Enhancing Biomethane Production from Citrus Waste: An Integrated Approach of Hydrothermal Carbonization and Anaerobic Digestion for Sustainable Waste Management

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Abstract: This study investigates the energy recovery potential of bio-oil derived from hydrothermal carbonization (HTC) of citrus waste through anaerobic digestion (AD). The bio-oil, a complex mixture containing 30-50% of the original carbon from biomass, serves as a valuable substrate for AD. Leveraging the HTC pretreatment, the hydrolysis step in AD becomes more efficient, facilitating faster degradation rates. Anaerobic digestion of the bio-oil was conducted in a high-loading hybrid anaerobic reactor. The reactor underwent stabilization using tomato liquid fraction, followed by bio-oil feeding with an applied volumetric loading of 5 g COD/L-d under mesophilic conditions. Remarkably, COD removals exceeded 90% when utilizing the tomato fraction and surpassed 80% in the bio-oil feed. Additionally, methane yield approached theoretical levels, highlighting the effectiveness of combining HTC and AD technologies. The study demonstrates that the integration of HTC and AD offers a promising alternative for the sustainable utilization of citrus industry wastes, showcasing high removal efficiencies and methane production. This approach aligns with circular economy principles, providing a pathway for efficient waste valorization and renewable energy generation.

Keywords: biomethane production, orange waste, waste to energy, sustainable waste management

Introduction

Efficient management of organic waste is a global imperative, posing challenges to both environmental sustainability and resource utilization. Addressing this challenge, innovative approaches, such as the integration of hydrothermal carbonization (HTC) with anaerobic digestion (AD), have been explored in recent studies (Li et al., 2023; Zhu et al., 2021; Al Ramahi et al, 2021).

HTC, involving the carbonization of organic materials is a process where biodegradable wastes are treated in hot water at temperatures between 180 and 250 °C in closed reactors with residence times between 0.5 and 9 hours and steam pressures between 10 and 50 bar. This process yields hydrochar and liquid products. In its initial stages, this technology was used to remediate soils contaminated with pesticides, explosives and other hazardous substances, making its benefits evident for the treatment of biomass waste (Al-Nuaimy et al., 2023; Islam et al., 2015). Coupled with AD, HTC presents a synergistic solution for elevating biomethane production and enhancing waste valorization (Lucian et al., 2020; Brown et al., 2020).

One of the main advantages of hydrothermal carbonization is that the process is applied to the feedstock without any drying treatment. Compared to pyrolysis, the treatment is carried out at lower temperatures and the product yield is generally higher, in addition to the fact that gaseous emissions are generally dissolved in the wastewater due to the pressure that exists in the reactor (Zaini et al., 2017).

This integrated approach has demonstrated its potential across diverse waste streams, including municipal solid waste (Adams et al., 2021), microalgal biomass (Marin-Batista et al., 2019), and macroalgae (Brown et al., 2020). Noteworthy improvements in biomethane production have been observed when HTC products are introduced into AD reactors, with the energy assessment emphasizing the efficiency of this combined approach, where biogas combustion significantly covers the HTC thermal demand (Lucian et al., 2020). The production and applications of hydrochar have been less studied than those of biochars obtained through the pyrolysis process. Some of the previous hydrothermal carbonization works have focused on the production of energy materials using diverse biomass sources such as residues from: potato, olive, miscanthus, palm oil, bamboo, pollinaza and obtaining in general a higher energy density (Missaoui et al., 2017; Saba et al., 2017; Zaini et al., 2017).

Within the citrus industry, where waste rich in limonene poses challenges for conventional AD processes, the application of HTC emerges as a promising solution. Limonene, known for its inhibitory effect on anaerobic digestion, can be mitigated through HTC, paving the way for enhanced biomethane production from citrus waste (Erdogan et al., 2015). This is particularly significant in regions like Mexico, a major global orange producer, where a substantial portion of the citrus industry waste remains underutilized.

Global and national energy demands have surged in recent years, driven by population growth, industrial activities, and increased energy consumption for transportation and heating. In 2019, Mexico's energy independence index, indicating the relationship between production and national energy consumption, stood at 0.71, signifying that energy consumption surpassed production. National energy consumption reached 10,477 PJ (SENER, 2022).

