for A-HA recovered from HT-solids: (Yang et al. 2019a) (A-HA,Y; tulip tree), (dos Santos et al. 2020) (A-HA,dS; sugarcane by-products)

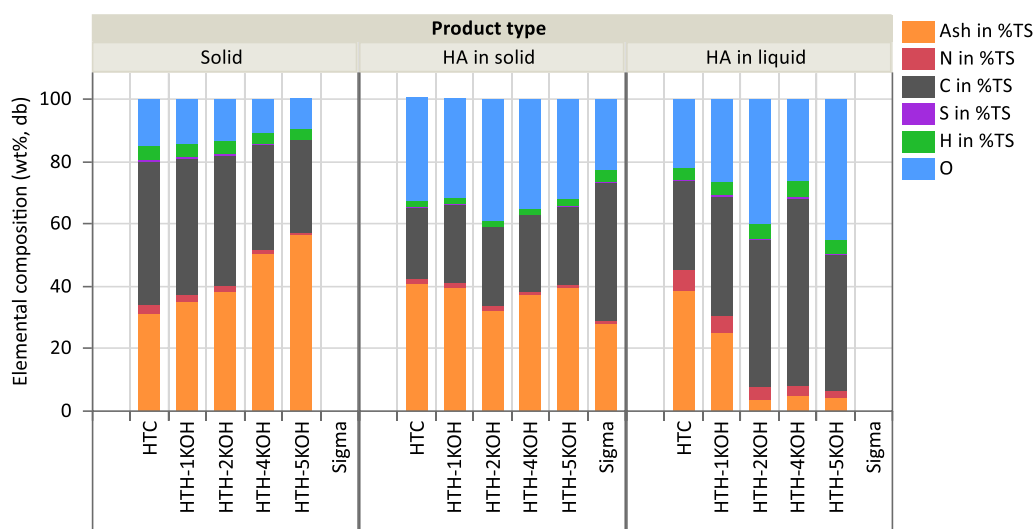


Fig. 5 Elemental composition of solids (wt%, db) from HTC and HTH runs and the humic acids recovered from the solids and process liquid compared to the digestate and humic acid from Sigma Aldrich Chemicals. (db: dry basis)

The ash content of the solids increased with the addition of KOH due to the accumulation of K and the reduction of C% in the solids, which aligns with the findings reported in previous works (Yoshimoto et al. 2023; Ghaslani et al. 2024). This occurred as the carbon dissolved in the liquid to form a wide range of organic compounds and A-HA. In Fig. 5, the distribution of the elements highlights the high ash content in the solids and in the HA from the solids again. However, when the elemental composition is compared on a dry, ash-free basis, we see that most solids have a similar C:H:O ratio (Additional file 1: Fig. S4).

3.4 Content of organic compounds in solids and process liquid

Figure 6 shows the effect of increasing the initial KOH content on various groups of organic compounds, such as acids, sugars, and alcohols. An important advantage of the HTH process for the use of the products in soil applications is the decreased generation of aromatic compounds (Ghaslani et al. 2024). This can be nicely seen in Fig. 6a for the solid and liquid phases. The concentrations of all aromatic compounds (HMF, furfural, phenol, catechol, guaiacol, cresol) decreased with the increasing KOH addition. In the solids, the composition of the aromatic compounds (g/kgDM) was similar in all five runs and mostly related to the already contained lignin, but as compared to HTC the concentrations decreased by more than one third, which reflects the suppression of new aromatic structures by chemical means. In contrast, the process liquid of the HTH-5KOH contained less than one tenth of the aromatics

produced in the HTC run, i.e. there were only very small amounts of soluble phenols and furans. This reduction in aromatics with increased KOH content is consistent with findings from prior studies (Tkachenko et al. 2023; Ghaslani et al. 2024) that instead of undergoing polycondensation to form aromatic hydrochar, aromatics underwent humification reactions, resulting in the production of A-HA (see Fig. 3a and b).

Organic acids and sugars, on the contrary, increased with KOH concentration, with fructose and arabinose appearing at the two highest KOH amounts (Fig. 6b). The increase in sugar content indicates that KOH contributes to the breakdown of more cellulose and hemicellulose units formerly not enzymatically split in the in cow manure digestate, transforming them first into sugars, then by retro aldol reaction into organic acids. The significant increase in organic acids content is seen in Fig. 6c. In the solid phase, the addition of KOH led to a significant increase in lactic acid concentration (g/kgDM), by almost a factor of 7 at the two highest KOH levels (4× and 5×). Formic acid also increased almost threefold, whereas acetic acid and the GC-fatty acids (measured by gas chromatography) showed slight increases. This suggests that the addition of KOH can have a significant impact on the production of various organic acids during the process, with a similar trend also reported in previous studies (Tkachenko et al. 2023; Ghaslani et al. 2024). However, the addition of KOH had little effect on alcohols (Fig. 6d), which suggests that KOH addition may not be a critical factor in the production of alcohols during the HTC process.

