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Organic waste biorefinery: implementation of combined treatments to enhance anaerobic digestion

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Abstract

Growing energy demand, greenhouse gas emissions, and dwindling fossil fuel reserves make it urgent to find sustainable solutions, such as using organic waste for renewable energy production. Traditionally considered a challenge, waste like sewage sludge, livestock manure, and agri-food residues is now emerging as a valuable resource for energy valorization and nutrient recovery.

This study examines the possible transformation of anaerobic digestion (AD) plants into biorefineries, optimizing the process through the co-digestion of the organic fraction of municipal solid waste (OFMSW) with four additives derived from sewage sludge innovative treatments such as pyrolysis and hydrothermal carbonization. Co-digestion of OFMSW with dewatered sludge, biochar, hydrochar, and HTC liquid was tested to evaluate the biomethane potential (BMP) in different industrial plant scenarios.

Results show that HTC liquid yielded the highest increase in methane production, followed by biochar and hydrochar which still demonstrated a synergistic effect with OFMSW. The study proposes innovative solutions to integrate multiple technologies into a centralized organic waste treatment hub, reinforcing the role of biorefineries in the transition toward a circular economy.

Photos of the full-scale AMIU Puglia combined plant (top right) and laboratory equipment for biomethanation tests

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Annamaria Giuliano

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13

D.R.S.A.T.E.

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Coordinator: Prof. Vito Iacobellis

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Organic waste biorefinery: implementation of combined treatments to enhance anaerobic digestion

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Bioraffineria di rifiuti organici: implementazione di trattamenti combinati per migliorare la digestione anaerobica

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“Education is the most powerful weapon
we can use to change the World”

Nelson Mandela, 1990

EXTENDED ABSTRACT *(Eng)*

The growing energy demand, rising greenhouse gas emissions, and dwindling fossil fuel reserves call for solutions to mitigate climate change using renewable energy sources. In this scenario, bio-waste is emerging as an alternative renewable source that is fundamental to meet the population's current and future energy needs.

Organic waste, such as sewage sludge, livestock manure, residues from the agri-food industry, and the organic fraction of municipal solid waste (OFMSW), has historically been regarded as a challenging waste stream, but now the perception is changing as these materials present significant opportunities for resource recovery. By leveraging advanced treatment technologies, organic waste can be utilized to generate renewable energy, and produce by-products that replenish essential nutrients in soils also resulting in minimize landfilling.

Transforming traditional waste treatment facilities based on anaerobic digestion (AD) into biorefineries represents a crucial opportunity in the framework of a circular economy.

This study highlights the potential of using combined technologies to optimize AD process and underlines how useful the joint processes of multiple organic matrices can be to increase material valorization.

For the scope, two different pre-treated OFMSW suspensions collected from two anaerobic digestion plants, wet and semi-dry, were tested through biomethanation tests

in combination with several additives. Co-digestions of OFMSW were tested with 4 organic waste from sewage sludge treatments, such as:

- Dewatered sludge coming out of the sewage treatment plant;
- Biochar from sludge pyrolysis;
- Hydrochar and liquid HTC from the hydrothermal carbonization of sludge.

Specifically, dewatered sludge and HTC liquid as they are characterized by high water content, were tested in a ratio of 1.0:2.3 to OFMSW; while biochar and hydrochar being carbonaceous solids were treated as solid additives by loading them in a concentration of 13 g/L to the amount of OFMSW.

Anaerobic digestion batch tests were conducted to evaluate co-digestion with four additives for both OFMSW from the wet plant (Scenario A) and the semi-dry plant (Scenario B). Mono-digestion of each OFMSW represents the baseline and was compared with its four co-digestion scenarios to assess variations in process efficiency based on methane production volume.

These tests were aimed at determining the BMP (Biochemical Methane Potential) of new substrates mixtures to evaluate the effectiveness of different industrial plant scenarios that, from the perspective of biorefinery, put multiple integrated technological solutions in series to improve process efficiency and achieve higher methane yields as well as digestate-derived products suitable for agricultural and industrial applications.

The results revealed that the additive yielding the highest increase in methane production during co-digestion with OFMSW is the HTC liquid. Meanwhile, hydrochar and biochar, both added at a concentration of 13 g/L_{OFMSW}, demonstrated a comparable synergistic effect, resulting in higher methane production during co-digestion than through the mono-digestion of each material.

In contrast, for dewatered sludge, the co-digestion ratio of 1.0:2.3 (additive:OFMSW) did not show a significant advantage in terms of methane production; it was below 10%, which is insufficient to confirm a synergistic effect from these materials.

For the investigated scenarios, some innovative layouts were proposed to enable the combined use of different substrates and different technologies arranged in series. The

aim is to create a centralized hub for organic waste treatment, where residues from one process can be repurposed to enhance the efficiency of another.

By addressing key challenges, such as the optimization of organic waste management and identifying scalable solutions, this work contributes to the advancement of innovative waste treatment strategies. The findings emphasize that biorefineries play a central role in converting organic waste into high-value outputs, aligning environmental and economic objectives.

Transforming waste treatment facilities into biorefineries capable of processing waste from multiple sectors is an opportunity that, within the framework of a circular economy, should not be missed.

keywords: biorefinery, BMP, methane, OFMSW, anaerobic digestion

EXTENDED ABSTRACT *(Ita)*

La crescente domanda di energia, l'aumento delle emissioni di gas serra e il progressivo esaurimento delle riserve di combustibili fossili richiedono soluzioni per mitigare il cambiamento climatico utilizzando fonti di energia rinnovabili. In questo contesto, i rifiuti organici stanno emergendo come una fonte rinnovabile alternativa, fondamentale per soddisfare il fabbisogno energetico attuale e futuro della popolazione.
I rifiuti organici come i fanghi di depurazione, gli effluenti di allevamento, i residui dell'industria agroalimentare e la frazione organica dei rifiuti solidi urbani (FORSU), sono stati storicamente considerati un flusso di rifiuti problematico. Tuttavia, questa percezione sta cambiando poiché tali materiali offrono opportunità significative per il recupero delle risorse. Sfruttando tecnologie di trattamento avanzate, i rifiuti organici possono essere utilizzati per generare energia rinnovabile e produrre sottoprodotti che reintegrano nutrienti essenziali nei suoli, riducendo al contempo lo smaltimento in discarica.

La trasformazione degli impianti tradizionali di trattamento dei rifiuti basati sulla digestione anaerobica in bioraffinerie, rappresenta un'opportunità cruciale nel quadro di un'economia circolare.

Questo studio evidenzia il grande potenziale dell'utilizzo di tecnologie combinate per ottimizzare il processo di digestione anaerobica e sottolinea l'utilità dei processi congiunti che coinvolgono più matrici organiche per incrementare la valorizzazione dei materiali.

A tal fine, sono state testate due sospensioni di FORSU pretrattate, destinate a due impianti di digestione anaerobica (uno wet e uno semi-dry), mediante delle prove di biometanazione in combinazione con diversi additivi. Le co-digestioni di queste FORSU sono state esaminate con quattro tipologie di rifiuti organici provenienti da trattamenti di fanghi di depurazione, quali:

- Fanghi disidratati provenienti da impianti di trattamento delle acque reflue urbane;
- Biochar derivato dalla pirolisi dei fanghi;
- Hydrochar e liquido HTC provenienti dalla carbonizzazione idrotermale dei fanghi.

In particolare, i fanghi disidratati e il liquido HTC, essendo caratterizzati da un elevato contenuto d'acqua, sono stati testati con un rapporto di 1.0:2.3 rispetto alla FORSU; invece biochar e hydrochar, essendo solidi carboniosi, sono stati trattati come additivi solidi, inserendoli in co-digestione con la FORSU in concentrazione di 13 g/L_{FORSU}.

Le prove di digestione anaerobica in batch sono state condotte per valutare la co-digestione con i quattro additivi sia per la FORSU proveniente dall'impianto wet (Scenario A) sia per quella proveniente dall'impianto semi-dry (Scenario B). La mono-digestione di ognuna delle due matrici rappresenta il punto di partenza e viene utilizzata come confronto per i rispettivi quattro scenari di co-digestione, in modo tale da determinare le variazioni di efficienza del processo in termini di volume di metano prodotto.

Questi test avevano l'obiettivo di determinare il potenziale biochimico di metanizzazione (BMP) di nuove miscele di substrati per valutare l'efficacia di diversi scenari impiantistici industriali che, in un'ottica di bioraffineria, combinano soluzioni tecnologiche integrate per migliorare l'efficienza del processo, ottenere rese di metano più elevate nonchè ricavare dal digestato dei prodotti, dall'alto valore aggiunto, adatti per applicazioni agricole e industriali.

I risultati hanno rivelato che l'additivo che ha determinato il maggior incremento della produzione di metano in co-digestione con la FORSU è stato il liquido HTC. L'hydrochar e il biochar, entrambi aggiunti in concentrazione di 13 g/L_{FORSU}, hanno dimostrato un

effetto sinergico tra loro comparabile, producendo una quantità di metano maggiore rispetto a quanto generato dalla mono-digestione delle singole matrici.

Al contrario, per i fanghi disidratati, il rapporto di co-digestione utilizzato di 1.0:2.3 (additivo:FORSU) non ha mostrato un vantaggio significativo in termini di produzione di metano, con una variazione inferiore al 10%, insufficiente per confermare un effetto sinergico di questi materiali.

Per gli scenari analizzati sono stati ipotizzati dei layout impiantistici innovativi che consentano l’uso combinato di substrati differenti e tecnologie complementari collegate tra loro. L’obiettivo è creare un hub centralizzato per il trattamento dei rifiuti organici, dove i residui di un processo possano essere riutilizzati per migliorare l’efficienza di un altro.

Affrontando sfide strategiche come l’ottimizzazione della gestione dei rifiuti organici e identificando soluzioni scalabili, questo lavoro contribuisce allo sviluppo di strategie innovative per il trattamento dei rifiuti. I risultati sottolineano il ruolo cruciale delle bioraffinerie nella trasformazione dei rifiuti organici in prodotti ad alto valore aggiunto, allineando obiettivi ambientali ed economici. Trasformare gli impianti di trattamento dei rifiuti in bioraffinerie capaci di trattare rifiuti provenienti da settori diversi rappresenta un’opportunità che, nel quadro di un’economia circolare, non bisogna lasciarsi sfuggire.

***keywords**:* bioraffineria, BMP, metano, FORSU, digestione anaerobica

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LIST OF ABBREVIATIONS

AD: Anaerobic Digestion
BC: Biochar
BMP: Biochemical Methane Potential
BOD$_5$: Biochemical Oxigen Demand
CHP: Combined Heat and Power
co-AD: Anaerobic co-digestion
COD: Chemical Oxigen Demand
dm: dry matter
DSS: Dewatered Sewage Sludge
EWC: European Waste Catalogue
FW: Food Waste
GHG: Greenhouse gas
HC: Hydrochar
HHV: Higher Heating Value
HRT: Hydraulic Retention Time
HTC: hydrothermal carbonization
HTC-L: liquid compound from hydrothermal carbonization
ISR: Inoculum to Substrate Ratio
LHV: Lower Heating Value
Mono-AD: anaerobic mono-digestion
MSW: Municipal Solid Waste
OFMSW: Organic Fraction of Municipal Solid Waste
OLR: Organic Loading Rate
om: organic matter
PE: Population Equivalent
SGP: Specific Gas Production
SS: Sewage Sludge
TA: Total Alkalinity
TOC: Total Organic Carbon
TS: Total Solids
VFAs: Volatile Fat Acids
WtE: Waste to Energy
WW-SS: Wastewater Sewage Sludge
WWTP: Wastewater Treatment Plant

INTRODUCTION

We live in a world of limited resources and, as is written in the Updated Bioeconomy Strategy of 2018 (EU, 2018), global challenges like climate change, land and ecosystem degradation, coupled with a growing population, force us to seek new ways of producing and consuming that respect the ecological boundaries of our planet.

Since 1972, with the report “The Limits of Growth”, it was realized that economic and population growth could not and will not be unlimited because of the finite amount of natural resources and because of the limitation of the planetary ecosystem, which cannot, in a natural way, absorb the waste products of human activity indefinitely. This is why human intervention, and specifically a worldwide collaboration, is needed so that the waste products can be reintroduced into productive cycles. This reconversion starts with changing the concept of waste from a “problem to be managed” to a “resource to be invested in.”

In 2019 the European Commission launched the European Green Deal and in 2021 the European Parliament adopted the European Climate Law, that makes mandatory the goal of reducing net greenhouse gas (GHG) emissions by at least 55 percent below 1990 levels by 2030, in order to achieve climate neutrality by 2050 (European Parliament, 2021). This challenge is intended to be faced by reducing the use of fossil fuels as the primary energy source and replacing them with renewable energies. For this reason, there is a growing interest in the development of innovative technologies for energy production from renewable sources.

In this context, among the main renewable energy sources such as wind, geothermal, solar and hydropower, biomass energy emerges; the advantages of biomass energy production are also enhanced by its ability to recover energy from organic waste. In fact, the need to recover material and energy from waste has become increasingly important (Blake et al., 2017; Cremiato et al., 2018) and the main organic waste streams are Food Waste (FW) and Sewage Sludge (SS) (Gadaleta et al., 2024) .

Among the municipal solid waste (MSW), focus is on the organic fraction (OFMSW) both because turns out it has an high potential for recovery and because it represents the highest percentage of separately collected waste considering also that about one-third of the food produced for human consumption is wasted (Schanes et al., 2018).

However, it is a complex and heterogeneous matrix characterized by a variable percentage of impurities that must be selected in order to optimize plant processes.

Several research groups are currently engaged in the development of innovative solutions to increase energy recovery (Lora Grando et al., 2017) and achieve a bio-based economy through the use of organic waste as resources for the supply of chemicals, nutrients and fuels (Wainaina et al., 2020).

The optimization of organic waste treatments is being studied to provide alternative energy sources to fossil fuels, to fight the problem of landfill saturation – which has always been used as the primary mode of disposal (Zaman, 2016) – and also to manage, in a more sustainable way, the large amount of organic waste generated, resulting from population growth and fast development of modern society (Lin et al., 2018).

For all these reasons, the management of the organic fraction of municipal solid waste emerges as one of the most important government-wide challenges and a hot topic of research worldwide (Wainaina et al., 2020).

The purpose of this research project is to optimize the anaerobic digestion (AD) of OFMSW, increasing its yield in terms of methane produced, and to test the co-digestion of this matrix with other organic additives, with the aim of recovering more and different types of waste that would otherwise end up in landfills, and to analyse the advantages and disadvantages of such joint processes.

To do that, two different suspensions of OFMSW – from two full-scale anaerobic digestion plants in southern Italy – were studied. Biometanation tests were carried out using OFMSW in combination with various additives: dewatered sewage sludge, biochar, hydrochar and HTC liquid obtained from sewage sludge innovative treatments to study the methane yields and determine aspects replicable on an industrial scale.

Based on experimental results, different layout schemes have been investigated in order to implement the concept of biorefinery, which involves the combined use of several innovative technologies for the valorisation of various type organic waste in a single treatment hub, exploit the most beneficial combinations for more effective and efficient bio-waste management.

1. ORGANIC WASTE

Organic waste is a macro-category of waste that includes all waste materials from biological sources that are generated either from domestic activities or from agricultural, forestry, food or industrial activities.

This kind of waste is maily composed of carbon, hydrogen, oxygen and nitrogen.

According to the European Waste Catalogue (EWC) (Directive 2000/532/EC as amended) which is a set of codes that allows waste to be classified according to its industry and/or origin, it's possible to define the macrocategories of waste among which organic waste can be found:

- 02 00 00: waste from agriculture, horticulture, aquaculture, forestry, hunting and fishing, food processing and preparation;
- 19 00 00: waste from waste management facilities, off-site waste water treatment plants, preparation of water intended for human consumption and water for industrial use;
- 20 00 00: municipal waste as household and similar, commercial, industrial and institutional waste, including separately collected fractions.

Among these, the categories of organic waste to which particular attention is paid in this work are: the Organic Fraction of Municipal Solid Waste (OFMSW) and the Sewage Sludge (SS) produced by Wastewater Treatment Plants (WWTPs).

Specifically, it is possible to identify into the 20th macro-category – related to municipal waste – the organic fraction of municipal solid waste (OFMSW) as that which includes the following EWC codes:

- 20 01 08: biodegradable waste generated by kitchens and canteens;
- 20 02 01: waste generated from garden and park maintenance;
- 20 03 02: waste from collection at markets.

On the other hand, sewage sludge is found within macro-category 19, with EWC code 19 08 05 as sludge produced by municipal wastewater treatment.

Organic waste due to its properties and degradation capacity can be treated with different technologies to recover valuable products such as nitrogen and phosphorus that can be re-used as fertilizers in agriculture, as well as treated to recover energy through the valorization of by-products such as biogas and bio-oils; for all these reasons it will be the main driver for tackling the challenges of this century.

1.1. Organic fraction of municipal solid waste (OFMSW)

In the past years, the increase in population and consumption level has led to a significant increase in waste generation.

In 2022 the amount of municipal waste generated per person in Europe amounted to 513 kg, 46 kg (and 9%) more than in 1995 (EUROSTAT).

The big variations across countries reflect differences in consumption patterns, economic wealth, and collection and management of municipal waste.

In fact, it is important to consider that over the years the attention to environmental issues and the sense of responsibility of citizens has also grown so, in terms of recycling, in 2022 the EU registered an average of 249 kg of waste recycled per person. In particular, in Italy in 2022, with municipal waste generation of 29.1 million tons, the percentage of separate collection stands at 65,2% (ISPRA, 2023).

European legislation over the years has set increasingly challenging recovery targets; in the 2018 with the circular economy directives regarding waste management, common EU targets were set such as:

- 65% of municipal waste to be recycled by 2035,
- 70% of packaging waste to be recycled by 2030,
- less then 10% of municipal waste to be sent to landfill by 2035.