Traditional energy generation methods, such as oil and nuclear energy, adversely impact the environment and human health. Consequently, alternative technologies focusing on renewable energy sources, notably thermochemical processes and anaerobic digestion, have gained prominence. Among these processes, hydrothermal carbonization

Anaerobic digestion, suitable for treating waste with high moisture content, produces biogas, primarily methane, as a renewable biofuel. The process, conducted in the absence of oxygen, necessitates sealed reactors to contain odors. Biomass, particularly organic municipal solid waste (MSW), emerges as a significant potential energy source with diverse applications. Despite environmental complications associated with MSW decomposition, it remains a valuable resource, especially in municipal markets where large waste volumes are generated daily.

Orange waste is one of the most abundant in municipal markets throughout the year, so methods for its utilization are required, integrating biological technologies to reduce processing costs, minimize dependence on fossil energy and reduce the ecological footprint. Considering the above, the objective of this work is to evaluate the performance of a hybrid anaerobic reactor in continuous mode in the removal of organic matter and biogas production by using the bio-oil generated by the hydrothermal carbonization of orange waste as a substrate. The findings of this study hold practical implications for enhancing waste-to-energy strategies, addressing the challenges posed by limonene-rich waste streams in the citrus industry, and contributing to the overall sustainability of waste management practices, particularly in regions like Mexico.

Materials and Methods

Collection of Citrus Waste

Citrus waste, comprising orange peels and whole oranges, was sourced from the "Emiliano Zapata" market in Orizaba, Veracruz, Mexico, specializing in the retail sale of fruits and vegetables. Periodic collection was carried out in proportion to the experimental requirements. The collected citrus residues underwent manual selection to eliminate inorganic matter or non-orange elements. Subsequently, the waste was weighed, and its size was reduced to approximately 2 mm using an Oster® brand food processor (model BLSTKAG-RPB).

Characterization of Citrus Waste

The conditioned citrus residues were characterized using analytical determinations presented in Table 1:

Table 1. Analytical determinations

Parameter	Nomenclature	Units	Method
Total Solids	TS	%	Gravimetric 2540 B SM
Volatile Solids	VS	% TS	Gravimetric 2540 E SM
Potential of hydrogen	pH	-	13-SCFI-2006 solid waste, determination of pH
Ash	-	%	NMX-F-607-NORMEX-2020

Hydrothermal Carbonization of Orange Waste

The hydrothermal carbonization (HTC) process was conducted using a high-pressure stainless-steel reactor (Toption Instruments), model CF-1, with a 1L volume and temperature control (Figure 1).

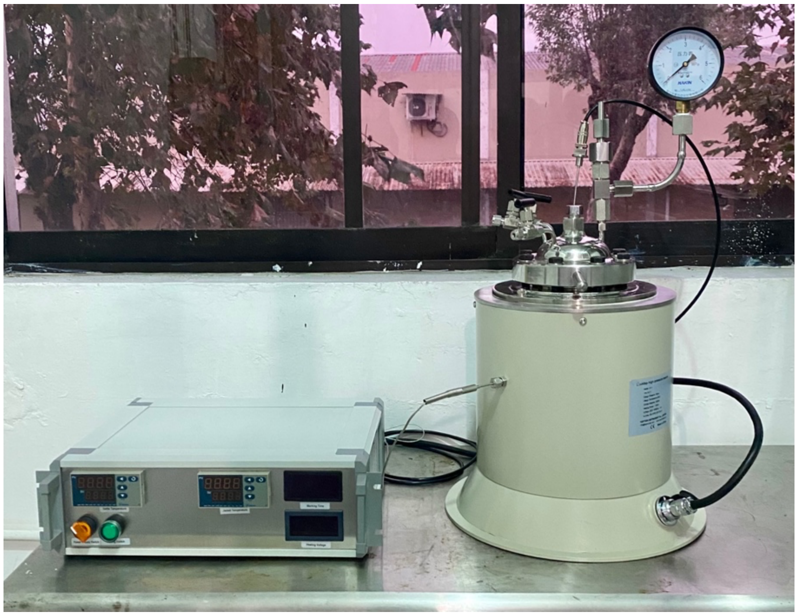

Figure 1. Hydrothermal carbonization equipment

Carbonization was conducted at 180 °C for varying durations (1, 2, and 3 hours per batch) with a consistent mixture of 350 g of citrus residue and 350 g of water. Additionally, experiments were carried out to explore the impact of different waste-to-water ratios (1:1, 1:2, and 1:3) under the conditions of 180 °C and 1 hour, aiming to assess the influence of solids content on the generated products.