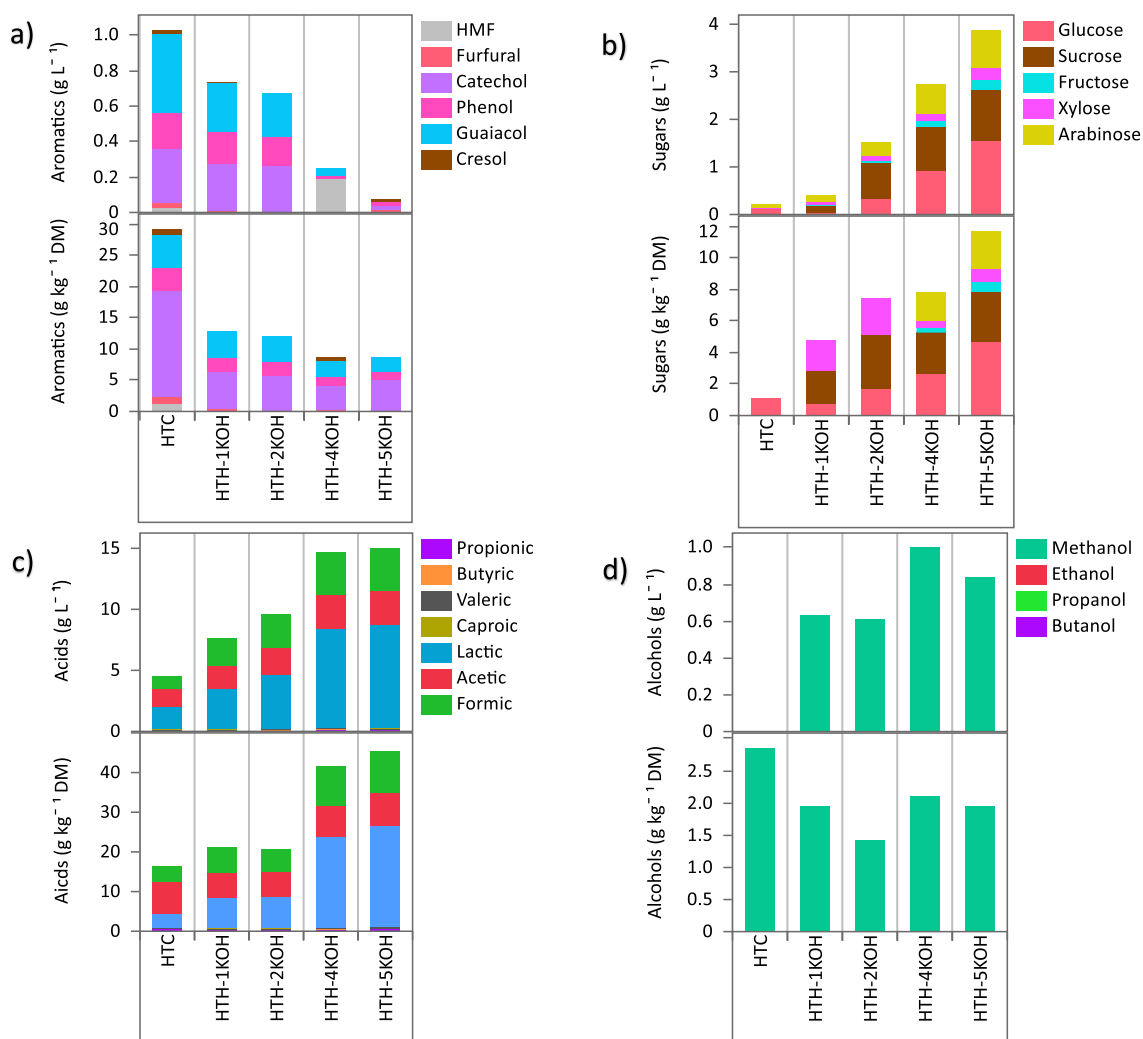


Fig. 6 Change in the concentration of **a** aromatics, **b** sugars, **c** acids, and **d** alcohols in the liquid (g L^{-1}) and solid ($\text{g L}^{-1} \text{DM}$) products with increasing initial KOH content

