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THE POTENTIAL OF PROCESS WATERS FROM HYDROTHERMAL CARBONIZATION AS A SUBSTRATE FOR ANAEROBIC DIGESTION – A BRIEF OVERVIEW

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ABSTRACT

Hydrothermal carbonization (HTC) is a thermochemical process to convert wet wastes into hydrochar. In HTC, process water (PW) is a byproduct whose treatment and valorization present a challenge due to its composition. Thus, anaerobic digestion (AD) emerges as a promising method for PW treatment and valorization by producing biogas, addressing renewable energy supply and waste management. Such an approach contributes to resource recovery and environmental sustainability of the whole HTC process. Therefore, this brief overview aimed to highlight the potential of PW as a substrate for AD by analyzing a few studies that performed AD of this HTC byproduct.

Keywords: Waste valorization. Hydrochar. Biogas. Biomethane. Biofuels.

1 INTRODUCTION

Hydrothermal carbonization (HTC) is a promising thermochemical process for waste valorization[1]. This process uses water both as solvent and catalyst[2] and is conducted at temperatures ranging from 140 to 370 °C with varying solid-to-liquid ratios (1/47 to 1/1) and reaction times (0.05 to 48 h). The resulting solid product from HTC is called hydrochar, a carbon-rich material. Hydrochar has the potential for various environmental applications, such as removing aquatic and atmospheric pollutants, amending soil, producing energy, and sequestering carbon[3].

In addition to hydrochar, it is important to note that HTC also produces a liquid fraction (effluent) known as process water (PW)[4]. HTC involves several reactions occurring simultaneously[5], which can result in PW with a high content of organic matter and nutrients[6,7]. However, PW characteristics depend on the type of waste used and the HTC conditions (e.g., temperature, solid-to-liquid ratio, and time). Thus, PW utilization poses a challenge due to its high chemical oxygen demand (COD) and variable nutrient content.

Therefore, anaerobic digestion (AD) emerges as a possible option for managing PW[8]. AD is a well-established technology that converts organic matter into methane-rich biogas through a series of biological stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis[9]. From this perspective, this work aimed to discuss the potential of the PW as a substrate for AD by analyzing a few studies that performed AD of this HTC byproduct.

2 MATERIAL & METHODS

The Scopus database was used to search the bibliography. The overview considered the period from 2019 to 2023, and it used the following query string: *TITLE-ABS-KEY(("hydrothermal carbonization" OR "hydrothermal co-carbonization" OR "co-hydrothermal carbonization") AND "effluent" OR "process water" OR "HTC liquor")*). The word clustering was performed using the software *VOSviewer*, version 1.6.20, the words were taken from the title and abstract of the articles.

3 RESULTS & DISCUSSION

The interest in AD within the context of HTC is evident when analyzing Figure 1. The process water from HTC generally presents high values of COD, such as those reported in Table 1, which range from 12 to 46 g/L. Consequently, it is necessary to implement an appropriate treatment to reduce the COD values of the PW. This can be achieved by AD, which not only reduces the COD but also yields biofuels. Recently, the possibility of coupling HTC and AD processes has been proposed. Such an approach could provide hydrochar – a carbon-rich material with the potential for various applications (e.g., adsorption of pollutants and energy production) – and biogas[10]. Biogas is mainly a mixture of CH_4 and CO_2 but can be cleaned and upgraded to biomethane by removing CO_2 and other impurities to enhance CH_4 content[3]. Against this background, Table 1 presents some examples of AD from PW from HTC of different biomass waste.