Following the carbonization processes, solid-liquid separation was achieved through filtration using a nylon filter bag with an 80-mesh size (150 µm pore). This step ensured the effective isolation of the resulting products for subsequent characterization and analysis.

Physicochemical Characterization of Bio-Oil

The resulting bio-oil underwent physicochemical characterization, including TS, VS, pH (using the techniques in Table 1), and COD (method 5220 D Standard Methods). The hydrochar obtained was dried.

Start-up and Stabilization of the Anaerobic Hybrid Reactor (AHR)

An Anaerobic Hybrid Reactor (AHR) was employed, which consisted of two sections: an upper fixed bed (FB) and a lower inverse fluidized bed (IFB) (Figure 2). The fixed bed was constructed from an acrylic tube, 23 cm in length, with a nominal diameter of 7.62 cm, and it was filled with 330 polymeric rings measuring, on average, 2.76 cm in length, serving as support material. Simultaneously, the inverse fluidized bed comprised an acrylic tube, 80 cm in length, with a nominal diameter of 8.89 cm. Silica sand named Extendosphere™, with a diameter of 170 µm, a specific surface area of 20,000 m^2/m^3, and a density of 0.69 kg/m^3, was utilized as the support medium.

Stage 1: Batch Operation

To initiate the AHR, a liquid fraction of tomato waste (10 gDQO/L) was used for 93 days, maintaining pH between 6.8 and 7.2 at 35 °C. Biogas production at Hydraulic Residence Time (HRT) of 72 hours were monitored.

Stage 2: Continuous Feeding with Tomato Waste

Continuous feeding with the liquid fraction of tomato waste (OLR 5 g COD/L*d, HRT 1 day) lasted for 43 days.

Stage 3: Continuous Feeding with Citrus Waste-Derived Bio-Oil

The substrate was switched to bio-oil from the hydrothermal carbonization of citrus waste, diluted with water to achieve a daily OLR of 5 g COD/L.d.
Throughout batch and continuous feeding, 3M NaOH solution was added at the inlet and outlet to regulate the substrate's pH close to neutrality.

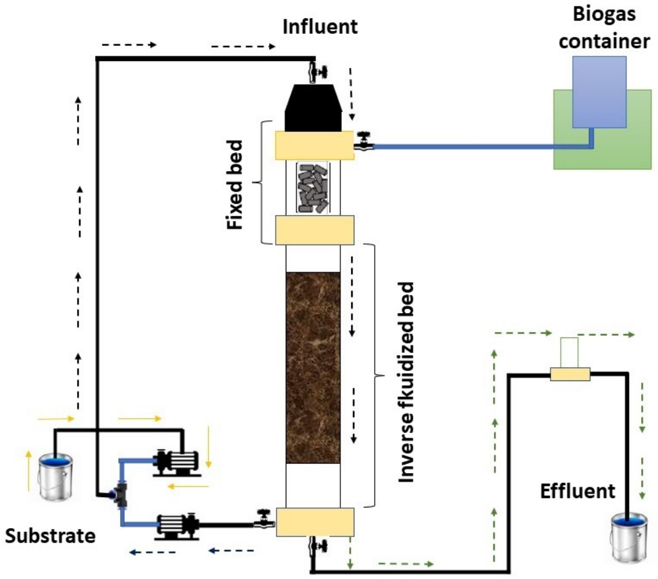

Figure 2. Anaerobic hybrid reactor

Results and Discussion

Composition of Substrates and Inoculum for Anaerobic Digestion:

In the initial start-up and stabilization stage of the hybrid anaerobic reactor, the liquid fraction of tomatoes served as the substrate, given its abundance in fruit and vegetable waste. The inoculum, characterized at start-up, exhibited an average attached volatile matter (AVM) concentration of 15.56 g VS/L support. Table 2 outlines the key characteristics of the substrates under consideration. A pivotal factor influencing the viability of hydrothermal carbonization is the moisture content of the residue, with a recommended minimum threshold of approximately 40% (Aragón-Briceño et al., 2020). In this study, the citrus residue exhibited an average moisture content of 79.46%, falling within the reported ranges for orange peel by Sharma et al. (2017), which were 75.3 ± 10.2%, and for pulp, 85.7 ± 0.0%.