In addition, a ban on landfilling of waste from separate collection is established, as well as a requirement for separate collection for textile waste and hazardous household waste by 2025.

In order to achieve circular economy goals, it is necessary to both increase the quality and efficiency of separate waste collection in order to intercept larger and more homogeneous waste streams and reduce the quantities sent to landfills. It is also necessary to have adequate industrial plants coverage ready to efficiently, sustainably and locally manage separate waste streams, ensuring the least possible impact on the environment.

In addressing these challenges, the organic waste stream plays a key role; in fact, this is the major fraction among the waste collected separately, with the 38% (Figure 1); so collecting and managing this stream in the right way is also the focus of this work in order to present the effectiveness of innovative treatment solutions.

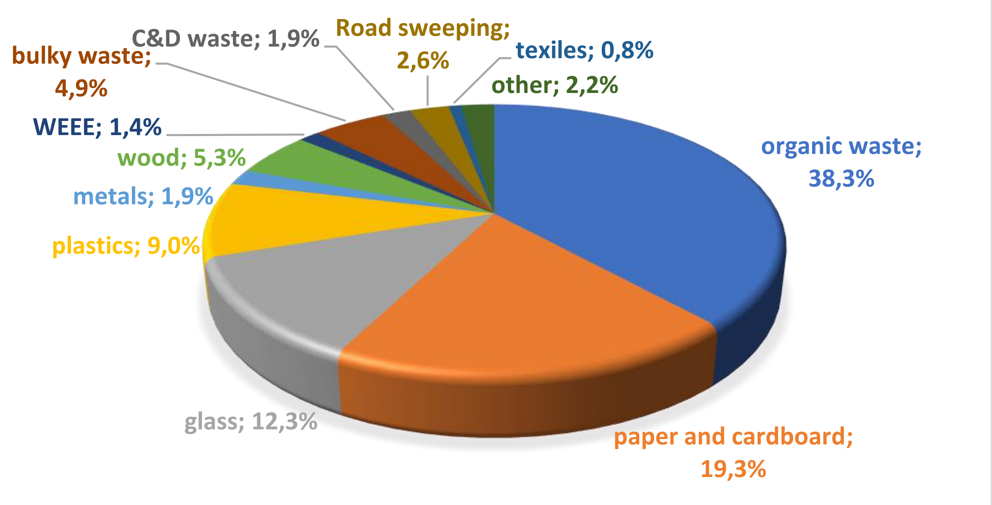


Figure 1 – Separate collection of the major merceological fraction of municipal solid waste, Italy 2022 (modified from: ISPRA, 2023)

Among the organic fraction of municipal solid waste, Food Waste (FW) is generally the highest one (almost 70%), followed by yardwaste (less than 30%) and then market waste (less than 1%).

In particular, in Italy in 2022 the OFMSW is composed of approximately (as in Figure 1):

- 70% organic waste from domestic and assimilated (with EWC 20 01 08);
- 26% garden and park maintenance waste (with EWC 20 02 01);
- 1% markets waste (with EWC 20 03 02);
- 4% waste sent for home composting (which do not have an EWC because they do not become waste).

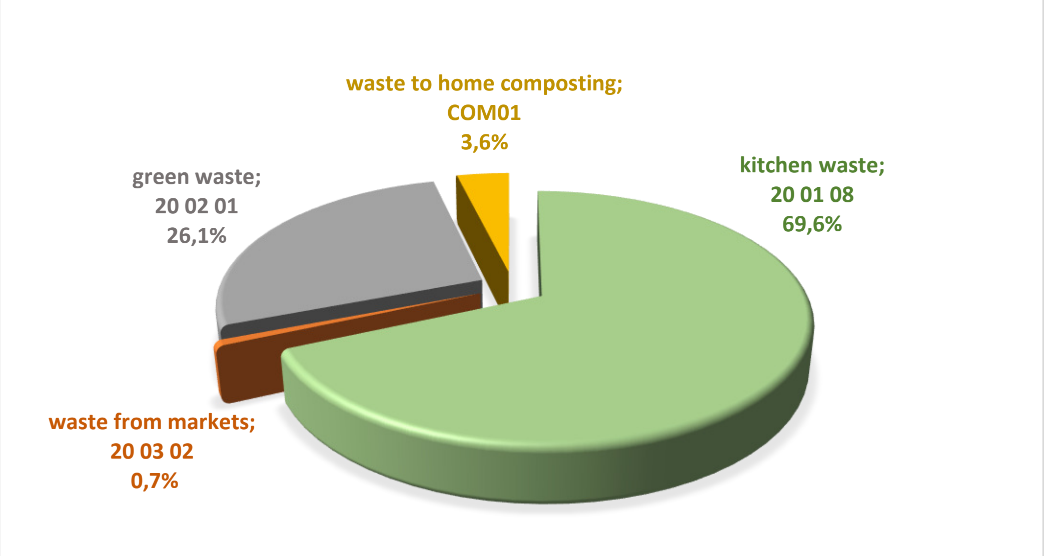


Figure 2 – Composition of OFMSW from separate collection, Italy 2022 (modified from: ISPRA, 2023)

It is important to consider that about 1.3 billion tonnes of FW are annually produced in the world (Gadaleta et al., 2024), but population growth and diet shifts are projected to stimulate a substantial increase in global food demand of 60% to 110% between 2005 and 2050 (Zan et al., 2022).

Food waste (FW) is the material intended for human consumption that are subsequently discharged, lost, degraded, or contaminated (Girotto et al., 2015).

It has an extremely variable composition because it varies seasonally and geographically depending on the consumption habits and collection system of that waste. Consequently, the variability is also into the physical-chemical nature of this kind of waste so it's possible to identify average values related to the percentage composition of sub- fractions (Table 1) and average values of physical-chemical parameters (Table 2).

Table 1 – Average values of FW composition according to the following sub-fractions (modified from: Gadaleta et al., 2024)

FW sub-fraction	Unit	Average value
fruit & vegeTables	%	51
bakery	%	15
meat & fish	%	7
dairy	%	7
dry food	%	7
ready meals	%	11
others	%	3

Table 2 – Average values of the physical-chemical composition of FW according to the following parameters (modified from: Gadaleta et al., 2024)

Parameter	Unit	Average value
Water content	%	70
Volatile solids	%dm	89-90
pH	-	5-6
N tot	%	2-4
C tot	%	45-55
C/N	-	15-30

This matrix, thanks to its nature, composition and human production, has great potential for energy and material recovery, for this reason is the topic of this research project.

1.2. Sewage sludge (SS)

Sewage sludge (SS) is a special waste identified with the EWC 19 08 05; it is the final solid residue produced by municipal wastewater treatment plants which treat, in addition to household effluent, also street runoff and non-hazardous discharges from industrial facilities within urban areas. Although technologies exist to minimize its production, sludge remains an unavoidable product of the depuration process and its amount is directly related to the level of refinement achieved. In fact, increased sludge production represents a virtuous element for depuration, since it is directly related to the pollutant load reduced.

Wastewater is subjected to primary physical treatment: with primary sedimentation, settled suspended solids are accumulated by gravity at the bottom of the tank and are removed, identifying that sludge as primary sludge.

For wastewater there is then a secondary treatment that is biological, in which microorganisms degrade the biodegradable dissolved matter by breaking down the concentrations of carbon, nitrogen and phosphorus, leading to the generation of a secondary sludge.

These two types of sludge are sent to an additional treatment known as sludge line which aims to stabilize the biodegradable substance and reduce the weight and volume of sludge to be handled; that makes the sewage sludge leaving the wastewater treatment plants sTable and palaTable.

The matrix coming out from these processes has an high content of organic compounds with macro and micronutrients, especially nitrogen and phosphorus, that makes SS an excellent fertilizer and a cheap and rich soil enhancer (Gadaleta et al., 2024), but is also to be considered that SS can contain high level of heavy metals as well as other undesirable and dangerous substances such ashormones, antibiotics, and pharmaceuticals (Agrafioti et al., 2013) which pose a huge risk for the ecosystem. It is crucial to manage this type of waste because this matrix has an impact not only on the water resources sector from which it comes, but also on the waste management that has to handle it to ensure the best treatment and the minimum impact on the environment as well as on the agricultural sector as a frequent final destiny in sludge recovery options.The first EU legislation that regulates the use of SS in agriculture was the Sewage Sludge Directive (86/278/EEC). It focuses on minimizing risks to human health and environment by controlling the levels of heavy metals (like cadmium, lead, and mercury) in the sludge and by imposing limits on its application in agricultural land (Table 3).

Table 3 – Maximum concentration of heavy-metals allowed in soils and in sludge (Directive 86/278/EEC – Annexes I A and I B)

Parameter	Unit	Limit value in soil (Annex I A)	Limit value in sludge used in agriculture (Annex I B)
Cadmium	mg/kg	1÷3	20÷40
Copper	mg/kg	50÷140	1,000÷1,750
Nickel	mg/kg	30÷75	300÷400
Lead	mg/kg	50÷300	750÷1,200
Zinc	mg/kg	150÷300	2,500÷4,000
Mercury	mg/kg	1÷1,5	16÷25

In addition, a range of organic chemicals may be present in sludge, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins (PCDDs), furans (PCDFs), and perfluorinated substances (PFASs) (Eljarrat et al., 1999).

The directive sets out specific rules on:

- Maximum permissible concentrations of heavy metals in sludge;
- Requirements for the safe use and disposal of sewage sludge;
- Monitoring and reporting requirements.

To this day, Directive 86/278/EEC appears to be out of step with the latest technical and scientific knowledge since it does not consider alternative sludge treatment and management techniques to agronomic use – including the recovery of matter and energy – which have since been successfully adopted in many other countries.

In 1999, the European Commission produced the "Working Paper on Sludge 3rd Draft of April 27, 2000" which imposed much stricter limits on metal concentrations in sludge intended for land spreading and introduced new parameters for trace organic pollutants.

In 2010, the "Working document sludge and biowaste" is published aimed at supporting the discussion on the revision of Directive 86/278/EEC in the light of the new European guidelines on organic waste and sludge and in particular the Directive 2008/98/EC on waste management.

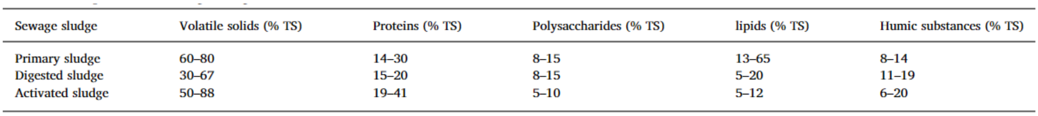
Additionally, the European Commission's 2020 Wastewater Treatment Directive includes updated provisions that affect sewage sludge treatment, especially regarding limits for pollutants and contaminants like heavy metals and persistent organic pollutants.

Great attention is placed on this waste because the large quantities and variable composition require that their treatment must be optimized to ensure adequate levels of environmental and human health protection. In fact, SS mainly consists of organic matter and nutrients, but its content is highly variable,since it depends on the SS treatment process and the seasonality (Romanos et al., 2019).

Is estimated that at least 50 million tons of sewage sludge with moisture content of 80% will be produced within the European Union annually (Kelessidis and Stasinakis, 2012).

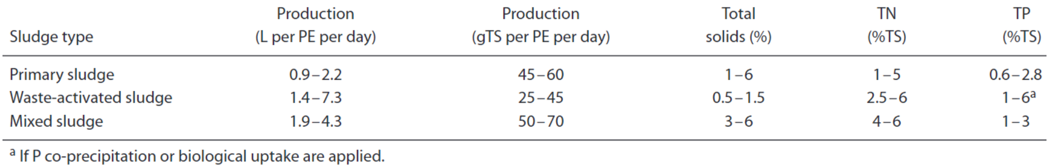
Regarding the composition of this waste, the chemical composition of sewage sludge is shown in Table 4 and Table 5 and the average characterization, distinguishing both by primary and secondary sludge and by raw and digested material, is shown in Table 6.

Table 4 – Chemical composition of SS (Wang et al., 2019)



Sewage sludge	Volatile solids (% TS)	Proteins (% TS)	Polysaccharides (% TS)	lipids (% TS)	Humic substances (% TS)
Primary sludge	60–80	14–30	8–15	13–65	8–14
Digested sludge	30–67	15–20	8–15	5–20	11–19
Activated sludge	50–88	19–41	5–10	5–12	6–20

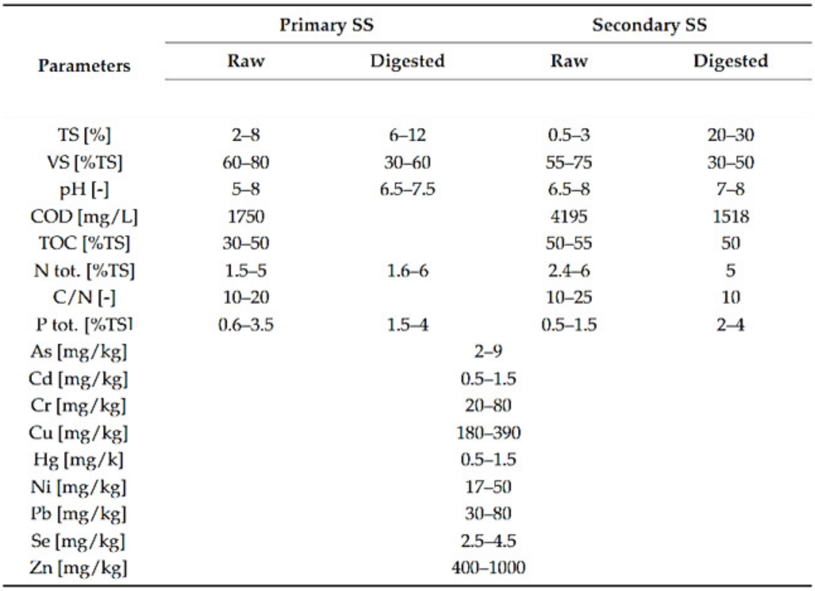
Table 5 – Characteristics and production of primary, biological and mixed sludge (modified from: Battista et al., 2019)



Sludge type	Production (L per PE per day)	Production (gTS per PE per day)	Total solids (%)	TN (%TS)	TP (%TS)
Primary sludge	0.9–2.2	45–60	1–6	1–5	0.6–2.8
Waste-activated sludge	1.4–7.3	25–45	0.5–1.5	2.5–6	1–6[a]
Mixed sludge	1.9–4.3	50–70	3–6	4–6	1–3

[a] If P co-precipitation or biological uptake are applied.

Table 6 – Average characterization of sewage sludge (modified from: Gadaleta et al., 2024)



Parameters	Primary SS		Secondary SS	
	Raw	Digested	Raw	Digested
TS [%]	2–8	6–12	0.5–3	20–30
VS [%TS]	60–80	30–60	55–75	30–50
pH [-]	5–8	6.5–7.5	6.5–8	7–8
COD [mg/L]	1750		4195	1518
TOC [%TS]	30–50		50–55	50
N tot. [%TS]	1.5–5	1.6–6	2.4–6	5
C/N [-]	10–20		10–25	10
P tot. [%TS]	0.6–3.5	1.5–4	0.5–1.5	2–4
As [mg/kg]	2–9			
Cd [mg/kg]	0.5–1.5			
Cr [mg/kg]	20–80			
Cu [mg/kg]	180–390			
Hg [mg/k]	0.5–1.5			
Ni [mg/kg]	17–50			
Pb [mg/kg]	30–80			
Se [mg/kg]	2.5–4.5			
Zn [mg/kg]	400–1000			

2. TECHNOLOGIES TO PROCESS ORGANIC WASTE

There is a wide range of technologies available for the treatment of organic waste, and they involve the use of biological, thermal, and chemical processes, as well as their use in a strategic and synergistic approach to utilize the advantages of some treatments and reduce their negative aspects. Among the various technologies adopted, from waste-to-energy (WtE) to waste recovery, those that use biological processes are the best known as well as the most widely used as they are able to enhance the biodegradable substance present within the organic matrix to the fullest. As is known from the waste management hierarchy, the last accepTable alternative remains landfilling, a method still widely adopted mainly for sewage sludge management.

This solution must be avoided or at least reduced in order to ensure material or energy recovery from organic waste in a such a way as to achieve a circular economy, reduce pollution, and provide greater environmental protection.

2.1. Biological treatments

Biological treatment refers to all those waste treatment technologies that use the natural processes of organic matter degradation by microorganisms within a biomass. A key role in these processes are environmental conditions such as temperature, humidity and oxygen. The solutions that result in the highest yields for organic waste are those in which biological processes are used, as they are the most functional in recovering the organic content of such waste.

In particular, both aerobic and anaerobic biological processes can be put in place, lately, however, a combined aerobic/anaerobic treatment is preferred, from which follows the advantage of obtaining and thus being able to dispose of both a biological gas, the so-called biogas, destined for subsequent energy valorization, and a soil conditioner suitable for agricultural use, namely compost.

2.1.1. Composting

Composting is a widely used aerobic biological process in which, through control of moisture, temperature and oxygenation of the waste, putrescible organic matter is decomposed, returning a compost with high fertilizing properties.

The process mainly consists of two phases: the active phase and the curing phase. In the first phase (2-3 weeks), with the presence of oxygen, bacteria break down easily biodegradable organic matter, releasing energy that results in an increase in temperature up to 50÷60°C. Under these conditions, the waste is also sanitized, with pathogens removal. The second phase (2-3 months) allows for the completion of the degradative processes, with a gradual reduction in temperature and the formation of humidified mineral-organic complexes. Thus, this approach makes it possible to recover nutrients and produce compost, as a material for further use in agriculture or floriculture. (Palaniveloo et al., 2020).

This process necessitates the use of bulky materials like garden waste or wood because they help create structure and porosity in the mixture, ensuring proper aeration, while also absorbing some of the leachate generated during the decomposition process (Gadaleta et al., 2024). The disadvantages of this technology include the requirement for extended treatment times, the need for large spaces, high energy consumption, and the potential for odor emissions.