The changes in concentration (g L^{-1}) of the organic compounds in the liquid phase are shown in Fig. 6a–d. The addition of KOH resulted in increased concentrations of lactic, acetic, and formic acid. The highest KOH addition led to a significant concentration of 8.5 g L^{-1} lactic acid, which was 4.5 times higher than the concentration achieved from the HTC process. This suggests that KOH addition can significantly improve the production of lactic acid (LA) obtained by the symmetrical splitting of all hexoses derived from hydrolysis of cellulose and hemicellulose (Wang et al. 2013), (Garlotta 2001). All fatty acids, except caproic acid, also increased with the addition of KOH. However; elevated levels of organic acids in the HTH products, particularly acetic acid (Bargman et al. 2013), may potentially inhibit seed germination and plant growth. This highlights the necessity for additional treatment (e.g., anaerobic digestion for methane

production) of the process liquid prior to its application to soil and plants. Overall, the results show that the addition of KOH indeed significantly impacts the production of various organic compounds during the hydrothermal treatment, with the effect depending on the specific starting products being investigated.

3.5 Inorganic distribution in solid and liquid

We also analyzed the distribution of inorganic compounds after hydrothermal processing. Initial statements for nutrients can be made based on results presented in Fig. 7a and b. The feedstock, cow manure digestate, contained high concentrations of nitrogen ($5.7 \text{ g N-Kjeld/kgFM}$), phosphorus (14.85 g P/kgFM) and potassium (47.3 g K/kgFM). These results are presented in Additional file 1: table S1. After hydrothermal treatment, the majority of the nitrogen was found in the process

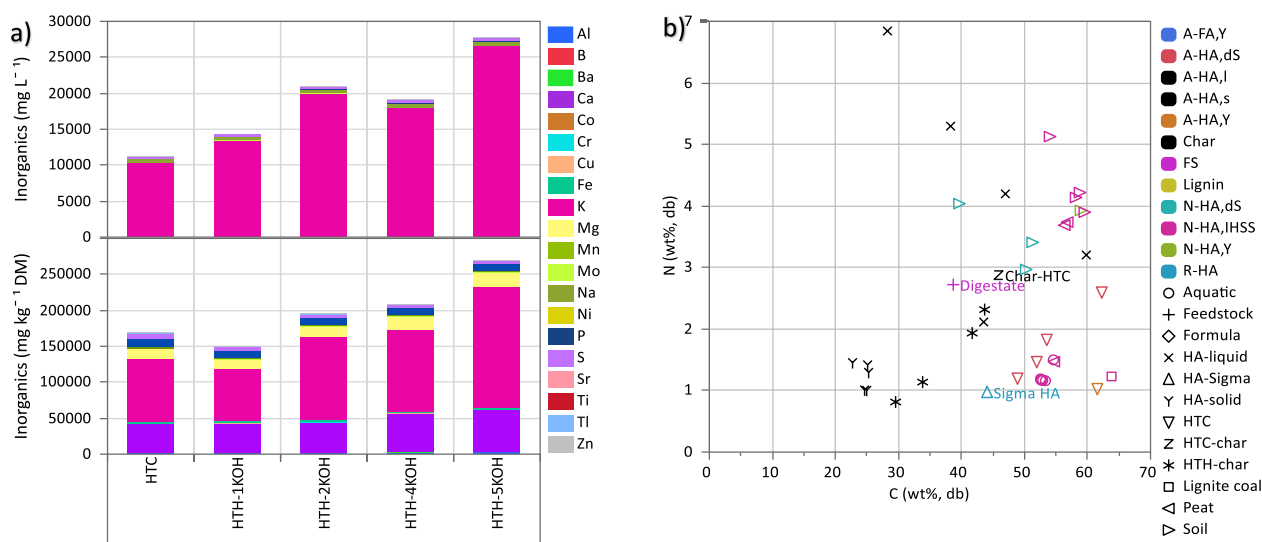


Fig. 7 **a** Content of ICP-OES elements found in HT-solid and process liquids, and **b** comparison of the molar composition of nitrogen vs. carbon in the HT-solids and humic acids (A-HA) to those found in natural humic substances (N-HA) and A-HA values in the literature

liquid as NH_4 in all experiments, causing very high liquid concentrations ranging from 3.7–4.3 g $\text{N-NH}_4/\text{L}$ (see Additional file 1: Fig. S5). The process liquid contained relatively low phosphorus concentrations, ranging from 6.5 mg P/L for HTC to 164.8 mg P/L for HTH-5xKOH. Potassium (K) concentrations were high again and ranged from 10.4 to 26.6 g K/L (Fig. 7a). The increase in K, resulting from the addition of KOH, aligns with findings from previous reports.