Table 2. Physicochemical properties of substrates used in anaerobic digestion

Parameter	**Tomato liquid fraction**	**Orange Waste (after juice extraction)**	**Orange Waste (whole fruit)**	**HTC bio-oil**		
				1 h	**2 h**	**3 h**
pH	4.56	4.06	3.48	3.6	3.52	3.59
TS (%)	3.19 ± 0.24	20.54 ± 1.25	13.22 ± 0.39	2.55 ± 0.19	2.45 ±0.05	2.36 ±0.14
VS (% TS)	81.23 ± 6.91	95.13 ± 0.32	96.73 ± 1.27	78.23 ± 4.6	79.36 ±0.50	81.86 ±0.32
Moisture (%)	96.79 ± 0.22	79.46 ± 1.25	86.78 ± 0.39	-	-	-
CODt (g/L)	51.96 ± 9.06	-	-	59.15 ± 9.74	54.22 ± 3.66	60.60 ± 3.99
CODs (g/L)	44.46 ± 8.52	-	-	53.28 ± 9.75	47.01 ± 5.36	55.88 ± 5.00

The inverse fluidized bed section, segmented into upper, middle, and lower zones, revealed distinct AVM concentrations and colonization percentages, offering valuable insights into biomass distribution within the reactor (Buffière et al., 2000).

The percentage of colonization varied across zones: 29.31% in the upper zone, 25.31% in the middle zone, and 30.95% in the lower zone. Correspondingly, biomass concentrations were 15.15, 13.96, and 17.56 g VS/L in the upper, middle, and lower zones, respectively.

Hydrothermal Carbonization Experiments:

Experiments with whole citrus residues under different dilutions (1:1, 1:2, and 1:3) produced varying bio-oil yields. For the 1:1, 1:2, and 1:3 CW:Water ratios, average bio-oil volumes were 138 mL, 502.5 mL, and 712.5 mL, impacting total solids with values of 2.19 ± 0.06, 1.63 ± 0.03, and 1.29 ± 0.03, respectively. Dilution effects on CODt and CODs revealed a 24% decrease in chemical oxygen demand for the 1:2 ratio and a 42% decrease for the 1:3 ratio compared to the 1:1 ratio (64.86 g COD/L for CODt and 57.12 g COD/L for CODs).

Hydrothermal carbonization of citrus residues at 180°C for 1, 2, and 3 hours demonstrated time-dependent shifts in phase distribution. With increasing reaction time, hydrochar formation was favored, leading to decreased bio-oil production and increased gas generation. Bio-oil volumes produced were 530.83 mL, 516.67 mL, and 499.0 mL on average for 1, 2, and 3 hours of carbonization, respectively. Figure 3 shows the percentages of each of the phases obtained.

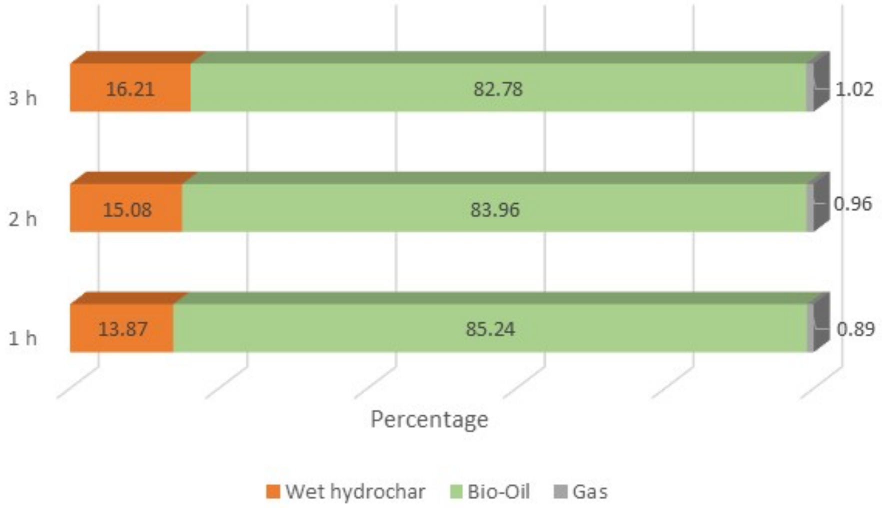

Figure 3. Distribution of the phases during the carbonization of orange waste

Upon completion of each carbonization run, liquid and solid phases were separated, and the bio-oil, characterized with COD values between 54 and 60 g COD/L, showcased dissolved organic matter.