In Italy in 2022, 45.2% of waste entering composting plants are from OFMSW, 14% from SS, 32.3% from green waste and 8.5% others (ISPRA, 2023).

2.1.2. Anaerobic Digestion

Anaerobic digestion (AD) is a biological process involving the degradation of organic matter under anaerobic conditions, i.e., in the absence of oxygen, resulting in the conversion of organic waste into biogas and digestate. The biogas is rich in methane (60–70%), while the remaining part is mainly composed of CO_2 (around 30%) and other gases (N_2, H_2, H_2S and NH_3) in trace amounts (Pramanik et al., 2019). Biogas production is encouraged with the aim of reducing CO_2 emissions and optimizing resource recovery from waste (Llano et al., 2021); in fact the biogas is usually used in thermal and electic energy production (Gadaleta et al., 2024), so it’s possible to define the AD also as a WtE process.

However, the production of another waste is also determined from anaerobic digestion: digestate, a nutrient-rich residual that is still considered a waste by current regulations. The degradation of organic matter occurs within the AD by a trophic chain of consecutive reactions involving different interacting microbial groups: hydrolytic bacteria, acidifying bacteria and methanigenic bacteria. The biodegradative process (described in detail in Section 3.1.1) consists of the following steps:

- **hydrolysis** of complex organic substrates, in which organic matter is decomposed into simpler compounds;
- **acidogenesis**, whereby volatile fatty acids (VFAs), ketones and alcohols are formed;
- **acetogenesis**, whereby acetic acid, formic acid, carbon dioxide and molecular hydrogen are formed from volatile fatty acids.
- **methanogenesis**, in which from acetic acid or formic acid the formation of methane is determined.

The anaerobic digestion process can take place in different modes discriminated according to the solids content that characterizes the treated waste. Thus, it is possible to have *wet* AD when the total solids content is less than 10%; *semi-dry* AD when the total solids content is between 15÷20%; and *dry* AD with a solids content between 25-40%.

The technology has limitations related to its stability; it requires specific pretreatment and careful monitoring of process parameters to ensure high biogas production yields (Arango-Osorio et al., 2019). The process scheme of an AD plant is reported in Figure 3.

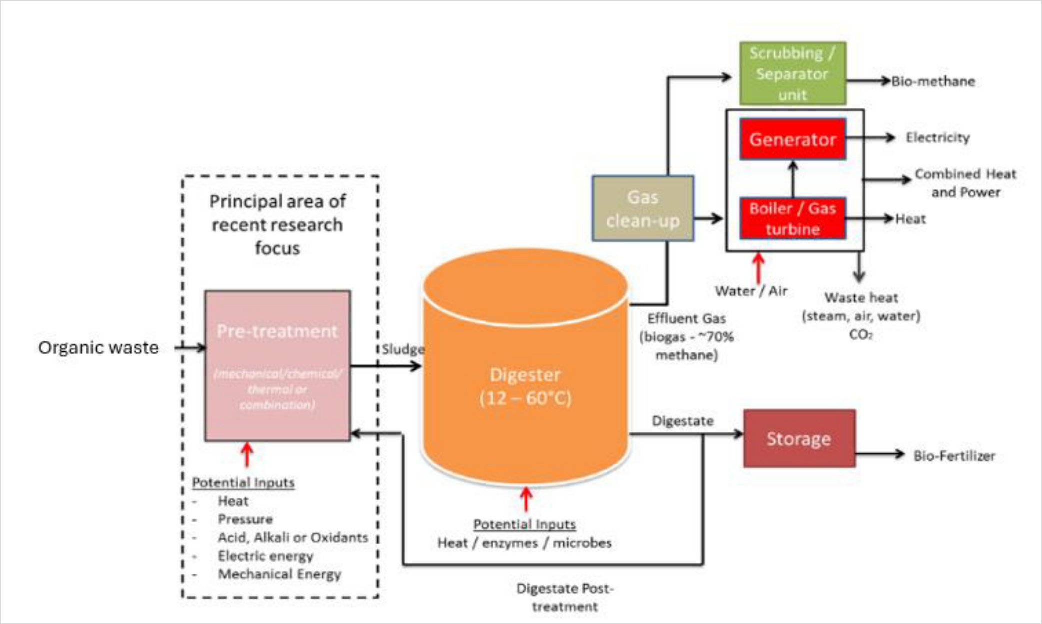


Figure 3 – General process scheme of AD plant (modified from: Oladejo et al., 2019)

In Italy, in 2022 the amount of organic waste treated with anaerobic digestion is about 880,000 tons of waste from 35% food waste, 1% green waste, 60% sludge, and 4% other (ISPRA, 2023).

2.1.3. Combined treatment of anaerobic digestion and composting

In recent years, in order to optimize the treatment of organic waste, innovative technology involving the combined processes of anaerobic digestion and composting (described in the preceding paragraphs) has emerged, leading to the gradual transformation of AD plants into combined ones. This phenomenon has occurred because the technologies of anaerobic digestion and composting are not in opposition to each other but, on the contrary, are highly integrable according to a process that involves, as a first step, the degradation under anaerobic conditions of the putrescible fraction, with the related production of biogas, and then the aerobic stabilization of the residual material, i.e., digestate, in order to obtain a product suitable for agricultural use

(APAT, 2005). In particular, Figure 4 shows the operation diagram of a combined treatment.

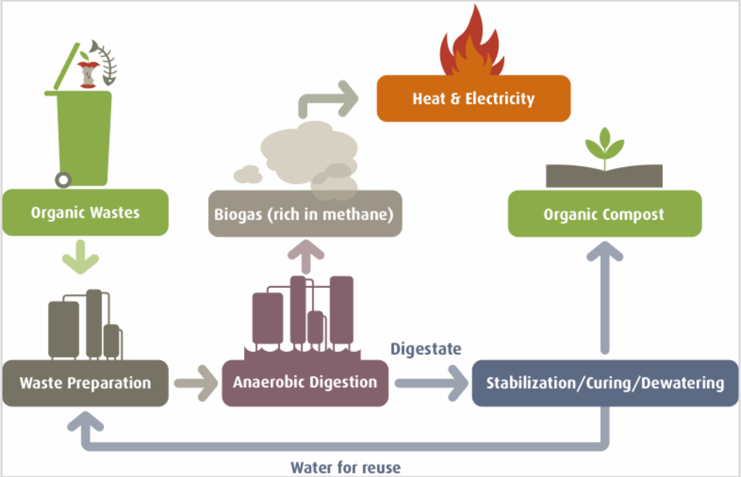


Figure 4 – Process scheme of a combined anaerobic-aerobic plant

The first stage of this integrated solution is mechanical-physical pretreatment to remove impurities from the incoming waste. It is important to consider that the pretreatment stage plays a key role in the whole process because it allows to:

- reduce the particle size of the waste;
- separate materials such as paper, plastic and glass as they are inert or unsuitable for biological treatment;
- prepare the waste for the AD process, with water dilution (including recirculation of process water) to achieve the appropriate total solids content for the particular AD process arranged.

The waste is subsequently sent to the anaerobic digester where particular microorganisms – in the absence of oxygen and under mesophilic conditions – start metabolic processes producing biogas.

The biogas, appropriately treated, can be used as fuel to feed a cogenerator with simultaneous production of electric and thermal energy. Digestate produced from the anaerobic phase is mixed with lingo-cellulosic material in certain proportions in order to start the composting phase. This one is subjected to the maturation and refining to obtain a quality compost that can be marketed in the agricultural sector.

Such a treatment provides a positive net energy balance associated with the methane energy recovery as well as the production of a soil conditioner (Cesaro et al., 2015). In fact, both matter and energy can be recovered from the organic fraction through compost production and biogas valorization. Other benefits from this technology are the reduction of the problems related to digestate odours emission and its potential phytotoxicity due to the presence of pathogens (Cesaro et al., 2015).

While the major problems encountered in using this technology are the high costs of operating and implementing the plant as well as the requirement for accurate monitoring of the processes present in a plant of such high technological complexity.

2.1.4. Dark fermentation

Dark Fermentation is a biological process that enables the production of molecular hydrogen H_2 through the fermentative activity of anaerobic bacteria (Siddiqui et al., 2011). From a circular economy perspective, this technology is considered highly innovative and is encouraged due to the potential for producing a renewable energy source, such as hydrogen (which has double the energy yield of methane), from a biological process that uses organic waste as raw materials.

Dark Fermentation is typically implemented in a two-stage anaerobic digestion system and occurs in an environment without both oxygen and light. It involves the degradation of complex polymers (such as carbohydrates, proteins, and fats) by specific microorganisms, resulting in the production of hydrogen and organic acids during the acidogenesis phase of AD process (Girotto et al., 2015).

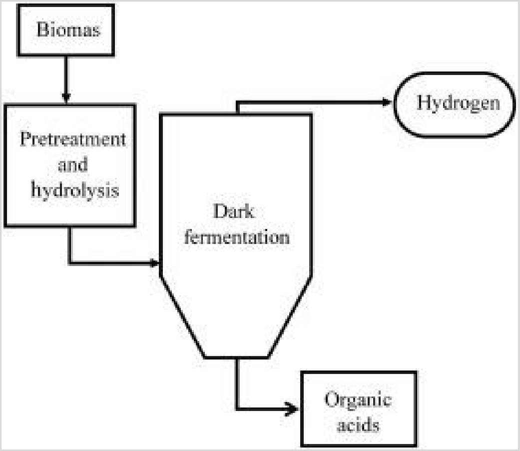


Figure 5 – Process scheme of Dark Fermentation (Kamran, 2021)

The entire process occurs at mesophilic temperatures ranging from 30 to 40°C. The first stage is typically maintained at an acidic pH of 5.5 to 6.5, with a short hydraulic retention time (HRT) of 2 to 3 days, promoting acid fermentation. In contrast, the second stage operates with a longer HRT of 20 to 30 days and a pH between 6 and 8, which supports the growth of slow-growing methanogenic archaea (Schievano et al., 2012).

A limitation of this technology is that the effluent obtained from Dark Fermentation remains highly putrescible, necessitating a subsequent stabilization treatment. Therefore, AD is required for the alkaline fermentation of volatile fatty acids (VFAs) into biogas (Cavinato et al., 2012).

2.2. Thermochemical treatments

Incineration, pyrolysis, and gasification are three thermochemical processes in which organic matter is degraded resulting in a reduction in both weight and volume of the waste. These technologies differ in terms of combustion environment and process temperatures. Hydrothermal carbonization, on the other hand, is an innovative technology that occurs in the presence of an aqueous phase and at a lower temperature compared to the aforementioned technologies.

2.2.1. Incineration

Incineration is a WtE technology that involves degrading organic matter at temperatures of 800–1000°C in the presence of oxygen, through an exothermic combustion process. This technology is widely established and commonly used for the disposal of municipal waste, as it not only reduces the amount of waste to be managed but also ensures significant energy recovery.

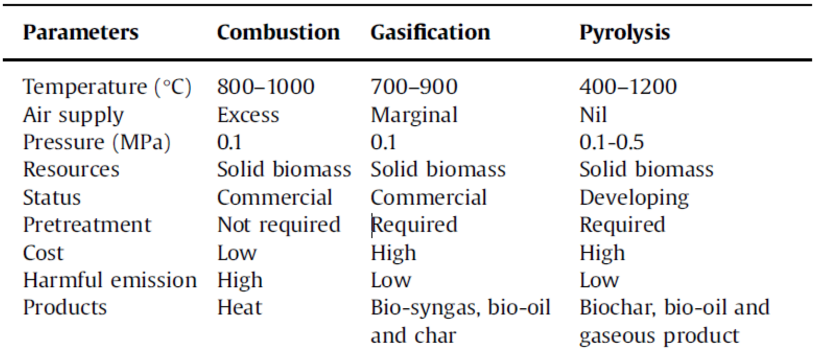
Due to its high moisture content, food waste has a low higher heating value (HHV) 27.92 MJ/kg_{dryFW} (Kim et al., 2013) and it is typically co-incinerated with other types of waste. While incineration can significantly reduce the volume of FW by 80-85% of the incoming waste (Xin-Gang et al., 2016), European countries do not recommend this technology because of the toxic air emissions it generates, such as dioxins and heavy metals (Yang et al., 2012).

In fact, among the limitations of this technology is the challenge of managing the residues of the process. In particular, combustion generates gases containing pollutants and heavy metals, which must be treated before being released into the atmosphere. On the solid side, the process leaves residues in form of ashes, which must be treated through specific disposal methods.

2.2.2. Gasification and pyrolysis

Gasification and pyrolysis are two innovative thermochemical technologies which differ from each other primarily by the temperature and environmental conditions under which they occur. While gasification takes place in limited oxygen conditions and temperature of 700-900°C, pyrolysis takes place in the absence of oxygen and with a temperature that can range from 400÷1200°C (Tripathi et al., 2016). In Table 7 is reported a comparison among these two technologies and incineration.

Table 7 – Comparison of thermochemical conversion techniques (Tripathi et al., 2016)



Parameters	**Combustion**	**Gasification**	**Pyrolysis**
Temperature (°C)	800–1000	700–900	400–1200
Air supply	Excess	Marginal	Nil
Pressure (MPa)	0.1	0.1	0.1-0.5
Resources	Solid biomass	Solid biomass	Solid biomass
Status	Commercial	Commercial	Developing
Pretreatment	Not required	Required	Required
Cost	Low	High	High
Harmful emission	High	Low	Low
Products	Heat	Bio-syngas, bio-oil and char	Biochar, bio-oil and gaseous product

The outputs of these processes are oil, char and gas for energy recovery; their relative proportions depend on the nature of the starting material and the operating conditions of the process. Specifically, lower temperatures tend to produce a higher fraction of liquid products, whereas higher temperatures primarily yield low-molecular-weight hydrocarbons, which are gaseous, as well as aromatic compounds.

The pyrolysis and gasification are considered more advanced technologies compared to incineration because they allow to recover energy from biomass and offer higher efficiency with less production of harmful gas emissions then incineration. Although the high moisture content of FW and the costs associated with these technologies are high, the advantages described allow pyrolysis and gasification to be increasingly considered as more sustainable alternatives for biomass treatment (Tripathi et al., 2016).

For treating sewage sludge, pyrolysis stands out as an optimal method as it offers benefits such as energy savings, material recovery, and the production of high-value materials (Samolada and Zabaniotou, 2014) as well as the possibility to immobilize carbon and heavy metals in the biochar matrix.

The main products of the pyrolysis process of a biomass are: biochar, bio-oil, and pyrolysis gas (Figure 6).

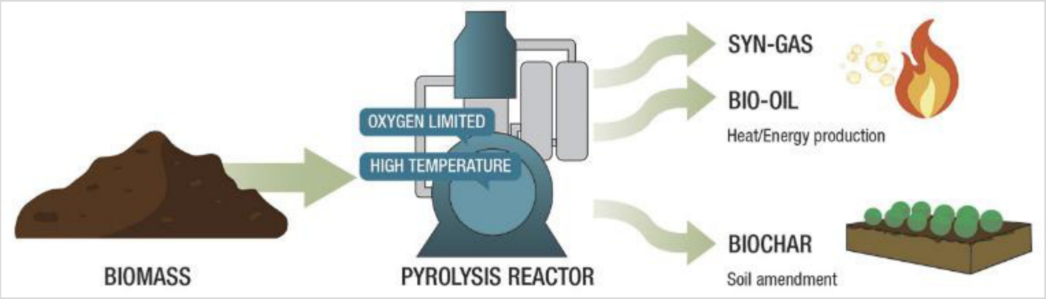


Figure 6 – Description of inflows and outflows from the pyrolysis process

Biochar is a solid, stabilized, sanitized, carbon-rich byproduct formed through the thermal stabilization of biomass (Mašek et al., 2013). On the other hand, bio-oil (a liquid) and pyrolysis gas (a gas) are energy-dense products that can be further utilized for energy generation. In particular, pyrolysis oil can be used as a fuel for heat or electricity generation, while biogas can either be burned as a fuel or converted into syngas for further use.

The relative proportions of these products depend on both the nature of the feedstock and the operating conditions of the pyrolysis process. Specifically, lower temperatures favor the production of a higher proportion of liquid products, while higher temperatures primarily generate low-molecular-weight hydrocarbons (which are gaseous) and aromatic compounds.

This technology is not yet widely adopted due to its complexity and the significant costs involved in investment, operation, and the treatment/disposal of residual byproducts. Furthermore, pyrolysis requires the sludge to have a low moisture content, which necessitates a drying step; this leads to further cost increases due to its high energy consumption (Oladejo et al., 2019).

2.2.3. Hydrothermal carbonization

Hydrothermal carbonization is an emerging technology which realize, with a wet process and subcritical conditions, a thermochemical conversion of the organic waste into a valuable, energy-rich resource trying to replicate the effects natural carbogenesis.

The process takes place at relatively low temperatures between 180÷230°C under the autogenously saturated pressures for several hours and in the presence of a liquid phase (process water). This process is suitable for waste with high moisture content (80÷90%), such as OFMSW or SS, and allows their conversion into high value-added products, such as clean biofuels and organic fertilizers (Wang et al., 2019). The moisture content is very important into hydrothermal process; in fact the carbonization is accelerated by water and it can be considered a good heat transfer and storage medium, which not only enhances the efficiency of heat transfer in preheating process but also avoids the local overheating due to the exothermal reactions during hydrothermal carbonization. The HTC process is governed by several chains of chemical reactions of hydrolysis, dehydration, decarboxylation, polymerization and coalification reported in Figure 7.