Some N was also incorporated in the solids and A-HAs as shown by the CHN analysis. The HTC-solid and HA contained the highest amounts of N, 2.9% and 6.8% (wt,db), respectively, while only 0.8% and 0.9% were found in the HTH-solid and HA at the highest pH. The molar composition of nitrogen vs. carbon in the solids and A-HAs is compared to those found in natural humic substances and A-HA values found in the literature in Fig. 7b. The A-HAs from the liquid processed from cow manure digestate contained a high amount of nitrogen compared to natural humic substances.

3.6 The HHV (MJ/kg DM) values of solids and A-HAs

Additional file 1: Fig. S6 shows the higher heating values (HHV) of solids and A-HAs. HTC increased the HHV of digestate from 17 to 21 MJ kg^{-1} . However, increasing the KOH content decreased the HHV. Since carbon and ash content are two important factors affecting the HHV of HTC solid product (Marzban et al. 2022), the HTH process is not recommended for producing solid products for biofuel applications due to the need for addition of inorganic alkaline agents,

such as KOH, in HTH. This increase not only reduces the carbon content of HTH solids (Fig. 5) by converting the carbon into organic compounds in the liquid but also leads to an accumulation of inorganics in the solids (K) (Fig. 7a). The observed behavior of HHV in HTC and HTH solids aligns with previous findings (Ghaslani et al. 2024)

3.7 Characterization of humic acids

The results of both FTIR and UV-vis spectroscopies confirmed that the products obtained in hydrothermal humification were analogues of humic acids. The UV-vis spectrum of commercial humic acid contained one well-defined maxima at around 200 nm with a decrease of the intensity in higher wavelengths. The UV-vis spectra of A-HAs in Fig. 8a are characterized by the absorption band at around 200 nm and gradual decay of the absorption intensity with an increase of the wavelength. This indicates the presence of the chromophores that absorb in the whole analyzed region (Cunha et al. 2009). The discrete shoulder at 270 nm in the spectra of HTH products vanished in HTH processes with larger amounts of KOH and was substituted by a shoulder at 345 nm in the spectra of HTH product obtained. Both shoulders are indicative of the presence of conjugated aromatic systems attributed to structural conjugation of quinones and ketones (Canellas et al. 1999), and light absorption of HTH products at longer wavelength corresponds to a higher degree of conjugation or aggregation induced involvement of the other conjugation systems into the optical transition.