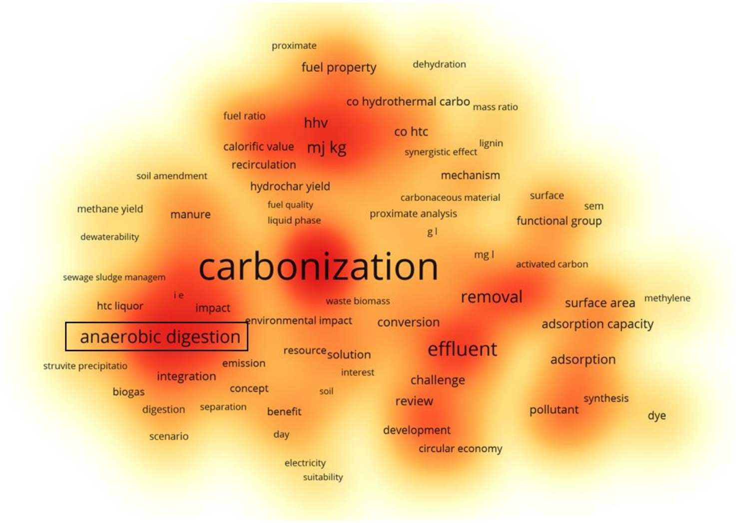

Figure 1. Clustering of the words present in the title and abstract of the articles found using the following query string: *TITLE-ABS-KEY((“hydrothermal carbonization” OR “hydrothermal co-carbonization” OR “co-hydrothermal carbonization”) AND (“effluent” OR “process water” OR “HTC liquor”))*.

The pH values of PW reported in Table 1 ranged from 3 to 9. This variation is attributed to different biomass wastes and the HTC conditions employed. During AD, pH is a crucial factor that impacts bacterial activity in breaking down organic matter into biogas[13]. AD involves several stages, each facilitated by different groups of microorganisms that thrive at specific pH ranges. For maximizing biogas production, the optimal pH values are slightly acidic, close to 6, during hydrolysis and acidogenesis[14], and between 6.8 and 7.2 during acetogenesis and methanogenesis[15].

TOC levels exhibit a direct correlation with biogas production, given that AD converts organic carbon into biogas[11]. Consequently, PW with higher TOC content might yield more biogas[12]. Notably, TOC levels in PW tend to rise with increased HTC temperatures, as one can observe in the study with water hyacinth (Table 1).

The optimal carbon-to-nitrogen (C/N) ratio for AD to maximize biogas production is generally between 20 and 30[16]. Increasing the C/N ratio can lead to a more stable pH and improve methanogenic activity due to the enhanced buffering effect of the digestion medium[16]. This effect is evident when comparing biogas yields from agricultural residue digestate to those from municipal solid waste digestate (Table 1).

Volatile fatty acids (VFA) are essential intermediates in anaerobic digestion, playing a crucial role in biogas production by serving as substrates for methanogenic bacteria[17]. Moderate VFA levels indicate healthy microbial activity and efficient organic matter breakdown. However, excessive VFAs can lower the digester’s pH, leading to methanogenesis inhibition[17]. Proper management of VFAs is vital to ensure a stable and efficient digestion process.

Regarding phenolic compounds, they can significantly inhibit biogas production in AD systems due to their toxicity to microorganisms[18]. In this case, the removal of phenolic compounds through the utilization of alternative materials, such as powdered activated carbon, biochar, and graphene, might be a potential avenue for enhancing methane yield [19,20].

Table 1. Examples of anaerobic digestion (AD) of process water (PW) from hydrothermal carbonization (HTC) of different biomass waste.