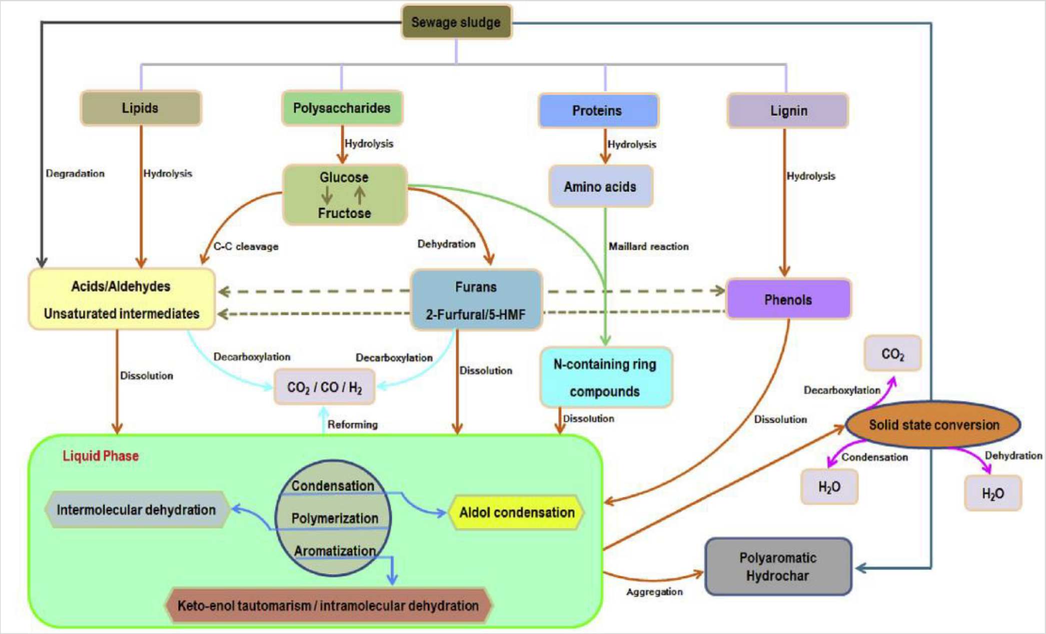


Figure 7 – Simplified reaction pathways for hydrothermal carbonization of SS (Wang et al., 2019)

This innovative treatment was first introduced by Bergius, the Nobel Prize winner in 1931 for invention and development of chemical high-pressure methods, with the aim of understanding the mechanism of natural coalification by hydrothermal transformation of cellulose into coal-like materials in laboratory as early as 1913 (Wang et al., 2019).

From the biomass, the reaction breaks water, carbon dioxide and other compounds generating hydrochar (a carbonaceous solid with lignite-like characteristics) and a nutrient-rich aqueous residue. The process is exothermic so once the required temperature is reached, it is self-sustaining from the energy released. HTC could be implemented in sewage treatment plants because it allows sterilization and reduction of sludge volume and compared to other WtE conversion methods using biological processes, HTC has various advantages including smaller treatment footprints, greater waste volume reductions, no process-related odors (Li et al., 2013) and significantly lowers transportation and management costs. The typical process diagram of an HTC plant is shown in Figure 8.

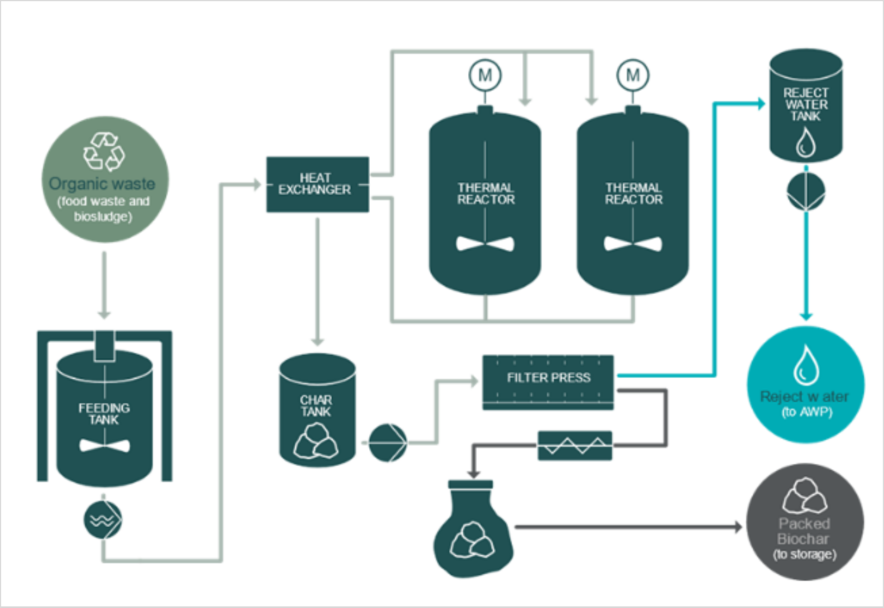


Figure 8 – Flow diagram of the HTC process

3. FROM ANAEROBIC DIGESTION PROCESS TO THE BIOREFINERY

The biorefinery is an innovative concept inspired by the traditional petrochemical refinery, but it operates on a fundamentally different principle. Rather than relying on chemical processes that utilize fossil fuels, a biorefinery focuses on the recovery of organic waste. It employs a hierarchical approach that prioritizes the extraction and production of high-value products, ultimately leading to the generation of bioenergy.

In particular, exploring treatment technologies for food waste and sewage sludge, has highlighted the potential of processing these urban waste streams in a single facility, creating what can be named as “urban biorefinery” (Figure 9).

This approach allows for the examination of the benefits not only of using multiple technologies in sequence but also of simultaneously treating different waste matrices and leveraging the products generated from each individual treatment.

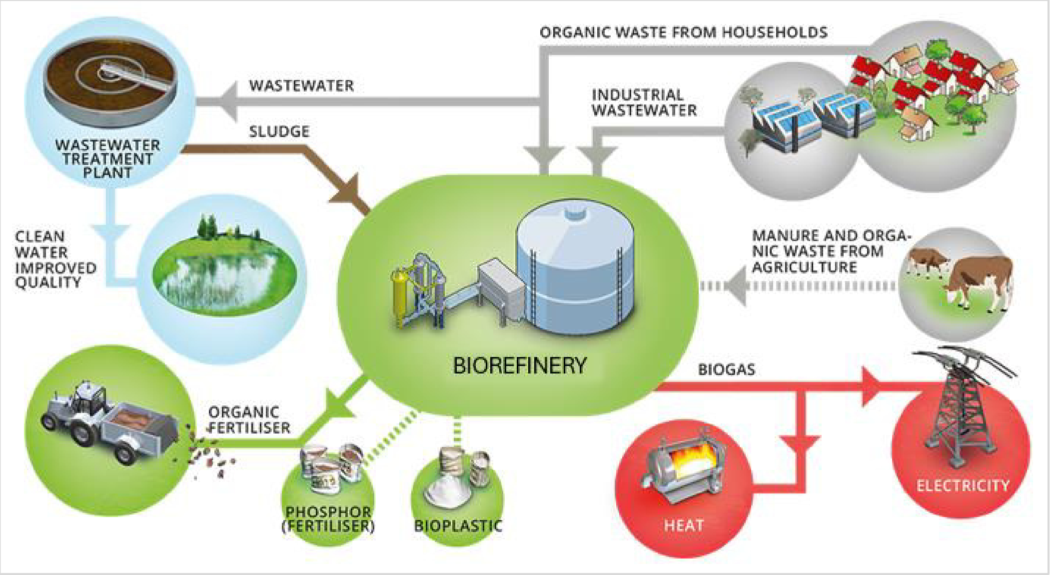


Figure 9 – Biorefinery flow chart

3.1. Focus on anaerobic digestion process

3.1.1. The AD process steps

Anaerobic digestion, as already introduced in section 2.1.2, is a biological process that occurs in an inert environment and it is one of the most economic ways to produce biogas from various biomass substrates (Demirel and Scherer, 2008). It means that is possible providing a clean fuel from renewable sources, replacing fossil fuel-derived energy and reducing environmental impacts.

The conversion of organic compounds into biogas occurs through natural metabolic processes carried out by microorganisms present within the biomass.

This process consists of 4 main steps in which biochemical reactions governed by enzyme kinetics and particular operating conditions occur (APAT, 2005); these are detailed below and shown in Figure 10. These phases can occur in separate sections of a plant or within the same reactor.

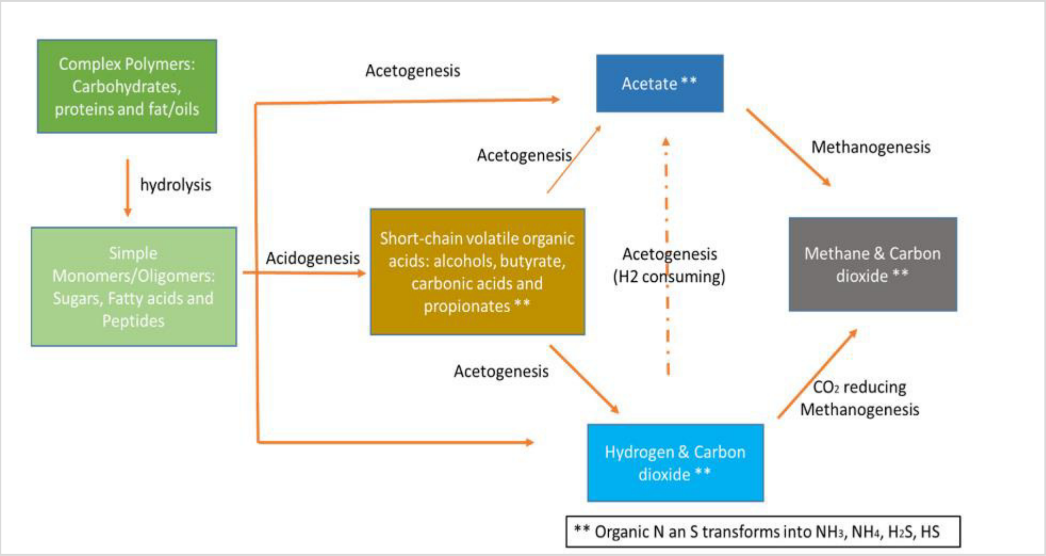


Figure 10 – Biological processes during anaerobic digestion (Oladejo et al., 2019)

Hydrolysis

The substrate consists of complex, particulate or soluble, organic substrates such as proteins, fats and carbohydrates that are hydrolyzed, broken down into smaller molecules by hydrolytic bacteria. This results in the production of simpler compounds such as aminoacids, fatty acids, and monosaccharides in soluble form that are available for transportation by acidogenic microorganisms. Hydrolysis is favored by the larger specific surface areas: therefore, this step can be preceded by pretreatments designed to reduce the substrate size, increase its specific surface area, and promote its breakdown. This phase is the slowest, so it also turns out to be the most limiting one.

Acidogenesis

In this phase, acidogenic bacteria lead to the fermentation of the previously formed soluble substances, going to oxidize simple organic substrates such as sugars and aminoacids resulting in the formation of short-chain volatile fatty acids (VFAs) including: acetic, butyric, formic, lactic, propionic, and valeric acids, as well as other products such as alcohols, carbon dioxide, and hydrogen.

Acetogenesis

This phase leads to the formation of acetic acid and can occur with two types of reactions, depending on the different types of bacteria operating:

- the **acetogenic bacteria**: convert VFAs or alcohols into acetic acid, carbon dioxide and molecular hydrogen;
- the **homoacetogenic bacteria**: from molecular hydrogen and carbon dioxide they produce acetic acid.

Methanogenesis

In the last step there is the production of methane, which, as the only non-reactive compound in the entire digestion process, is considered as the final product. It can be produced from two different reactions:

- by the **hydrogenotrophic pathway**, operated by hydrogenotrophic microorganisms that lead to the anaerobic oxidation of hydrogen with consequent formation of methane
  $4H_2+CO_2\rightarrow CH_4+2H_2O$
- through the **acetoclastic pathway**, operated by acetoclastic microorganisms that break down acetic acid with the formation of methane and carbon dioxide. More than 70 percent of the methane produced comes from this mechanism
  $CH_3COOH\rightarrow CH_4+CO_2$

The two strains of methanigenic bacteria described in these two pathways and operating at this stage allow: by degrading acetic and formic acid, to avoid the inhibition of the process that might occur under conditions of excess acidity, the conversion of fatty acids to acetate and H_2 while maintaining H_2 concentrations at low levels. It is also to be considered that methane turns out to have low affinity for the liquid phase so it quickly moves away into the headspace of the reactor where it will accumulate; carbon dioxide and the other minor gases formed, on the other hand, show greater affinity for the liquid phase and take longer to separate from it and accumulate in the headspace.

3.1.2. Management parameters of an AD reactor

Inside an anaerobic digester, the substrate introduced is considered and defined in terms of total solids (TS or “dm” stands for dry matter), volatile solids (VS or “om” stands for organic matter), chemical oxygen demand (COD), or five-day biochemical oxygen demand (BOD_5), but before introducing a biomass into a digester, it’s necessary to evaluate also its fibrous components (cellulose, hemicellulose, lignin), total nitrogen, organic carbon and its potential biogas production with the corresponding percentage of methane. Therefore, it is necessary to define the meaning of these parameters and the method by which they are determined.

- **Total solids (TS):** represent the dry matter content, obtained by drying a sample in the oven at 105°C for 24 hours. In this condition, water in the sample evaporates, so the TS represent the sum of the organic fraction and the inert fraction.

- **Volatile solids (VS):** represent the organic matter in the TS that volatilizes when the sample is subjected to combustion in a muffle furnace at 550°C. After this process, the residual material is the inert contribution present in the substrate, called “ash".
- **Chemical Oxigen Demand (COD):** represents the amount of oxygen required to chemically oxidize the organic matter in the substrate, and this parameter is determined by using a strong oxidizing agent in an acidic environment.
- **Biochemical Oxigen Demand (BOD_5):** is a parameter used to measure the amount of oxygen consumed by microorganisms to decompose the organic matter in the sample over a period of 5 days, at a temperature of 20°C.

Once the main characteristics of the substrate are known, it is necessary to define the reactor monitoring parameters such as the hydraulic retention time, organic loading rate, and specific gas production; considering the following quantities:

Q	Influent flow rate to the reactor [m^3/d]
Q_{biogas}	Biogas production rate [m^3/d]
S	Substrate concentration in the influent flow [kg_{VS}/m^3]
V	Reactor volume [m^3]

The operational parameters of an anaerobic digestion (AD) reactor are defined:

- **Hydraulic Retention Time (HRT)**: The average time in which the matrix to be treated remains in the reactor (expressed in days). This parameter is influenced by temperature and type of substrate. It is calculated as the ratio between the reactor volume and the influent flow rate, as indicated in formula (1). This value ranges from 10 to 30 days, with an initial phase of bacterial community growth followed by a stationary phase with constant methane production.

$$HRT = \frac{V}{Q} \tag{1}$$

- **Organic Loading Rate (OLR)**: The volumetric organic loading of the substrate related to the reactor volume; it is the amount of substrate entering the reactor per unit of usable volume and time; it is expressed in $kg_{VS}/m^3/d$. In mesophilic wet anaerobic reactors, OLR is in the range of 2÷4 $kg_{VS}/m^3/d$ to a maximum of 6 $kg_{VS}/m^3/d$ (APAT, 2005).

$$OLR = \frac{\mathrm{Q} * \mathrm{S}}{\mathrm{V}} \tag{2}$$

- **Specific Gas Production (SGP)**: The amount of biogas produced per unit of volatile substance fed into the reactor; it is expressed in $m^3_{biogas}/kg_{substrate}$ and is a parameter correlated to the biodegradability of the substrate being treated.

$$SGP = \frac{\mathrm{Qbiogas}}{\mathrm{V}} \tag{3}$$

  It’s important consider that the amount of biogas that can be produced from a substrate is closely correlated to: the substrate composition (in terms of quantity and type of carbohydrates, lipids, and proteins), the presence of lignocellulosic structures, which are not easily degradable and the material particle size.

- **Biochemical Methane Potential (BMP)**: is a parameter for estimating the biodegradability of a substrate through its ability to produce methane under anaerobic conditions; it is determined through a specific laboratory test (described in section 5.2.2) and it is expressed in $NmL_{CH4}/gVS_{substrate}$ given by the ratio of the standardized volume of methane produced over the grams of volatile solids of the initial substrate.

3.1.3. Stability parameters of AD process

Anaerobic digestion is a highly complex process so monitoring its parameters is essential to ensure that the reactions described in the previous paragraphs can take place completely and the yield of the entire process can be maximized.

- **Temperature:** is a fundamental parameter for the AD process, since heterogeneous microbial populations are involved in the process which are particularly sensitive to even small variations in temperature. In fact, such variations do not result in a different rate of processes, but in replacement of the entire bacterial population. Depending on the temperature chosen, it is possible to have psychrophilic (between 10÷25°C), mesophilic (between 25÷45°C) and thermophilic (between 45÷70°C) processes. For mesophilic digestion processes (which are the most common), the best biogas yields occur for temperatures between 30÷35°C.
- **pH and Buffering Capacity**: pH values too high or too low can create unsuitable conditions for the metabolic activity. Therefore, in AD process is necessary to maintain pH between 6.5÷7.5. This parameter provides information about the stability of the process; in fact, changes in pH are linked to both the buffering capacity of the system and shifts in equilibrium between the species involved in the process. When higher pH values are reached, it indicates the accumulation of ammonia, which inhibits acidogenic and methanogenic bacteria, leading to excessive production of H_2 and H_2S (Jain et al., 2015). The buffering capacity, on the other hand, is determined by the total alkalinity (TA) of the system, expressed as the concentration of calcium carbonate. For a sTable AD process the alkalinity should range between 3,000÷5,000 mg_{CaCO3}/L.
- **FOS/TAC[1]:** This parameter relates the sum of VFAs to the alkalinity buffering capacity of the solution. This is a crucial parameter for monitoring the AD process because when the system moves away from a sTable condition, the VFAs concentration tends to increase, while alkalinity decreases. Therefore, their ratio is a quick indicator of system unbalance. An optimal FOS/TAC ratio is considered between 0.3÷0.4.