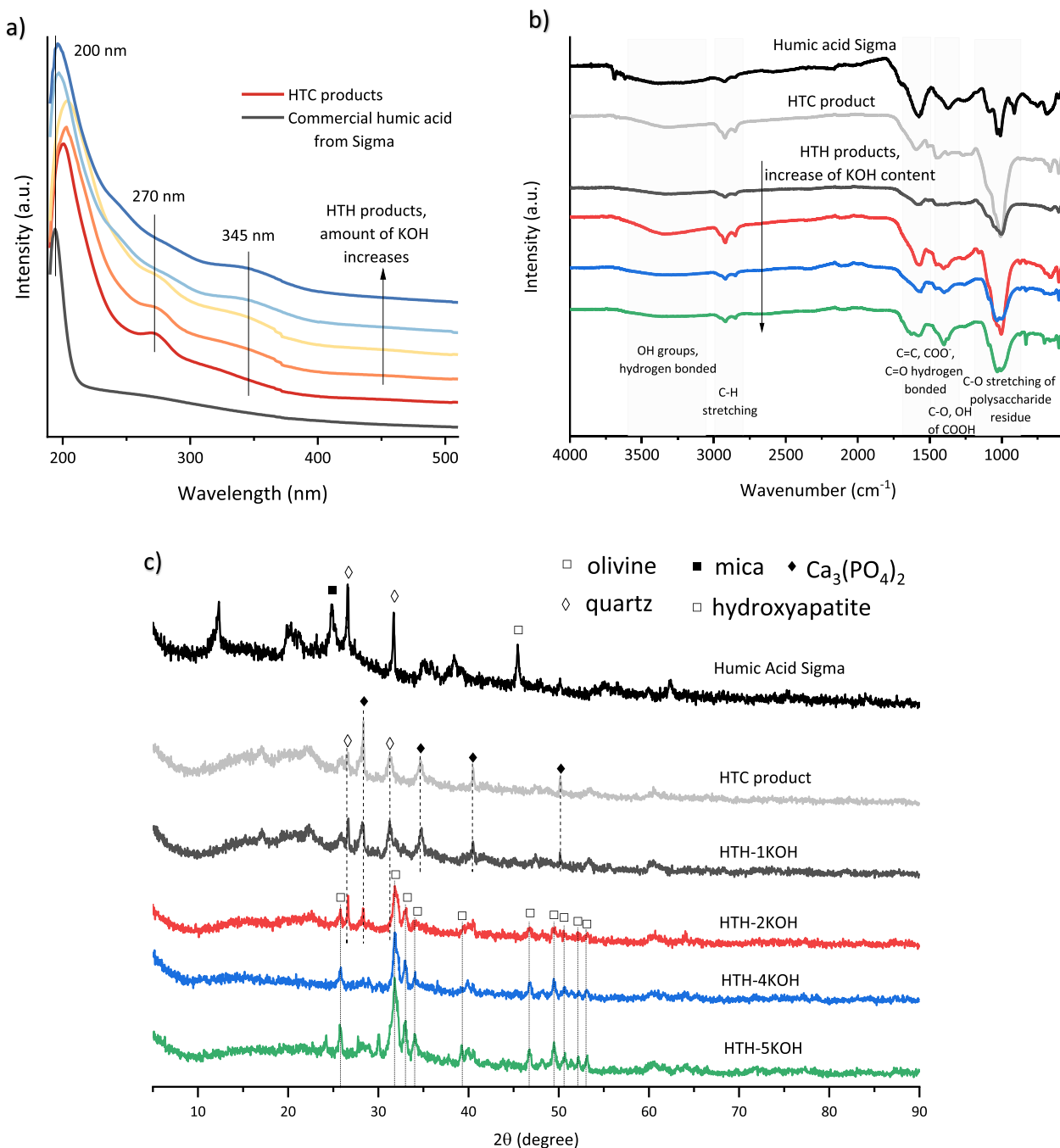


Fig. 8 **a** UV-vis spectra of the A-HAs and commercial HA from Sigma. The arrow shows a gradual increase of the KOH added before the reaction, **b** ATR-IR spectra of the HTC and HTH products obtained with the different KOH content in comparison to the commercially available humic acids supplied by Sigma Aldrich, **c** XRD patterns of the commercial and A-HAs; increase of the pH during the hydrothermal treatment results in crystallization of calcium phosphates as neutral salt (lower pH) or basic salt (higher pH), and appearance of the quartz at lower pH

The FTIR spectra of A-HAs revealed the presence of carboxylic and hydroxyl functional groups, as well as conjugated aromatic system, characteristic for humic substances (Fig. 8b). The spectra revealed a decrease in the adsorption intensity with an increase in the

wavelength typical for humic substances (Cunha et al. 2009). The FTIR spectra of the HTH products in Fig. 8b reveal diversity of the bands typical for the humic substances (Aiken et al. 1986; Stevenson 1994). Major absorption bands were in the regions of 3600–3050 cm⁻¹

(broad band corresponding to the hydrogen bonded OH groups), 2940–2900 cm^{-1} (aliphatic C–H stretching), 1690–1500 cm^{-1} (aromatic C=C, COO^- , hydrogen bonded C=O), 1465–1300 cm^{-1} (C–O stretching and OH deformation of COOH), 1185–864 cm^{-1} (C–O stretching of polysaccharide residues).

Due to the amorphous nature of all humic acids, the XRD analysis allows to quantify the presence of minerals (Fig. 8c). The mineral composition of the isolated natural humic acids or the synthetic ones depends on the place of isolation or starting materials, correspondingly. The minerals bond or not bond to the humic acids can be removed during the base extraction. The reference commercial humic acid is rich in quartz, apparently extracted together with the humic acid from the soil. Also, mica and olivine were identified in the commercial humic acid. The signal at $12^\circ 2\theta$ can be attributed to the typical layered silicates of soil: smectite, vermiculite, chlorite or mica (Naidja et al. 2002). The products of hydrothermal carbonization or humification were enriched with calcium phosphates. The HTC process and HTH with lower pH (1KOH and 2KOH) resulted in crystallization of the neutral salt, $\text{Ca}_3(\text{PO}_4)_2$. Increasing the pH during the synthesis results in the crystallization of the basic calcium phosphate, hydroxyapatite $\text{Ca}_5[\text{OH}(\text{PO}_4)_3]$. Doubling the amount of the base used in the reaction resulted in a higher amount of hydroxyapatite than the neutral salt. Further increase led to solely basic phosphate crystallization. In the HTC and HTH with the lower alkaline content, XRD analysis revealed the presence of quartz. Apparently, higher pH of the synthesis led to the formation of water soluble potassium silicates that were washed out from the HTH products (A-HA). The SEM–EDX analysis of the A-HAs from HTC and HTH process liquids, and the commercial reference from Sigma are shown in Additional file 1: Figs. S7. The EDX analysis also showed the presence of above mentioned inorganics, found by XRD, in the recovered A-HAs and Sigma HA.