Waste	Hydrothermal Carbonization Conditions	Process water characteristics	Anaerobic Digestion Conditions	Methane production	Ref.
Agricultural residue digestate	T: 200; S/L: 1/5; t: 1	COD: 42.2; pH: 6.2; TN: 1.9; TOC: 14.9; C/N: 8.0; VFA: 2.1; Phenols: 1.6		180.7 $NmlCH_4/gCOD$	
	T: 250; S/L: 1/5; t:1	COD: 46.3; pH: 6.1; TN: 2.2; TOC: 16.5; C/N: 7.4; VFA: 4.2; Phenols: 0.8		155.5 $NmlCH_4/gCOD$	
Municipal solid waste digestate	T:200; S/L: 1/5; t:1	COD: 18.1; pH: 7.1; TN: 2.4; TOC: 5.7; C/N: 2.4; VFA: 0.9; Phenols: 0.4	Mesophilic – 15 days	137.7 $NmlCH_4/gCOD$	12
	T:250; S/L: 1/5; t:1	COD: 16.4; pH: 7.8; TN: 1.7; TOC: 6.0; C/N: 3.6; VFA: 1.3; Phenols: 0.6		134.6 $NmlCH_4/gCOD$	
Sewage sludge digestate	T:200; S/L: 1/5; t:1	COD: 38.9; pH: 6.2; TN: 4.5; TOC: 17.1; C/N: 3.8; VFA: 1.8; Phenols: 0.9		181.7 $NmlCH_4/gCOD$	

	T:250; S/L: 1/5; t:1	COD: 43.6; pH: 7.6; TN: 4.7; TOC: 18.4; C/N: 3.9; VFA: 5.3; Phenols: 0.8		151.9 $NmlCH_4/gCOD$	
Oat husk	T: 219.2; S/L: 1/12.5; t: 0.5	COD: 13.18; pH: 3.46; TN: 1.76	Mesophilic – 51 days	144 $NmLCH_4/gCOD$	21
Water hyacinth	T: 150; S/L: 1/10; t: 1	COD: 19.0; pH: 5.6; TOC: 7.1; VFA: 0.4; Phenols: 79.7	Mesophilic – 30 days	213.4 $mLCH_4/gCOD$	22
	T:200; S/L: 1/10; t: 1	COD: 27.5; pH: 4.4; TOC: 11.1; VFA: 1.4; Phenols: 342.3		137.9 $mLCH_4/gCOD$	
	T:250; S/L: 1/10; t: 1	COD: 31.4; pH: 5.1; TOC: 12.1; VFA: 1.6; Phenols: 424.8		148.8 $mLCH_4/gCOD$	
Grape Marc	T:220; S/L: 1/10; t: 1	COD: 33.28; pH: 4.40; TOC: 9.69	Mesophilic – 36 days	135.7 $mLCH_4/gCOD$	23
Grape Marc extracted		COD: 31.08; pH: 4.37; TOC: 7.68		113.9 $mLCH_4/gCOD$	
Sewage sludge digestate	T: 160; S/L: 1/1; t: 0.5	COD: 12.6; pH: 9.15: TOC: 4.6; VFA: 0.2	Mesophilic – 21 days	260.0 $mLCH_4/gCOD$	24
	T: 220; S/L:1/1; t: 0.5	COD: 12.9; pH: 7.14; TOC: 4.6; VFA: 0.4		277.2 $mLCH_4/gCOD$	
	T: 250; S/L: 1/1; t: 0.5	COD: 12.16; pH: 8.08; TOC:4.8; VFA: 0.7		225.8 $mLCH_4/gCOD$	

T = temperature (°C); S/L= solid-to-liquid ratio; t = time (h); COD = chemical oxygen demand (g/L); TN = Total nitrogen (g/L); TOC = total organic carbon (g/L); C/N = carbon-to-nitrogen ratio; VFA = total volatile fatty acids (g/L); Phenols = total phenols (g/L).

4 CONCLUSION

AD emerges as a viable solution for managing PW from HTC, converting it into biogas/methane. However, the PW characteristics influence its anaerobic degradation into biogas/methane. In other words, the biogas/methane yield from PW is related to HTC feedstock and conditions, which govern the PW composition. Therefore, it is always necessary to evaluate the potential of biogas/methane production from PW of different HTC processes. The production of biogas/methane in addition to hydrochar could enhance the feasibility of the entire HTC process. However, an evaluation must be conducted for each scenario considered. Therefore, coupling the HTC and AD processes might represent a promising pathway for efficient sustainable waste management and renewable energy production, which would be aligned with the principles of the circular economy.

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