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[1] FOS in German stands for «Flüchtige Organische Säuren» and it means Volatile Fat Acids (VFAs); while TAC stands for «Totales Anorganisches Carbonat» which means Alkaline Capacity

- **C/N**: the ratio between carbon and nitrogen is a fundamental parameter because microrganisms require nitrogen for protein synthesis and cellular structure formation. Carbon, on the other hand, is used as an energy source. According to the literature, the optimal C/N ratio is 25:1, although this value can vary depending on the type of feedstock supplied to the reactor (Jain et al., 2015). A ratio that is too high indicates that nitrogen is rapidly consumed by methanogens, which require proteins, while a ratio too low leads to the accumulation of free nitrogen in the ammonia form, causing a rise in pH to critical levels.
- **Nutrients**: the major nutrients for bacteria are C, H_2, O_2, N_2, P and S. Small amounts of sodium, potassium, calcium, magnesium and ammonia stimulate growth but at high concentrations can also be toxic.

3.2. Organic matrices in co-digestion

Beginning with the well-established anaerobic digestion process, scientific activity in recent years has directed its attention into the optimization of this process by the joint treatment of several organic matrices, in order to study the effects, advantages and also critical aspects. In particular, for organic matrices that are currently managed in landfills, such as sewage sludge, the possibility of co-digesting them with organic fraction of municipal solid waste has been explored to enhance recovery. In fact, this could be a win-win strategy (Massaro et al., 2015) because if OFMSW is added in the sewage sludge AD process, it results in an increase in biogas production and consequently also in energy recovering; while also giving the proper disposal to organic waste thus determining a clear benefit for the environment (Nakakubo et al., 2012).

Given that both sewage sludge and OFMSW are wet organic matrices, it is evident that optimizing this combined treatment is crucial in order to fully leverage the environmental, energy, and economic benefits of this approach.

Sewage sludge could, therefore, be recovered and valorized ensuring a high content of carbon and significant production of biogas (thanks to its high biodegradability), without affecting the yield of the delicate biological process, but profiting from the synergistic action between the matrices.

Some studies have already pointed out some disadvantages of co-digestion of food waste with sludge from municipal WWTPs including the return of nitrogen to the water line and reduced dewaterability of sludge (Mattioli et al., 2017).

3.2.1. Co-digestion of Primary Sludge and Food Waste

An interesting study, concerning the co-digestion of these organic matrices, is that conducted by Xie et al. (2017) by using BMP tests in which is determined that from mono-digestion of primary sludge the BMP is 159 mL/gVS; from the mono-digestion of food waste the BMP is 652 mL/gVS and from the co-digestion of them in a 1:1 ratio (VS basis) there is an higher specific methane yields of 799 mL/g VS. The VS removal resulted from the co-digestion is 118%, far from the mono-digestion of primary sludge (VS removal: 75.8%) and monodigestion of FW (VS removal: 93.4%).

3.2.2. Co-digestion of Sewage Sludge (SS) and diluted Food Waste (FW)

Another comparison of BMPs resulting from different co-digestion ratios of FW and SS is that presented by Pan et al. (2019) in which the substrates are: diluted FW (5.2% TS; 90.9%VS) and SS (4.5% TS; 49.5%VS).

BMP tests were conducted with seven groups of tests with different SS:FW ratios (at VS basis): 1.0:0.0 (i.e.mono-digestion of SS), 0.8:0.2, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.2:0.8 and 0.0:1.0 (i.e. mono-digestion of FW). The inoculum added into each bottle and the ratio of inoculum to substrates was controlled at 2.0:1.0 (based on VS).

From the cumulative curves of methane production, is evident that the lowest production is from the mono-digestion of SS, only 124.43 ± 20.10 mL/gVS; similar results for SS mono-digestion were also reported by Kim et al. (2003) with 116 mL/gVS and Zhen et al. (2015) with 176.36 mL/gVS. While the highest methane production occurs by FW mono-digestion with BMP of 417.72 mL/gVS. Co-digestion ratios, on the other hand, return intermediate curves, with biogas production increased with increasing proportion of FW. The addition of FW has also been shown to be beneficial in enhancing digestate dewatering, resulting in a reduction in the volume to be handled and associated treatment and disposal costs.

3.2.3. Co-digestion of Dewatered Sludge (DSS) and Food Waste (FW)

An example of the co-digestion of dewatered sludge (DSS) and food waste (FW) is described by the experimental work of Dai et al. (2013) in which, comparing the high-solids[2] co-digestion of DSS and FW with the respective mono-digestions discovered that system stability was improved in co-digestion because the co-substrate acted as a diluting agent to toxic chemicals like ammonia or Na^+. In detail, known matrices features (DSS: 20.4% TS, 56.7% VS; FW: 21.4% TS, 92.8% VS) the mixing ratios for co-digestion of DSS and FW ranged from 2.4:1.0 to 0.4:1.0 based on VS and 4.0:1.0 to 2.0:3.0 based on wet mass, respectively.

As results, the addition of FW into the DSS high-solids digestion improved system stability and greatly enhanced volumetric biogas production; while the addition of DSS into the FW high-solids digestion reduced the inhibition level of Na^+ concentration and helped maintain satisfactory stability during the conversion of FW into biogas. It was found that biogas production and VS reduction in digestion of the co-mixture of DSS and FW increased linearly with higher ratios of FW.

3.2.4. Co-digestion of Sewage sludge and OFMSW

Also the experimental study of Mattioli et al. (2017) turns out to be of particular attention as it investigates the effects of mono-digestion of sludge (a mix of primary and secondary sludge) produced from an industrial WWTP and then the co-digestion of this sludge mix with the OFMSW. The primary and secondary sludges have 3-5% TS and 77% VS. Compared to the sludge mono-digestion, its co-digestion with OFMSW determines an increase in biogas production. In fact, co-digestion of SS and FW

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[2] It's referred to total solids (TS) content of the feedstock greater than 15%w/w.

provides general environmental improvements compared to SS mono-digestion and SS-FW composting, mainly due to the higher energy recovery during the anaerobic digestion step (Francini et al., 2019).

In general, as declared into the Thecnical Proposals of the End-of-Waste Criteria (Saveyn et al., 2013), the organic waste chosen as co-substrate of sewage sludge for the implementation of the co-digestion processes should guarantee a high content of carbon and significant production of biogas (high biodegradability), a low content in terms of nitrogen and phosphorous in order to avoid additional loading of nutrients to the water line, a low content of inert materials, heavy metals and organic micro-pollutants as well as pathogens to obtain a digestate of good quality.

3.3. The concept of biorefinery

Waste biorefineries are complex systems due to the variability, heterogeneity and low purity of waste materials as opposed to dedicated biomasses; for this reason an unique layout of the most suitable processes to be included in an organic waste biorefinery cannot be defined, because it needs to be related to the quantity and characteristics of the waste, the specific local conditions, market trends and legislative constraints (Alibardi et al., 2020).

Although biorefineries represent a sustainable option for producing bio-based goods through decarbonization pathways, they must meet the market demand and preferred over the fossil-based ones. Moreover, as reported by European Commission (2018), the exploitation of organic waste according to a pyramidal hierarchy in which the extraction of valuable biomolecules, which will be used as they are or as precursors of high-added-value compounds, is a priority in biofuel production.

The most abundant waste produced in the urban context are FW and SS (Battista et al., 2019), so the co-treatments of these matrices need to be investigated to produce high-added-value molecules and biofuels and to recover nutrients through a biorefinery approach.

In this scenario, anaerobic digestion as a well-established biological process – able to treat complex matrices – may be a suitable candidate to play a central role in biorefinery schemes (Alibardi et al., 2020).

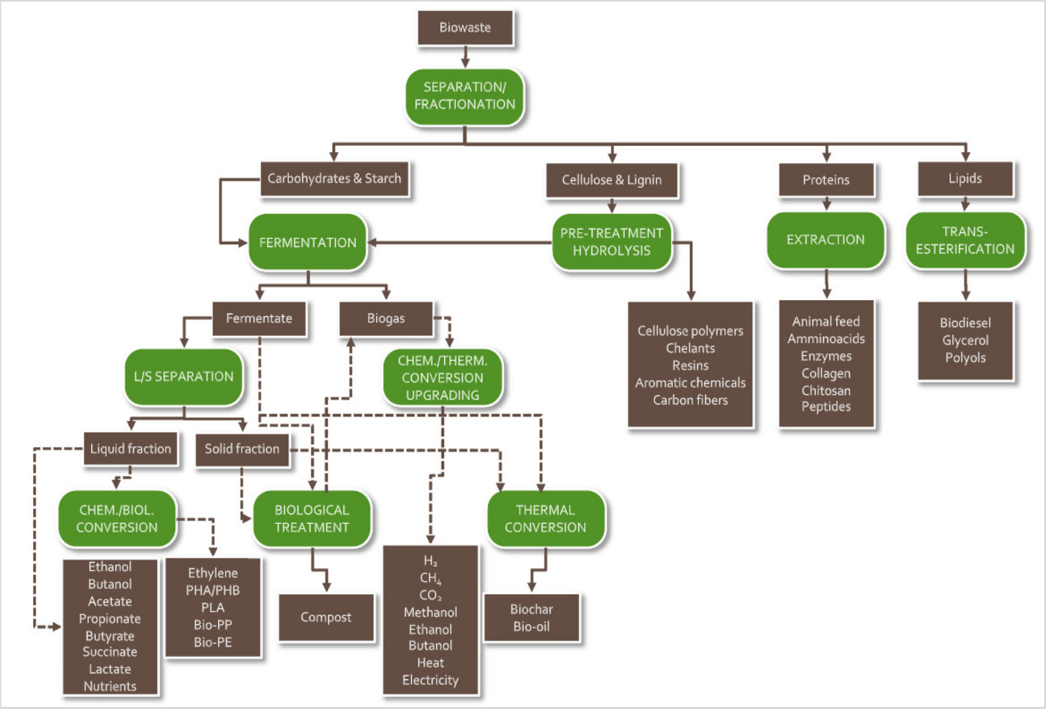


Figure 11 – Layout for a multi-platform anaerobic biorefinery producing biofuels and biomolecules (Alibardi et al., 2020)

Figure 11 presents the layout of a multiplatform waste biorefinery in which some bioproducts and technologies presented are alternatives to each other, depending on the desired end products.

In all biorefineries, the crucial step is pretreatment because it enables to remove unwanted constituents, change the physical properties of the solid matrix to speed up downstream processes (Tonini and Astrup, 2012). In detail, the scheme shown in Figure 11 involves the initial separation of the individual components of the waste feed (carbohydrates, starch, cellulose, lignin, proteins and lipids), followed by dedicated treatments of each component to maximise the yield of biofuels and biomolecules recovery (Alibardi et al., 2020).

To analyze practical cases, as reported in the work of Battista et al. (2019), some examples of full-scale biorefineries can be found in Germany and Italy. In Moosburg (Germany) there is an AD plant which receives the substrates from a centralized FW processing facility (Koch et al., 2016); these substrates are pre-treated with a hammer mill to remove the inert materials, then a centrifuge divide solid and liquid phase and the liquid one is sent for AD processing with other co-substrates such as: contaminated milk, lacto-rich waste, fat oil and grease. The AD process takes place at 35°C with HRT of 25 days.

Another example is the co-digestion plant in Rovereto (Italy) where FW from separate collection is mixed with SS to form a mixture of 12 %TS. It works under mesophilic condition (35°C) with HRT less then 12 hours (Mattioli et al., 2017).

Organic waste biorefineries are complex systems because the target of increasing recovery must take into account the difficulties of having a heterogeneous and variable waste input.

4. RESEARCH PURPOSES AND PLAN

4.1. Research purposes

This research project arises from the dual need to optimize the process of anaerobic digestion of the organic fraction of municipal solid waste (OFMSW) and to maximize the recovery of wastewater sewage sludge (WW-SS). Anaerobic digestion is a well-established and widely applied technology, that continues to attract interest and innovation due to its capacity to produce methane from organic waste. This study concerns the development of anaerobic digestion plants into integrated biorefinery systems. Such facilities would function as treatment hubs for organic waste matrices, improving the synergistic recovery of resources in terms of material reutilization and energy production.

The research specifically focuses on testing OFMSW co-digestion processes with additives derived from innovative sewage sludge treatments, including hydrothermal carbonization (HTC) and pyrolysis. These technologies generate scraps (such as hydrochar, biochar, and liquid fractions) which, despite being classified as waste, may serve as valuable additives to enhance the anaerobic digestion process.

The yield of these co-digestions in terms of methane production is evaluated to determine which additives provide the greatest benefits and whether the matrices interact synergistically during anaerobic digestion. The ultimate goal is to propose integrated solutions capable of processing heterogeneous organic waste streams in joint processes using combined technologies to increase the synergic recovery of resources, from both material and energy perspectives.

To address these objectives, biomethanation tests were conducted to assess both the methanation potential of individual substrates and the performance of new substrate mix tested in co-digestion configurations. The research purposes are:

- Optimization of the anaerobic digestion process for OFMSW by increasing methane yields and improving overall process efficiency;
- Enhancing the recovery of organic waste that would otherwise be destined for landfill disposal, thus promoting circular economy principles;

- Investigating synergistic actions among organic matrices of different origins to exploit their complementary characteristics and boost process performance;
- Proposing centralized plant configurations that integrate multiple technological solutions, allowing for more efficient management, recovery, and valorization of organic waste materials.

This approach aims to bridge the gap between conventional anaerobic digestion practices and innovative biorefinery concepts, offering practical and scalable solutions to handle diverse organic waste streams while maximizing biogas production and resource recovery.

4.2. Research plan

For achieving the purposes described in Section 4.1 an experimentation study has been made at laboratory of Environmental Technologies of Politecnico di Bari. The experimental activity – following chemical-physical characterisation OFMSW – included exsperimental tests to assess the impact of various additives from sewage sludge processing on the anaerobic digestion performance of OFMSW. The experimental phases are briefly shown in Figure 12.

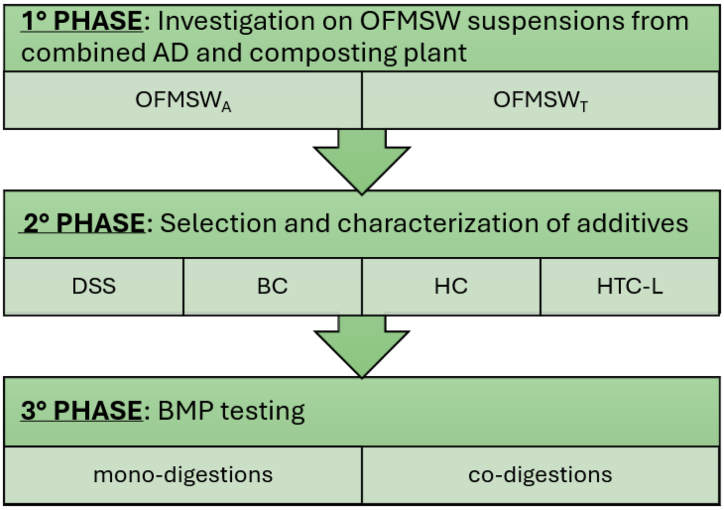


Figure 12 – Research plan

The **first phase** involved the study of two industrial anaerobic digestion and composting plants located in Southern Italy. The investigation focused on characterizing the OFMSW suspensions obtained after mechanical pretreatment prior to anaerobic digestion, which became the central matrices of the study. Specifically, the $OFMSW_A$ matrix originated from a wet-type anaerobic digestion plant; the $OFMSW_T$ matrix came from a semi-dry anaerobic digestion plant.

The **second phase** focused on identifying, collecting, and characterizing additives to be used during the experimentation to evaluate their performance in co-digestion with the pretreated OFMSW suspensions. The selected additives included:

- Dewatered Sewage Sludge (DSS): residual biosolids obtained from wastewater treatment.
- Biochar (BC): produced through the pyrolysis process of sewage sludge, offering high carbon content and adsorptive properties.
- Hydrochar (HC): derived from the hydrothermal carbonization (HTC) of sludge, characterized by enhanced porosity and reactivity.
- HTC Liquid (HTC-L): the liquid phase recovered from the hydrothermal carbonization process, rich in soluble organic compounds and nutrients.

The **third phase**, the core of the experimentation, consisted of conducting several biomethanation tests. Each test was performed using nine batch reactors with a 600 mL capacity, operating under batch conditions. These trials were designed to determine the Biochemical Methane Potential (BMP) of the different substrates and their combinations.

First, BMP tests were conducted for each substrate individually, maintaining an ISR (Inoculum-to-Substrate Ratio) of 2, these represented the mono-digestion tests of each substrate. The tests conducted for the OFMSW matrices were the baseline scenarios from which to implement the co-digestions.

Following, co-digestion trials were carried out to assess the synergistic effects of combining the OFMSW matrices ($OFMSW_A$ and $OFMSW_T$) with the selected additives (DSS, BC, HC, and HTC-L).

A summary of the scenarios investigated is presented in Figure 13.

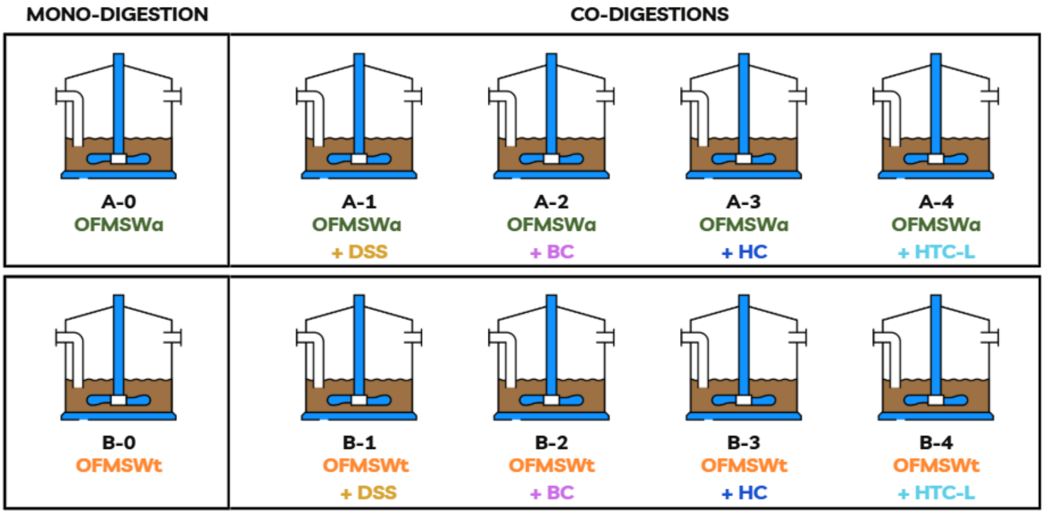


Figure 13 – Co-digestion scenarios starting with $OFMSW_A$ (type A) and $OFMSW_T$ (type B)

Specifically, the addition of 13 mg/L of OFMSW was tested for biochar and hydrochar, while the addition in 1.0:2.3 of additive:OFMSW was tested for dewatered sludge and HTC liquid. The overview of the seven BMP tests conducted (reported as T_i) is shown in Figure 14, indicating the corresponding substrates investigated.