3.8 Anaerobic digestion of HTC and HTH process liquid

The feedstock used in the hydrothermal processes had previously undergone anaerobic digestion, recovering a large amount of energy from the original cow manure slurry. According to the average biogas yield found in 119 previous studies (Dandikas et al. 2021), anaerobic digestion of fresh cow manure slurry produces an average of 27 (I_N/kgFM) biogas with 59.9% methane content. The extended biogas experiments conducted in this study showed that the cow manure digestate still had the potential to generate 4.9 (I_N/kgFM) biogas with 59.2% methane content. The HTH-5KOH process liquid produced 10.1 (I_N/kgFM) biogas with 73.1% methane content, whereas the HTC process liquid produced 5.0 (I_N/kgFM) biogas with 67.4% methane content (Table 1). The methane and biogas production of the HTH-5KOH process liquid was two times higher than the HTC process liquid, showing its better performance. In theory, 1 kg of COD can produce 350 L of methane (Michaud et al. 2002). This was used as the basis for calculating the theoretical methane production for 1 kg of fresh matter (FM) of HTC and HTH liquids from their COD concentrations (Additional file 1: Table S4). The HTH-4OH-HCl process liquid also produced higher amounts of methane than the HTC process liquid, but 16.2% less than that of the HTH-5OH process liquid. This can partially be explained by the lower level of organic compounds solubilized at the lower KOH level, resulting in a 10.1% lower COD value and theoretical methane yield, and differences in the composition of the organic compounds. The experimental results showed that only 35.6% and 36.6% of the expected theoretical methane production for HTH-5KOH and HTC liquids, respectively, was achieved, suggesting that the A-HA contained in the liquids was not an accessible substrate in the digestion process.

The results also show that a high K concentration in HTH-5KOH may inhibit biogas production (Chen et al. 2008), or cause a delayed start due to an adaptation

Table 1 The summary of biogas (I_N/kgFM) and methane yield ($\text{I}_N \text{CH}_4/\text{kgFM}$), theoretical methane yield for digestate, HTC, and HTH process liquids, compared to literature values for fresh cow manure from (Dandikas et al. 2021)

Substrate	Biogas yield (I_N/kgFM)	Methane yield ($\text{I}_N \text{CH}_4/\text{kgFM}$)	Methane %	Theoretical methane (L/kgFM)	Practical yield of methanisation (%)*
Digestate	4.9 ± 1.56	2.9 ± 0.85	59.2 ± 1.3	28.4	10.2
HTC	5.0 ± 0.15	3.4 ± 0.14	67.4 ± 0.67	9.2	36.6
HTH-5KOH	10.1 ± 0.26	7.4 ± 0.17	73.1 ± 0.26	20.7	35.6
HTH-4KOH-HCl	8.7 ± 0.02	6.2 ± 0.02	71.3 ± 0.39	18.6	33.3
HTH-4KOH-pH 8	8.4 ± 0.11	6.1 ± 0.04	72.6 ± 0.49	16.5	37.0
HTH-4KOH-pH 6.86	10.9 ± 0.2	7.5 ± 0.04	68.9 ± 0.24	15.5	48.4
Fresh cow manure (Dandikas et al. 2021)	27	16.17	59.9	–	–

*Practical yield of methanisation was calculated based on (experimental methane yield / theoretical methane yield) × 100