Bio-oil Anaerobic Digestion:

In the anaerobic digestion experiment, conducted in three stages, the hybrid reactor initially stabilized with the tomato liquid fraction (Stage 1) achieved COD removals exceeding 95% after day 43. Continuous feeding in Stage 2, utilizing the liquid fraction of tomatoes, showed an initial COD removal drop to 52%, but stability was regained within 22 days, reaching removal values close to 90%.

In Stage 3, a substrate change introduced bio-oil from citrus waste carbonization. Although a drastic decrease in COD removal occurred initially, recovery took place, with removal increasing to a maximum of 80% in the last days of operation (Figure 4). These results align with previous studies using similar reactor configurations with citrus waste specifically orange press liquor (Rosas-Mendoza et al., 2018).

The promising results obtained with the bio-oil product of hydrothermal carbonization underscore its potential as a substrate for anaerobic digestion, addressing challenges associated with efficient bio-oil treatment (Ipiales et al., 2021). Future research should explore higher organic loads and assess scalability and stability under more substantial loads drawing on insights from studies on various substrates (Juárez-García et al., 2022; Alvarado-Lassman et al., 2008).

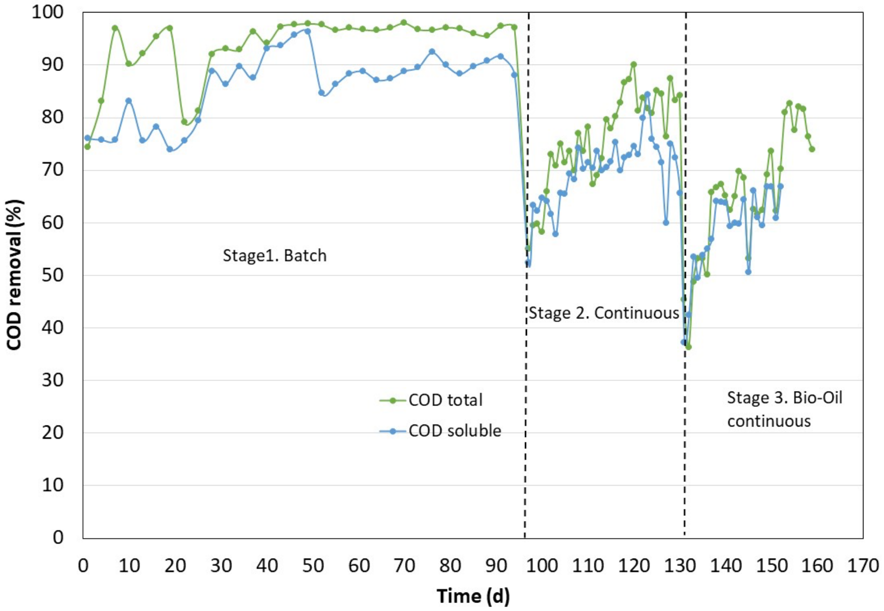

Figure 4. COD removal in anaerobic hybrid reactor

Conclusions

The integration of hydrothermal carbonization (HTC) with anaerobic digestion (AD) presents a promising strategy for the efficient management and valorization of organic waste, addressing environmental sustainability and resource utilization challenges. This study, conducted using citrus waste as a model substrate, highlights the potential of HTC-derived bio-oil as a substrate for anaerobic digestion in a hybrid reactor configuration.

The hydrothermal carbonization of citrus waste, characterized by varying reaction times and dilutions, demonstrated the production of bio-oil with distinct physicochemical properties. The time-dependent shifts in phase distribution during carbonization revealed an increasing favorability towards hydrochar formation with extended reaction times. The resulting bio-oil, characterized by high COD values, holds promise for subsequent anaerobic digestion processes.
The findings of this study contribute to the growing body of knowledge on the potential of HTC-AD technologies, particularly in the context of citrus waste. The successful adaptation of the hybrid anaerobic reactor to different substrates, including bio-oil derived from HTC, underscores its versatility and potential for addressing challenges associated with waste streams rich in limonene.

In conclusion, the study presents a step forward in the exploration of innovative solutions for waste management, emphasizing the role of HTC-AD technologies in sustainable and efficient organic waste treatment. Further research and scaling efforts in this direction are crucial for realizing the full potential of these integrated systems in addressing the complex challenges posed by diverse organic waste streams.

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