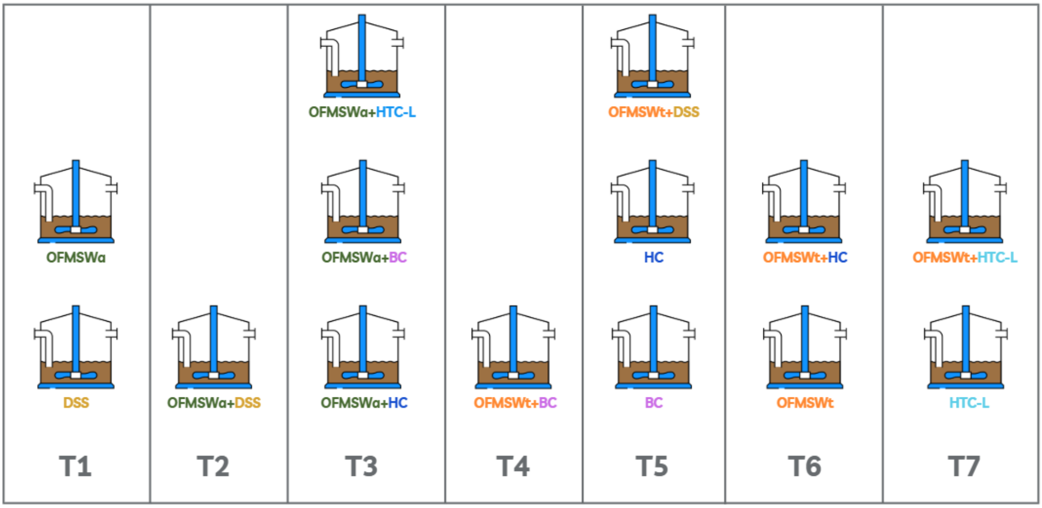


Figure 14 – Overview of the BMP tests

Each trial lasted approximately 33 days, during which the cumulative methane volume was monitored. Data normalization was performed to ensure comparability under standard temperature and pressure conditions (273.15 K and 101.325 kPa).

The trials provided BMP values by correlating the cumulative methane volume to the grams of volatile solids (VS) in each substrate. The approach allowed the identification of optimal configurations for maximizing methane yield. Furthermore, the study analyzed the effects of solid and liquid additives, emphasizing their potential to:

- Provide essential nutrients (e.g., nitrogen, phosphorus, and organic acids) to stimulate microbial activity;
- Enhance process stability by buffering pH variations and adsorbing potential inhibitors;
- Improve the structural quality of the digestate for downstream applications.

This research ultimately aims to contribute to the advancement of anaerobic digestion technologies, promoting resource-efficient treatment systems within a circular economy framework.

The experimental activity facilitated the development of hypothetical process layouts that integrate anaerobic digestion, pyrolysis, and hydrothermal carbonization (HTC) technologies. This integrated approach aims to optimize the management of organic waste by leveraging the complementary benefits of each process.

5. MATERIALS AND METHODS

5.1. Materials involved in the experimentation

Anaerobic digestion is a highly versatile process that can be applied on a wide variety of organic biomass. Theoretically, any organic material could be utilized to generate energy within the digesters, offering the potential for energy recovery from waste or resources. However, the effectiveness and sustainability of this process depend on several critical factors. Among these, process microbiology plays a fundamental role, as the presence of specific microorganisms is essential for the proper fermentation process and optimal biogas production. Additionally, the technological limitations of the plants, which need to be properly designed and sized to ensure efficient treatment, can affect the ability to process certain substrates. This is further compounded by environmental regulations and laws that set specific requirements for the management of organic waste and biogas production, as well as economic considerations regarding the feasibility of using specific materials.

Therefore, the adoption of anaerobic digestion requires a deep understanding of the characteristics of each substrate, to optimize operating conditions and ensure efficient and sustainable energy production. Integrating all these variables is crucial for achieving a process that is not only technically sound, but also economically and environmentally advantageous.

It has a great relevance to make proper assessments to identify the biomass to be treated in the AD process, there are several factors that can influence this choice:

- physical characteristics, and the related methanogenic potential;
- availability;
- economic value of the substrate and costs associated with its use.

The first step of the experimental activities was the identification, production and characterization of different organic matrices – from full-scale or pilot-scale waste treatment plants – that were to be used in the research project. The whole experimentation was conducted at the *Environmental Technologies* Laboratory of the Polytechnic of Bari.

The substrates were characterized by laboratory analysis to determine the moisture content and volatile solids content; they were stored in refrigerated cells at 4°C to prevent decomposition of organic matter and ensure the proper execution of the tests and reliability of the results. After that, the BMP tests were performed.

OFMSW represents about 40 percent of the waste collected separately (ISPRA, 2023), so solutions that maximize recovery must be used for this matrix. In particular, at the entrance to the organic waste treatment plants, an essential first step is the mechanical treatment stage. These operations are used to open bags for waste delivery, to reduce the grain size and to obtain a material that has the suitable characteristics to proceed in the subsequent treatment steps according to the technological solution adopted. Frequently, the shredded waste is then mixed with recirculating water in such a way as to obtain a suspension suitable to be subjected to the anaerobic digestion process. This liquid suspension, characterized by a different content of total solids depending on the process and the heterogeneity of the starting material, is the target of the experimental activity.

Specifically, two different OFMSW suspension matrices, both from combined digestion and composting full-scale plants, were used for experimentation. The difference between them is that the first, called from now on $OFMSW_A$ and described in the section 5.1.1, comes from the combined plant of AMIU Puglia, where wet digestion of OFMSW is performed; the other one called $OFMSW_T$ is described in section 5.1.3 and comes from the combined plant of TERSAN Puglia, where a semi-dry digestion is performed.

5.1.1. Pre-treated OFMSW from full scale combined wet-AD and composting plant

The experimental activity was carried out with the aim of testing different organic matrices to evaluate the efficiency of their combined treatment. For this purpose, the suspension of OFMSW produced by pre-treatment processes of the AMIU Puglia plant was collected and is now defined as $OFMSW_A$. Specifically, the matrix was collected before entering the digester to obtain a sample that is representative of the material currently undergoing the wet AD process.

In general, the plant processes 40,000 tons/year of OFMSW and 8,000 tons/year of ligno-cellulosic waste according to the process scheme shown in Figure 15.

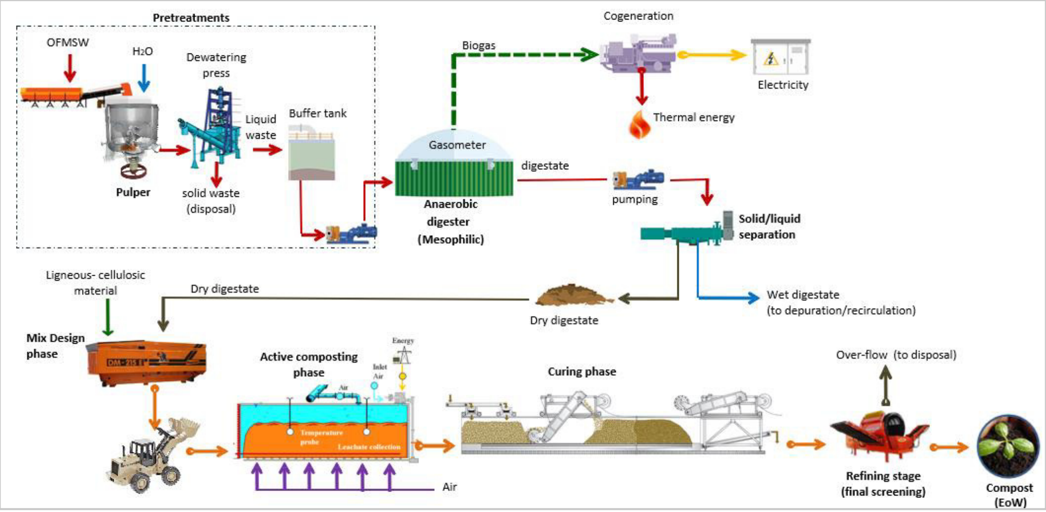


Figure 15 – Process flow diagram of the combined anaerobic digestion and composting plant of AMIU Puglia

From the separate waste collection of the municipality of Bari, the organic fraction of municipal solid waste is delivered to the palnt and subjected to mechanical pre-treatments, which are essential to give the matrix the proper characteristics for the subsequent biological process (including a total solids content lower than 10%). This is followed by the anaerobic wet digestion section, which utilizes a digester of approximately 6000 m^3 with a gasometer on top that allows the accumulation of biogas produced and its transfer to the cogeneration (CHP) stage.

The digestion process operates continuously, so the produced digestate is sent to the spin-dryer that separates liquid phase, which is recirculated as process water, from the solid material. The dry-digestate is then combined with the incoming ligno-cellulosic material and sent to the composting process in aerated bio-cells. The process is followed by a curing phase and a screening for refinement, from which compost is finally obtained; when it meets specific criteria, the end-of-waste target is reached having a markeTable product.

Specifically, the mechanical-physical pre-treatments that produce the $OFMSW_A$ suspension, which is the subject of this experimental activity, are represented by the equipment shown in Figure 16.

Figure 16 – Equipment for organic waste pretreatments

- **Shredder**: The shredding process, carried out by a slow-speed twin-shaft shredder, allows to open waste collection bags and reduce the material size, which is then transported by a screw conveyor to the pulper.
- **Pulpers:** The pulper is a 12 m^3 mixer where the incoming waste is combined with recirculated water in a 1.0:1.5 ratio and mixed for 20 minutes, resulting in a pumpable slurry. By gravity, the heavier and bigger material settles at the bottom and then removed.
- **Rejector**: The suspension is sent to the rejector, which further shreds the material and, using a screen with 16 mm diameter holes, retains any coarse solid fragments still present.
- **Press:** The solid fraction retained by the pulper and rejector is sent to the press to recover a part of its liquid fraction which is then joined with the suspension; the solid part is stored for disposal in landfill.
- **Hydrocyclone**: The slurry passed through this device to remove sand and fine inert materials from the suspension.
- **Buffer Tank**: This is a storage tank from which the suspension is sent to the anaerobic digester.

It is possible to monitor all pre-treatment steps through sensors installed on the devices and the control screen shown in Figure 17.

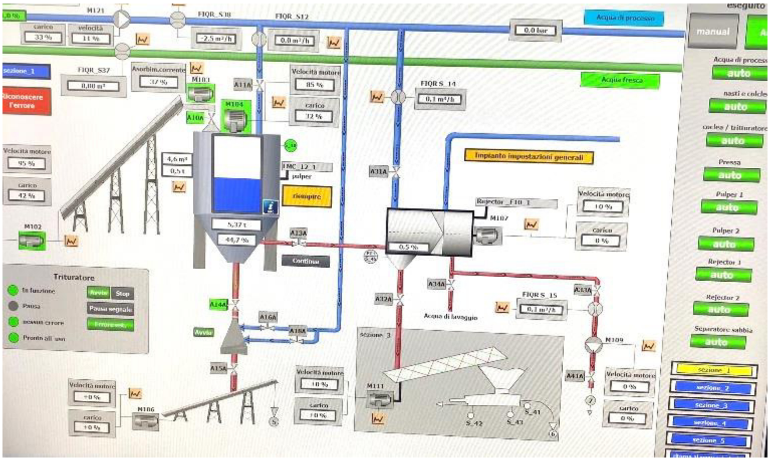


Figure 17 – Simplified plant layout for process monitoring

The suspension thus pretreated, achieves characteristics suitable for wet anaerobic digestion. So, downstream of the buffer tank, a sample of $OFMSW_A$ suspension was taken for the experimental activity. In all, about two kilos of this material was used for the experimental activities.

5.1.2. *Pre-treated OFMSW from full-scale combined semi-dry AD and composting plant*

The second type of organic fraction of municipal solid waste being tested is called $OFMSW_T$, as it comes from the combined plant of TERSAN Puglia, located in Bari. The matrix is the liquid suspension collected before entering into the semi-dry anaerobic digestion. The process line of the TERSAN plant is shown in Figure 18.

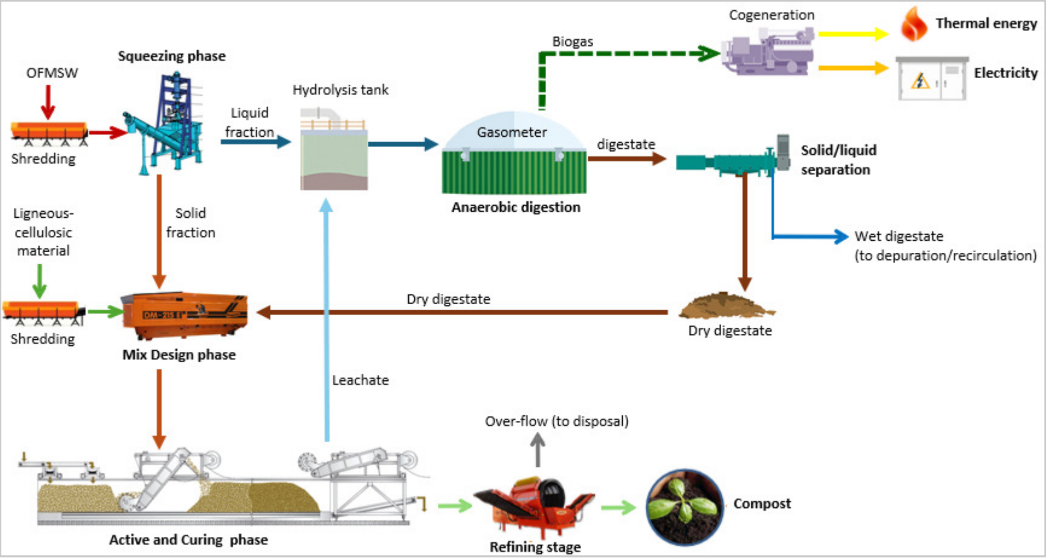


Figure 18 – Process flow diagram of the combined anaerobic digestion and composting plant of TERSAN Puglia

The plant collects organic waste both from the separate collection of municipal solid waste and from agro-industrial activities, amounting to approximately 90,000 tons/year. The process involves the shredding of the OFMSW to reduce the size and open the bags, followed by pressing. The liquid fraction resulting from this squeezing phase is sent to anaerobic digestion along with process water from scrubbers, biofilters, and leachate from composting. The AD process produces biogas, which is subsequently upgraded to biomethane and injected into the grid, as well as digestate. The digestate is then dehydrated using a centrifuge, with the liquid fraction being sent to treatment, while the solid fraction is directed to the composting section and mixed with the shredded OFMSW and lignocellulosic waste. The composting process involves biosoxidation in piles with turning, followed by a maturation step and two refining screenings, which result in the production of compost.

The liquid fractions of this process, such as:

- the liquid from pressing the OFMSW,
- the water drained from the composting areas,
- the wastewater from the scrubbers,

are collected in a tank equipped with a mixing system to ensure the homogeneity of the substrate. These fractions are recovered as they are characterized by a high organic matter content, which can be valorized through anaerobic digestion. In fact, as also reported by Cesaro et al., (2015), although the solid fraction out of the press-extruder still contains some organic, this accounts for approximately 4–5% of the one contained in the fed material, whereas the fluidized materials is mainly composed of the readily fermenTable organic substances. This mixed substrate is then pumped into the hydrolysis tank (Figure 19), where the first stage of the digestion process takes place; it is then sent to the 3000 m^3 anaerobic digestion reactor for the other stages of the process. For experimentation, a one-kilogram sample of substrate was collected from the tap before entering into the hydrolysis tank.

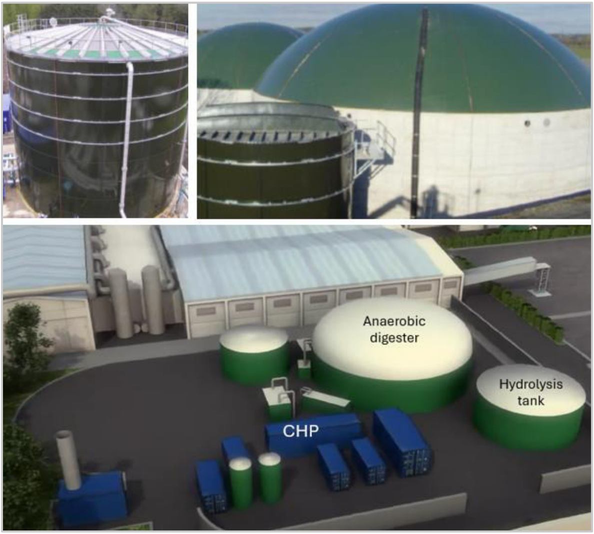


Figure 19 – Hydrolysis tank and anaerobic digester in the AD area of TERSAN plant

5.1.3. Digestate from full-scale AD plant as inoculum

All biological processes are based on the degradation activity of organic matter conducted by microorganisms in the matrix itself. It is necessary, especially for anaerobic digestion, to ensure the presence of a bacterial flora capable of activating the decomposing processes of organic matter, and this is accomplished through the use of an inoculum, a material that has already been digested and contains the bacterial diversity necessary to activate the methanization process.