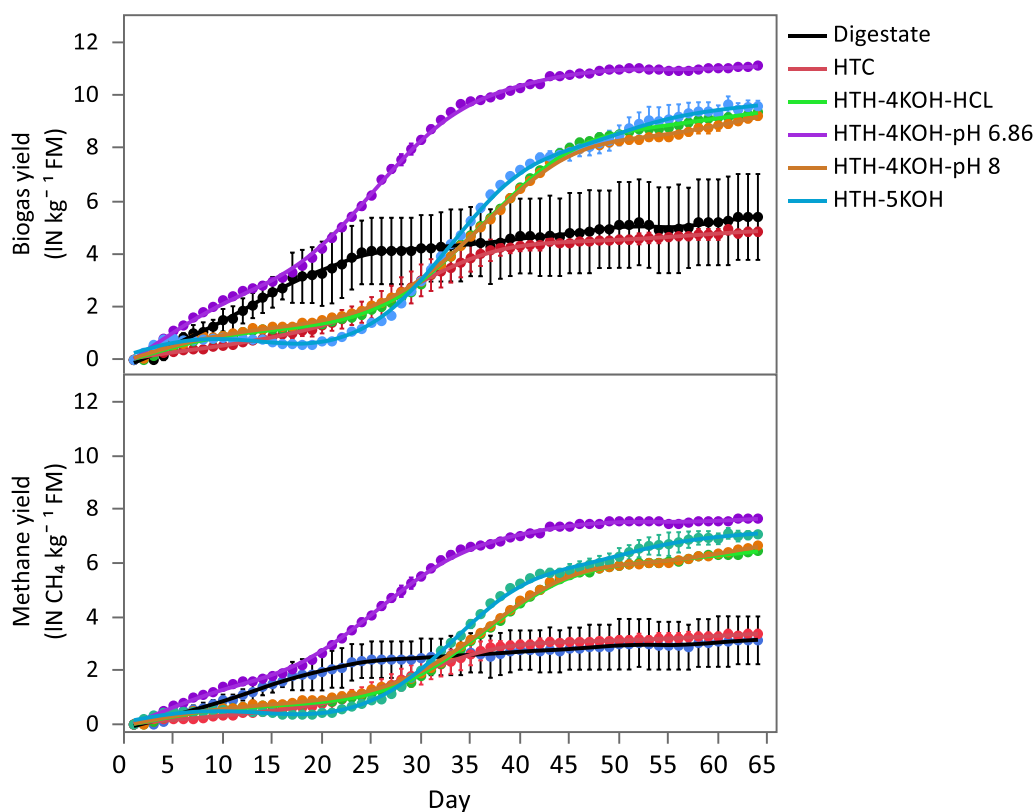


Fig. 9 Biogas and methane yield ($\text{IN kg}^{-1}\text{FM}$) of HTC and HTH process liquids. The pH of HTH-4KOH process liquid was adjust using HCl (labeled HTH-4KOH-HCl) the same as HTH-5KOH. In addition, the pH of HTH-4KOH was adjusted using cation exchange resins (HTH-4KO-pH 8, and HTH-4KO-pH 6.86)

period compared to HTC, in which fermentation started on the first day but at a slow rate (Additional file 1: Fig. S9). To mitigate the adaptation period, the K concentration and pH of the HTH-4KOH process liquid were adjusted using cation exchange resins (pH of 8 and 6.86). The HTH-4KOH process liquid was chosen because it initially had a lower K concentration compared to HTH-5KOH (Fig. 7a). This approach using resin was then compared to the HTH-4KOH-HCl method, where HCl was utilized for pH adjustment. The results showed a more than two times increase in biogas and methane yield for HTH-4KOH-pH 6.86 compared to digestate, while avoiding any inhibition period compared to the HTH-4KOH-HCl and HTH-5KOH, in which the pH was also adjusted to 8 using HCl (Figs. 9, and Additional file 1: S10). The increase in methane yield from HTH liquids was significantly higher than HTC, when the digestate was considered as reference for this comparison (Additional file 1: Fig. S9). Furthermore, HTH-4KOH-pH 6.86 produced 48.4% of theoretical methane yield (Table 1). The reduction in ammonium concentration, from 4.5 to 1.7 g N-NH₄/L, and potassium, from 18 to 13.5 g K/L, could explain the more rapid biogas production observed

in the HTH-4KOH with a pH of 6.86, as compared to the HTH-5KOH treatment. The reduction in ammonium and potassium concentration in the HTH-4KOH liquid over time (24 h) using cation exchange resin is illustrated in Additional file 1: Fig. S3. However, further studies are required to investigate the individual effects of ammonium and potassium on the timing of biogas and methane production.

The results of the anaerobic digestion experiments indicate that full recovery of HA after the biogas process is possible. In fact, measurement of HA in the supernatant of the biogas digestate after the experiments showed a slight increase in the concentration of A-HA in the HTH-5 samples (11.6%), while the content increased significantly in the HTC liquid (162.5%) (Additional file 1: Table S9). However, since the initial A-HA content in the process liquid from HTH-5KOH was more than seven times higher than that in the HTC liquid, the final content in the HTC liquid was still one third that in the HTH liquid. The rise in A-HA levels in the samples may result from ongoing humification reactions throughout the anaerobic process. The continuation of humification reactions was already observed during the storage of

HTC process liquid produced from digestate cow manure (Marzban et al. 2023), because the various compounds, such as aromatics, amino acids, and sugars, can be considered to be reactive building blocks for humic acid formation (Yang and Antonietti 2020a, 2020b). Nonetheless, further research is required to investigate this aspect in more detail. The reduction in acetic acid content, a substantial increase in methane yield, and the rise in A-HAs content, however, collectively position the HTH process as a viable pretreatment technology for biogas production.

4 Conclusion

Our study analyzed the effect of the addition of alkaline species in hydrothermal processing of cow manure digestate on the formation of organic and inorganic compounds, carbon distribution, and production of artificial humic acids (A-HAs). Our study highlighted the transition from carbonization to humification reactions with the increase of KOH, emphasizing the superior performance of the HTH process over HTC. Notably, HTH enhanced the production of artificial humic acids (A-HAs) and demonstrated efficient carbon distribution across liquid and solid phases without generating gaseous byproducts, highlighting its environmental advantages. In particular, HTH resulted in a higher total organic carbon (TOC) content and organic acids, while significantly reducing aromatics compared to HTC. Therefore, recycling HTH liquid into anaerobic digestion significantly increased methane production and reduced organic acids, demonstrating HTH's efficiency in enhancing bioenergy outputs. This two-step combination of thermochemical and bioconversion processes had the potential to transform biowaste into humic-rich products, while its organic byproducts increased the methane productivity. Application of the A-HAs-rich side products of biogas manufacturing to soils can enhance phosphorus supply for plants, thus reducing the reliance on chemical fertilizers. This offers, in our opinion, an innovative approach for managing wet biomass and enhancing its impact on soil health and biogas production. However, these possibilities require further investigation.

Future research should prioritize HTH process optimization, considering a wide range of temperatures and time, and solid content of feedstock, and explore the complex relationship between lignin, cellulose, and hemicellulose in the production of A-HAs in more detail. Comparative studies assessing the potential phytotoxicity of HTH products are recommended, which explore the potential of HTH products (solid, liquid, A-HA, and mixture as slurry) for promoting seed germination and plant growth. Future research should also investigate

co-hydrothermal humification, where digestate can be humified together with lignocellulosic biomass. Exploring alternative alkaline agents, such as agricultural lime or wood ashes as substitutes for KOH, could expand the sustainability of the process.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1007/s42773-024-00334-1>.

Additional file 1: Table S1. The mean value and standard deviation of organic compounds, N, P, K, Ash%, COD, TS%, VS%, and pH of cow manure digestate. **Table S2.** Fiber analysis of digested cow manure using VLUDFA method for determination of cellulose, hemicellulose, and lignin content. **Fig. S1.** Schematic of A-HA extraction from solid (A-HAs), process liquid (A-HAL) and anaerobically digested HTC and HTH process liquid. **Fig. S2.** A-HA extraction from solid: visual appearance of a) supernatant including A-HA extracted from solid products, and b) supernatant after precipitation and removal of A-HA, c) dried extracted A-HA.s. **Table S3.** Analysis performed for the feedstock digestate, HT-solids and process liquids and A-HAs produced from HTC and HTH processes. **Table S4.** Content and lumped parameters of HTC and HTH liquids, the inoculum used for biogas experiments. **Fig. S3.** Changes in pH, and reductions in K and ammonium concentrations of HTH-4KOH using cation exchange resins. Analytical method. **Table S5.** Results for solids and humic acids produced in the five runs: mass recovered, yields, % volatile solids (%VS). **Table S6.** Process conditions, inputs and yields for digested cow manure as feedstock (%solids = 8.3%). **Table S7.** Comparison of the concentrations of total (TC), inorganic (TIC) and organic (TOC) carbon in the process liquid from the five runs and the TOC after the precipitation of the A-HA (TOC(HA)). **Fig. S4.** Elemental composition of solids (wt%,daf) from HTC and HTH runs and the humic acids recovered from the solids and process liquids compared to the digestate and humic acid from Sigma Aldrich Chemicals. (daf: dry ash-free). **Table S8.** Average values and standard deviations (SD) of individual sugars, aromatics, acids, and alcohols in HTC and HTH solid and liquid products. **Fig S5.** The content of N-Kjeld, NH₄-N, NO₂-N, NO₃-N (g L⁻¹) in feedstock, and process liquids of HTC and HTH. **Fig. S6.** HHV (MJ/kg) of feedstock, solids, and A-HAs extracted from solid and liquid products of HTC and HTH processes. **Fig. S7.** SEM of HA from Sigma and A-HAs recovered from HTC and HTH process liquid. **Fig. S8.** SEM-EDX analysis of the HA from Sigma Aldrich and those extracted from HTC and HTH liquid phase. **Fig. S9.** Percentage increase of biogas and methane yield compared to digestate used as feedstock of hydrothermal experiments. **Fig. S10.** Individual figures for the cumulative biogas and methane production for HTC and HTH liquids compared to digestate (feedstock of hydrothermal experiments). **Table S9.** Comparison between the values of A-HAs, acids, sugars of digestate, HTC and HTH-5KOH process liquids, before and after biogas production.

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Author contributions

All authors contributed to the study's conception and design. Material preparation, experiments, data collection and analysis were performed by Nader Marzban. The first draft of the manuscript was written by Nader Marzban and Judy. A Libra, and all authors, commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability

All data generated or analyzed during this study are included in this published article and its additional files.

Declarations

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

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