Digestate from an industrial anaerobic digestion plant in Southern Italy was used as inoculum for the experimental activity. This plant, of Agrolio s.r.l. company, realize the anaerobic digestion of olive pomace, an organic waste from olive milling for the extra virgin olive oil production process.

Before the start of each trial, the necessary amount of inoculum was taken from the plant to be loaded into each BMP reactor, depending on the substrates to be analyzed. A total of 14 kilograms of inoculum was used for the eight trials.

The company Agrolio s.r.l. provided the characterization of this substrate carried out by an accredited laboratory and it is shown in the following Table 8.

Table 8 – Chemical-physical characterization of the inoculum

Parameter	**Unit**	**Value**	**Method**
Total solids	%	8.4	DIN EN 12880
Water content	%	91.6	DIN EN 12880
Ash	% dm	20.1	DIN EN 12879
Volatile solids	% dm	79.9	DIN EN 12879
Ammonium_NH4+	mg/L	618	MI C03 07 Photometric Method
Ammonium_NH4+-N	mg/L	480	MI C03 07 Photometric Method
Acetic Acid	mg/L	38	MI C03 09 HPLC for Volatile Fatty Acids
Propionic acid	mg/L	<12	MI C03 09 HPLC for Volatile Fatty Acids
Iso-butyric acid	mg/L	<14	MI C03 09 HPLC for Volatile Fatty Acids
Butyric acid	mg/L	<14	MI C03 09 HPLC for Volatile Fatty Acids
Iso-valeric acid	mg/L	<16	MI C03 09 HPLC for Volatile Fatty Acids
Valeric acid	mg/L	<16	MI C03 09 HPLC for Volatile Fatty Acids
Total VFAs	mg/L	38	-
pH	-	7.8	APHA. 20th Edition. 4500-H+ B
Electric conductivity	mS/cm	13	APHA. 20th Edition. 2510 B
Redox Potential	mV	-206	APHA. 20th Edition. 2580

TAC	mg_{CaCO3}/l	8,320	MI C03 11 Titrimetric Method
FOS	mg_{HOAC}/l	2,190	MI C03 11 Titrimetric Method
FOS/TAC	-	0.26	-

It is important to highlight that the inoculum used for testing was fresh and quite homogenous, taken from the above mentioned active anaerobic plant which was at steady-state at the time of sampling. Moreover, the inoculum was stored at ambient temperature (20÷25°C) as suggested by Holliger et al., (2016).

5.1.4. Dewatered sewage sludge from WWTP

The sludge exiting the wastewater treatment plants is a dewatered sludge with total solids content around 20%. Sewage sludge is characterized by low organic matter, but a preliminary dewatering process increase its organic matter concentration (Battista et al., 2019).

For the experimental activity was collected sludge produced by 6 WWTPs with capacity greater than 20,000 population equivalent (P.E.), located in the Apulia region and managed by Acquedotto Pugliese. The average chemical-physical characterization of the sludge produced by these plants is shown in Table 9.

Table 9 – Chemical-physical composition of SS from 6 selected wastewater treatment plants

WWTPs	**pH**	**Total solids**	**Water content**	**Ash**	**N**	**K**	**P**	**TOC**
	-	%	%	%	%	%	%	%
1	7.2	24.2	75.8	4.1	9.2	0.7	1.5	39.2
2	6.8	25.1	75.0	5.8	5.7	0.2	1.8	39.9
3	7.5	17.3	82.8	4.1	7.9	0.5	3.1	38.9
4	6.8	22.2	77.8	4.2	7.1	0.4	4.0	40.6
5	7.3	17.9	82.2	4.1	7.9	0.7	2.3	40.5
6	7.6	22.3	77.7	6.8	6.1	0.2	2.4	34.2
Average value	**7.2**	**21.5**	**78.5**	**4.8**	**7.3**	**0.4**	**2.5**	**38.9**

Based on the annual sludge production from these plants, the percentage (shown in Table 10) to be taken from each plant was determined to make a mean composite sample that was representative of the sludge produced by these plants.

Table 10 – Composition of the representative mean composite sample of the sludge

WWTPs	SS production	Mean composite sample
	tons/year	%
1	5,822	31
2	3,415	18
3	3,120	17
4	2,260	12
5	2,182	12
6	1,937	10

This mean composite sample is the SS that is used during the biomethanation trials in order to evaluate both its own biomethanation potential and the potential obtained from codigestion treatment with OFMSW.

In literature, is known that the high level of carbohydrates, lipids, and proteins in SS allows for a potential methane production of about 300 L/kgVS, ranging from a minimum of 175 L/kgVS to a maximum of 475 L/kgVS. (Thorin et al., 2018).

5.1.5. Biochar from pilot-scale sludge pyrolysis

Biochar is a solid product derived from the sludge pyrolysis process that takes place under anaerobic conditions. In general, its characteristics and potential depend mainly on the organic matrix involved in its production and the operating temperature (Pan et al., 2019).

Biochar has various applications: direct combustion as a solid fuel, adsorbent in catalytic applications, agricultural applications (Oladejo et al., 2019). Now the application of biochar is typically prioritized in the agricultural sector, as it is an excellent fertilizer rich in essential nutrients such as phosphorus, nitrogen, and magnesium, which are crucial for improving soil quality and maintaining its structure. Moreover, biochar has the ability to trap pollutants within its structure that would otherwise be released into the environment, helping to mitigate environmental contamination.

Biochar can reduce potential inhibition of the process caused by Ammonia, as it has a high capacity to absorb substances that could otherwise be harmful to the microorganisms involved in the AD process. It also improves microbial enrichment (Luo et al., 2015), acts as an electrical conductor, and facilitates inter-species electron transfer even in methanogenic bacteria, leading to higher methane production (Zhao et al., 2016), accelerating the decomposition of volatile fatty acids (VFA) (Wang et al., 2021).

In this experimental project, biochar is used as an additive to the OFMSW suspension during the AD process. This substrate is chosen because it has an high specific surface area and contains numerous functional groups that can interact with the biological diversity within an AD process. In addition to being chemically compatible with the molecules present in the feedstock, biochar has a highly porous structure, making it an excellent physical support for the growth of microbial communities, aiding their development and metabolic functions.

For these reasons, biochar was selected as an additive for the experimental activity. Literature shows that adding biochar allows the management of a higher organic loading rate (OLR) with the same reactor volume and time, thereby improving the AD performance and increasing biogas production (Chiappero et al., 2020) (Qiu et al., 2019). Additionally, it enhances the mineral content of the digestate.

For this experimental activity, the biochar used as an additive was produced by testing the pilot-scale pyrolysis technology developed by the Danish company Aquagreen ApS. The pyrolysis process required dried sludge as input material; a detailed description of the procedure and activities involved in this process is provided below.

Identification of the dewatered sludge sample

The sludge to be subjected to the pyrolysis process was selected by creating a mean composite sample from sludge collected from six wastewater treatment plants with a capacity of over 20,000 PE in Apulia region.
Based on the annual sludge production of each plant, the composition of the mean composite sample was defined, as shown in Table 11.

Table 11 – Composition of the representative mean composite sample of sludge

WWTPs	**SS production** **tons/year**	**Mean composite sample** **%**
1	6,534	39
2	3,836	23
3	1,861	11
4	1,687	10
5	1,567	9
6	1,428	8

This dewatered sludge sample was found to have a dry matter content of 22.8%.

Drying phase

Since the pyrolysis technology requires the input sludge to have a dry matter content of at least 90%, the sample was subjected to a drying process using the DRYWA belt dryer from ISOTEX (Figure 20).

Figure 20 – DRYWA dryer and detail of the loading hopper

This technology involved loading the sludge via a hopper, where two rollers ensured the uniform distribution of the sludge onto a perforated moving belt. The sludge then passed through the drying chamber, where moisture was removed from the sample by circulating hot, dry air at temperatures ranging from 50÷75°C. As the air passed through the sludge, it absorbed moisture and, after exiting the chamber, was cooled through a heat exchanger, causing the condensed water to separate. The exhaust air flow was recirculated and reheated, ensuring a closed-loop system. At the end of the process, which did not result in any emissions to the atmosphere, a screw conveyor expelled the dried sludge (Figure 21).

Figure 21 – Sample of dried sludge

The equipment was set with belt speed at 3% and ventilation at 60%, this required a sample residence time inside the dryer of 4 hours. In detail, an extract of the dried sludge characterization carried out by accredited laboratory is shown in Table 12.

Table 12 – Extract of the chemical-physical characterization of the dried sludge

Parameter	Unit	Value	Method
Fixed residue (at 105 °C)	%	95.21	UNI EN 14346 A 2007
Fixed residue (at 600 °C)	%	29.2	CNR IRSA 2 Q64 vol. 2
pH	-	8.09	CNR IRSA 1 Q64 Vol.3 1985+APAT CNR IRSA 2060 man 29 2003
Flash point	°C	> 75	ASTM E502-07
TOC	%	34.7	IRSA Q.64 vol.3
LHV	kJ/kg	11,450	UNI EN 15400:2011
Salinity	meq/100 g	45.2	ANPA all. 9 man. 3 2001
C/N ratio	-	12	Calculation
Volatile solids	%ss	64	UNI EN 15169:2007

The same dried sludge, before being subjected to the pyrolysis process, was subjected to further laboratory characterization from which a dry matter content of 93.2% and an ash content of 28.4% were found. The values differed slightly from those found by the accredited laboratory due to the time between the drying and pyrolysis tests, so there was a physiological increase in moisture with a consequent decrease in dry matter content (from 95.21% to 93.2%).

Pyrolysis phase

After drying the sample, it was subjected to the pyrolysis process within a pilot plant of the Danish company Aquagreen, shown in Figure 22, which was built and tested at the Technical University of Denmark (DTU).

Figure 22 – Pyrolysis pilot-scale plant and detail of the external burner for gas combustion

The plant consists of:

- a loading hopper;
- a cylindrical reactor;
- an airtight container for collecting the biochar;
- a pipe for removal of the produced gas;
- an external burner for gas combustion.

The dried sludge sample was manually loaded into the hopper and through internal handling screws arrived in the cylindrical reactor. Thanks to the presence of six semi electric cells, the oven reached a temperature of 650°C – considered to be the target temperature with which the best yields were recorded – and under anaerobic conditions, thanks to the insufflation of nitrogen, the material was pyrolyzed.

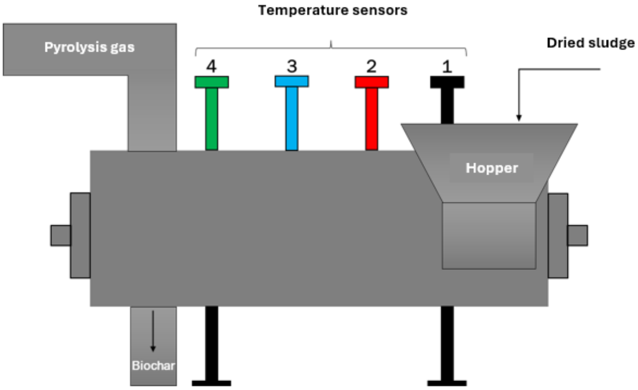
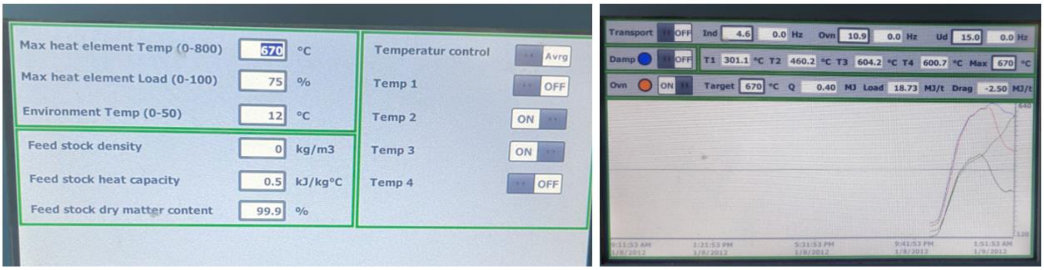


Figure 23 – Schematization of the pyrolysis pilot plant

The process was monitored through the presence of a control panel in which the measurements taken by four temperature sensors placed along the entire reactor were returned; on the panel it is possible to set the maximum temperature and the speed of the screws, as well as to view the temperature trend as shown in Figure 24.



Max heat element Temp (0-800) 670 °C
Max heat element Load (0-100) 75 %
Environment Temp (0-50) 12 °C
Feed stock density 0 kg/m3
Feed stock heat capacity 0.5 kJ/kg°C
Feed stock dry matter content 99.9 %

Temperatur control Avrg
Temp 1 OFF
Temp 2 ON
Temp 3 ON
Temp 4 OFF

Transport OFF Ind 4.6 0.0 Hz Ovn 10.9 0.0 Hz Ud 15.0 0.0 Hz
Damp OFF T1 301.1 °C T2 460.2 °C T3 604.2 °C T4 600.7 °C Max 670 °C
Ovn ON Target 670 °C Q 0.40 MJ Load 18.73 MJ/t Drag -2.50 MJ/t

Figure 24 – Control panel of the pyrolysis pilot plant

The reactor needed about 2 hours to reach temperature, after which about 25 kg of dried sludge was loaded and the hopper was hermetically closed. Inert nitrogen was then insufflated and the screw movement started. At industrial scale, the sludge pyrolysis time at 650° C was 20 minutes; at pilot scale, however, a residence time of at least one hour was required because effective pyrolysis at 650° C could only be guaranteed in the central/terminal part of the reactor. The products of the process were pyrolysis gas and biochar.

The pyrolysis gas is a high-energy-density gas that, unlike what usually happens in the industrial-scale plant, was not monitored in terms of quantity and composition; it was directly piped and burned at a temperature of about 900°C using an external combustion flashlight.

The biochar, on the other hand, consisting mainly of carbon and ash, was collected in an airtight container and allowed to cool for at least 12 hours so as to prevent oxidation in contact with air; it was then analyzed.

The test determined that 43% biochar and 57% pyrolysis gas were produced from the incoming dried sludge sample. The biochar was analyzed and found to have an ash content of 66.3%.

It is finally concluded that the biochar used in the experimental activities was obtained from the process of pyrolysis of dried sludge at 650°C for about 30 minutes. From this trial, 1 kilogram of biochar was sampled, and about 40 grams was used for the experimental tests.

5.1.6. Hydrochar and HTC liquid from pilot-scale sludge HTC

Hydrochar and HTC liquid are two of the substrates used in the experimentation as additives for the anaerobic digestion of the OFMSW, and they originate from the hydrothermal carbonization process of dewatered sludge. As is well known, sewage sludge contains a significant amount of organic matter, which is predominantly composed of proteins, polysaccharides, lipids, humic substances, and nucleic acids (Wang et al., 2019). The HTC process allows the conversion of these organic ingredients through depolymerization into monomers, followed by decomposition with hydrolysis, dehydration, decarboxylation, and deamination, and then by the recombination of the produced reactive fragments through condensation polymerization (Wang et al., 2019); these reactions occur simultaneously as shown in Figure 25.

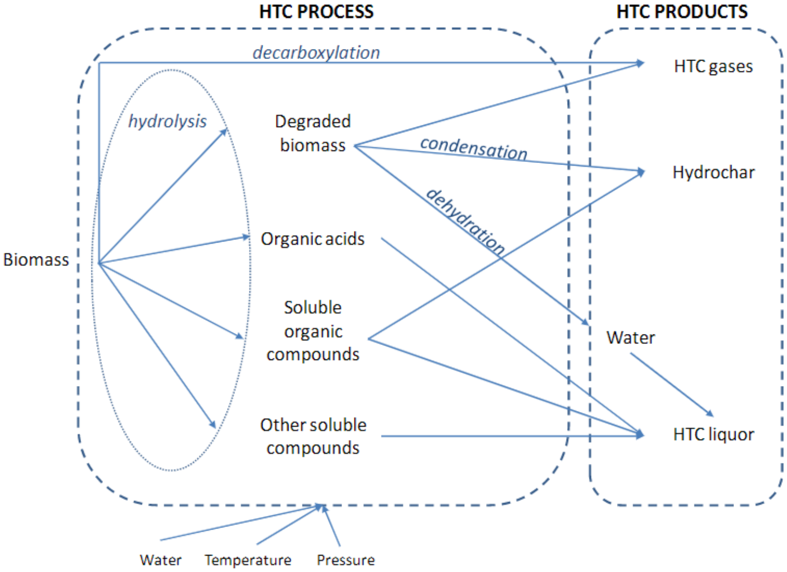


Figure 25 – Reactions of the hydrothermal carbonization process (Langone and Basso, 2020)

This thermochemical process produces a solid carbonaceous product known as hydrochar and a liquid product called HTC liquid, both of which still contain recoverable organic matter. The carbon content in the sludge, following the HTC process under standard conditions, is distributed with 60% into the hydrochar and less than 40% in the liquid phase, while approximately 2% is dispersed in the gas phase (Saetea and Tippayawong, 2013). Regarding phosphorus, after HTC, more than 90% of the total phosphorus present in SS is contained in the hydrochar as precipitated phosphate salts (Heilmann et al., 2014); this gives hydrochar the significant advantage of being usable as a medium for nutrient recovery.

The high temperature and alkaline conditions also facilitate the immobilization of heavy metals in the solid structure of hydrochar, leading to a significant reduction in ecological risk (Huang and Yuan, 2016).

The additional environmental benefit arises from the removal of nitrogen and sulfur during HTC, which consequently eliminates the potential risk of forming gaseous pollutants such as NO_x and SO_x if sludge hydrochar is used as a solid fuel instead of fossil fuels (Zhao et al., 2013).

Compared to initial sewage sludge, hydrochar generally has lower volatile matter content and higher ash content, which is probably the limiting factor for its potential applications in energy and functional materials (Wang et al., 2019)

But the liquid fraction also has value for recovery: some short-chain organic acids such as acetic, propionic and butanoic acid, as well as other organic compounds, are detected into the liquid fraction (Danso-Boateng et al., 2015). It has been reported that 40-70% of the nitrogen (N), 50-70% of the potassium (K), and 10-15% of the phosphorus (P) in sewage sludge could be transferred to the liquid phase, which is then averaged to have 2,000-5,000 ppm N, 100-600 ppm K, and 10-200 ppm P (Wang et al., 2019). Due to the content of macro- and micronutrients, the liquid HTC has great potential for application as an organic fertilizer. For this research project, hydrochar and HTC liquid, which were used as additives in the experimentation, were produced during an additional experimental activity conducted at the Green Propulsion Lab in Fusina (VE), which involved the testing of a pilot-scale HTC reactor with a capacity of 1,000 L, designed by the HBI Group company. A detailed description of the pilot-plant, procedure and activities involved in this process is provided below.

Identification of the dewatered sludge sample

The sludge to be subjected to the HTC process was selected by creating a mean composite sample from sludge collected from six wastewater treatment plants in the province of Foggia, considered the most significant and with a capacity over 20,000 PE. Based on the annual sludge production of each plant, the composition of the mean composite sample was defined as shown in Table 13.

Table 13 – Composition of the representative mean composite sample of sludge from the province of Foggia

WWTPs	**SS production**	**Mean composite sample**
	tons/year	**%**
1	5,807	24
2	4,164	17
3	3,787	16
4	2,370	10
5	4,447	19
6	3,335	14

This dewatered sludge sample was found to have a chemical-physical composition as reported in Table 14.

Table 14 – Extract of the chemical-physical composition of the mean composite sample of the dewatered sludge

Parameter	**Unit**	**Value**
Fixed residue (at 105°C)	%	15.7
Fixed residue (at 550 °C)	%	2.6
LHV	kJ/kg	1,090
LHV	kJ/kg dm	19,150
Carbon	%dm	46,5
Hydrogen	%dm	4,2
Total Nitrogen	%dm	5,5
Total Sulfur	mg/kg dm	8,900

A moisture content of 84% was found in the sample; since for the HTC process it was verified that the best yields were obtained with an initial sample having 90 percent moisture, it was necessary to add water to the sample.

Sample rehydration

The dewatered sludge sample was manually placed into the loading hopper, and then into the mixer the necessary amount of water to reach the target moisture value of 90 percent was added.

Figure 26 – Loading hopper and mixer of the pilot-scale HTC plant

Hydrothermal carbonization

The HTC pilot plant is composed of 2 storage tanks, 2 HTC reactors, and a heat exchanger (as in Figure 27).

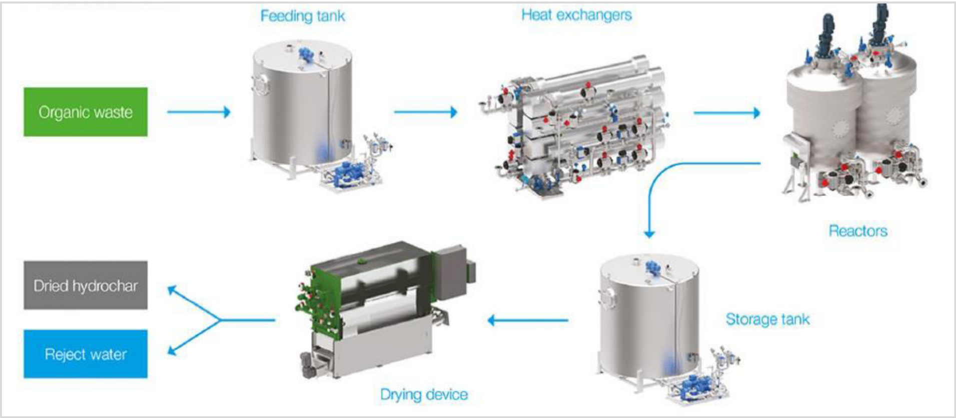


Figure 27 – Flow chart of the pilot-scale HTC plant

The heat exchanger is used to increase the temperature of the sludge entering the reactors.

After the mixing step, a heating time of 120 minutes was required for the reactors, then the sludge was transferred inside them for a residence time of 30 minutes at a temperature of 200°C.

Solid/liquid separation

The slurry exiting the reactor is then sent to the dryer, which allows separation of solid and liquid fraction.

5.2. Experimental protocol of treatability tests

The experimental activities conducted during this research project were carried out at the Environmental Technologies Laboratory of the Polytechnic of Bari. The activities involved the preliminary characterization of the waste to be tested, as well as the activation and monitoring of BMP tests to evaluate the biomethanation capacity of individual substrates and that of their joint treatment.

In 2009, an IWA[3] task group proposed a standard protocol (Angelidaki et al., 2009) to define guidelines for evaluating methane potential to reliable and reproducible assessment of the anaerobic biodegradability of any compound to methane and carbon dioxide.

The BMP test determine the ultimate biogas potential for substrates which means their anaerobic biodegradability; this is a key parameter for assessing design, economic and managing issues for the full scale implementation of anaerobic digestion processes.

In 2015, an international workshop was held to agree on common solutions about BMP test results; the necessary elements for validation and proper execution of BMP tests were defined in the work of Holliger et al., (2016).

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[3] Task Group for the Anaerobic Biodegradation, Activity and Inhibition (ABAI Group) of the Anaerobic Digestion Specialist Group of the International Water Association (IWA).

The protocol adopted to carry out the treatability tests of this experimental project follows the guidelines defined by Angelidaki et al.,and Holliger et al. and it is described in detail in the following sections.

5.2.1. Matrices characterization

Characterization of the substrates to be treated represents the first necessary step in conducting any laboratory test, in order to determine the initial conditions of the matrices and the changes they have undergone as a result of the tests performed.

The characterization assays involve the determination of total solids (TS) and ash content in a material. These data allow for the calculation of the sample's moisture content and its volatile solids (VS) content.

The determination of total solids content is carried out using a thermostatic oven (Figure 28, on the left): an insulated electric furnace that allows temperature regulation.

Figure 28 – Furnaces used for samples characterization: stove (left), muffle furnace (right)

According to the UNI EN 14346:2007 standard, Method A, for the determination of dry matter, the samples to be analyzed (in at least two repetitions) are placed in vessels of known mass and then placed in the stove at 105°C for at least 24 hours. The net weight of the initial sample is defined as "m sample."

The thermal process at this temperature causes the evaporation of water, resulting in the drying of the sample. After the 24-hour period, during which it is assumed that the sample has reached a constant weight, net of tare, the sample is weighed again, thus determining the dry residue at 105°C (denoted as "m 105°C"), which represents the dry matter content (dm), defined as total solids (TS).

$$TS\ (\%) = \frac{\mathrm{m\ 105°C\ (g)}}{m\ sample\ (g)} \times 100 \tag{4}$$

The difference between the final weight and the initial weight represents the mass of evaporated water. By expressing this difference as a percentage of the initial weight of the sample, it is possible to calculate its moisture content.

$$H20\ (\%) = \frac{\mathrm{m\ sample\ (g) - m\ 105°C\ (g)}}{m\ sample\ (g)} \times 100 \tag{5}$$

The dry matter content of a substrate represents the sum of its organic matter and the inert material. Determining the total solids (TS) is essential to understand the concentration of the material to be subjected to digestion.

To remove the inert material from this concentration, the total solids sample obtained from the previous test is subjected to an additional thermal process in a ceramic furnace called muffle furnace (Figure 28, on the right). This specific furnace is made of refractory material, allowing it to reach high temperatures, up to 1000°C.

The dry matter sample to be analyzed, in at least two repetitions, is placed in special ceramic pots (of known tare) and then placed in a muffle furnace, according to the CNR IRSA 2 Q64 vol. 2 ,at temperature of 600°C for at least 6 hours to ensure complete combustion of the sample.

The sample is then removed from the furnace, ensuring it has reached a constant weight, and, net of tare, the residue at 600°C (denoted as "m 600°C") is determined, corresponding to the inert material content of the sample.

$$ASH\ (\%dm) = \frac{m\ 600°\mathrm{C\ (g)}}{m\ 105°C\ (g)} \times 100 \tag{6}$$

The difference between the weight of the sample placed in the muffle and the weight remaining at the end of the process represents the organic matter that has volatilized, which is the volatile solids content (VS) of the sample.

Since the sample placed in the muffle furnace was related to the dry matter, the determination of volatile solids (VS) will be based on the total solids, as in Formula (7).

$$VS\ (\%dm) = \frac{m\ 105°C\ (g) - m\ 600°\mathrm{C}\ (\mathrm{g})}{m\ 105°C\ (g)} \times 100 \tag{7}$$

However, having also determined the percentage of total solids in the original sample, it is thus possible to calculate the volatile solids content relative to the initial sample using the following formulas:

$$VS(\%) = \frac{TS(\%) \times VS(\%dm)}{100} \tag{9}$$

$$VS(g) = \frac{m\ sample\ (g) \times VS(\%)}{100} \tag{10}$$

It can thus be defined that 100% of the sample is the sum of the total solids and the moisture content (Formula 11), while the total solids are the sum of the ash and volatile solids (Formula 12). Therefore, the initial sample is considered to consist of three fractions: moisture content (defined as H20), volatile solids (defined as VS), and ash content (defined as ASH) reported in Formula (13).

$$sample = H20(\%) + TS(\%) \tag{11}$$

$$TS(\%) = ASH(\%) + VS(\%) \tag{12}$$

$$sample = H20\ (\%) + ASH(\%) + VS(\%) \tag{13}$$

5.2.2. Definition of quantities for BMP testing

After characterizing the matrices to be used, it is necessary to identify the combinations of substrates to be treated in each test. Specifically, BMP tests were conducted on the individual substrates to determine the biomethanation potential of each matrix subjected individually to the batch AD process. For each of these tests, an inoculum to substrate ratio (ISR) of 2 was chosen. This parameter represents the ratio between the grams of volatile solids of the inoculum and the grams of volatile solids of the substrate.

$$ISR = \frac{m\,SV\ inoculum\ (g)}{m\,SV\ substrate\ (g)} \tag{14}$$

The ISR is a key parameter of BMP tests; in the work of Holliger et al., (2016), is recommended to use a portion of VS from the inoculum which is greater than that from the substrate, in order to minimize acidification or inhibition problems. In fact, in general is reported to use ISR between 2÷4; but for easily degradable substrates (where rapid accumulation of VFAs could lead to inhibition of AD) an ISR greater than 4 should be applied, while with less degradable substrates (such as lig-nocellulosic), it's better to use an ISR less than 2.

During this experimental project, an ISR of 2 was chosen for all BMP trials. This means that in each reactor, a substrate quantity was added to achieve a mass of volatile solids equal to half of that in the inoculum.

The ISR of 2 was also maintained for the co-digestion tests, but for the new substrate, which itself consists of a mixture of different matrices, the balance among them was chosen on a case-by-case basis. Specifically, for the co-digestion of dehydrated sludge and OFMSW, a ratio of 1.0:2.3 was chosen, corresponding to 30% and 70% by weight, respectively. The same ratio was used for the co-digestion of HTC liquid and OFMSW. This ratio was determined following the regulatory limit (Annex 2 of Legislative Decree 75/2010 and subsequently the Ministerial Decree of 10/07/2013), which stipulates that a '*composted amendment with sludge*' must not contain more than 35% by weight of sludge in the initial mixture. Since, in the context of a biorefinery, the composting of the digestate produced follows the AD process, it was chosen a weight fraction lower than the limit imposed by Italian regulations, in order to ensure that the produced digestate could then be further treated in a composting process.

For substrates such as biochar and hydrochar, is reported that their use as additives to enhance the anaerobic digestion of OFMSW. Therefore, it was decided to add these substrates at a concentration of 13 g per liter of OFMSW suspension.

Since the inoculum, although already digested, continues to produce methane, it is necessary to include some reactors for blank assays in each test, to determine the background methane production from the inoculum. These reactors record daily methane production, and therefore, the BMP of the substrates is determined by subtracting the methane production of the blanks from the gross methane production of the substrate assays (Holliger et al., 2016).

An additional expedient, defined in the protocol, is the use of the microcrystalline cellulose as positive control, because it has a well knowm BMP value, so using this material makes it possible to provide feedback on the reliability of the trial conducted. Indeed, the average theoretical BMP of cellulose is between 340÷395 NmL_{CH4}/gVS; considering a certain data tolerance, if the BMP of the positive control is less then 352 $NL_{CH4}/kgVS$ (<85%) or more then 414 $NL_{CH4}/kgVS$ (>100%) the test cannot be assumed to be valid (Holliger et al., 2016).

5.2.3. Preparation of the CO_2 absorption solution

Before proceeding with the activation of the BMP tests, it was necessary to prepare an alkaline solution to capture CO_2 in order to determine the amount of methane produced during each test. Considering that the biogas derived from AD is a gas mixture composed of 60÷70% CH_4, approximately 30÷40% CO_2, and other trace gases, a basic solution was prepared to precipitate CO_2, thus removing it from the gas phase. This allows the remaining gas to be considered as entirely methane.

The "CO_2 trap" is composed of sodium hydroxide (NaOH) in 3N solution in distilled water. Thymolphthalein is also added to this solution, an indicator that turns blue if the pH is above 9.3÷10.5 in an aqueous environment; otherwise, it remains colorless at lower pH values (Figure 29).

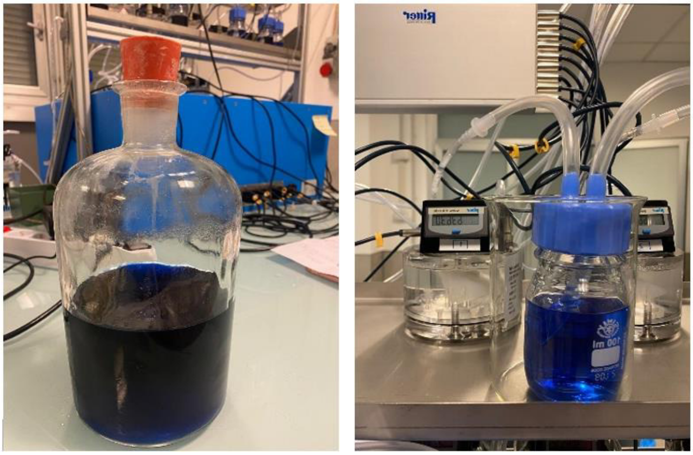

Figure 29 - Device containing the solution defined as “the CO_2 trap”

The fermentation bottles in which biogas is produced are hydraulically connected to the vessels containing this solution; the biogas flows through a dip pipe into the absorption bottle containing the absorption solution and the CO_2 reacts with NaOH, forming sodium carbonate (Na_2CO_3), a salt dissolved in the solution. This neutralization reaction leads to a decrease in the pH of the solution, as the NaOH present decreases by reacting with CO_2. As a result, the solution will gradually be able to remove a smaller amount of CO_2, which would skew the volumetric analysis of the methane produced, overestimating it. For this reason, the addition of Thymolphthalein is necessary, as its blue coloration decreases in intensity as the pH become lowers, i.e., as the NaOH is consumed. Therefore, when it becomes colorless, the solution needs to be replaced with a fresh one. This color change can be observed in Figure 30, where three CO_2 absorption bottles are shown at three different stages: as the NaOH content decreases, due to the lowering of pH, the color of the solution changes from deep blue to colorless.

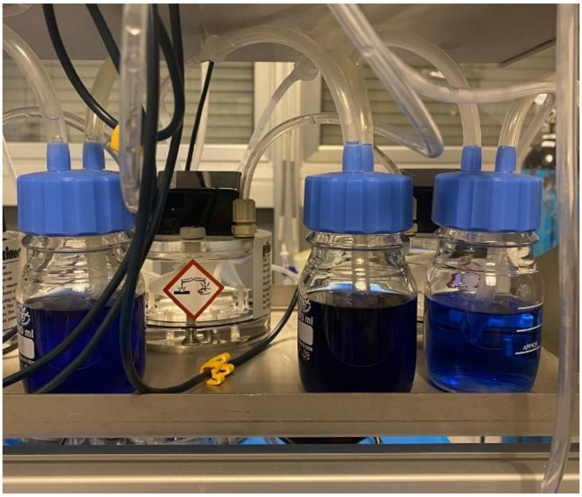

Figure 30 – CO_2 capture solution in different pH stages

5.2.4. Fermentation reactors setup

Biomethanation tests were carried out using the RITTER's Biogas Batch Fermentation System - Type BBFS V4.x equipment (Figure 31).

Figure 31 – Biogas Batch Fermentation System - Type BBFS V4.x

The equipment consists of a central metallic body that acts as an oven: it allows the reactors placed inside, which contain the substrates to be analyzed, to be heated by circulating hot air set at 37°C. The device includes 9 fermentation bottles with a stirring device, each with a volume of 0.5 L. These reactors are filled with the substrate up to a maximum of ¾ of their capacity, leaving free space at the top for the accumulation of the biogas produced. After loading, each reactor is sealed with a lid that not only isolates the substrate but also allows for electrical and hydraulic connection to the rest of the equipment. The reactors are stirred by a mixter powered by an electric motor placed on the lid of each reactor.

There is a pipe on each lid which allows the biogas produced in the reactor to reach the so-called CO_2 trap where, due to the presence of the solution described in section 5.2.3, the CO_2 contained into biogas is absorbed, and the remaining gas can be assumed to be only methane. From the traps, the gas is then directed to the milligas counters, which are 9 devices, one for each reactor. These are filled with a liquid, and the gas enters the vessel through a hole at the bottom; as it moves up, it is found to accumulate below a bascule (Figure 32) with a capacity of 3.25 mL.

Figure 32 – Milligas counter detail

Each time the bascule reaches its maximum capacity, it performs an oscillation that allows the gas to move into the headspace of the milligas, from where it is then expelled. The described oscillating system serves as the volumetric counter for the methane produced by each reactor. The cumulative volume is recorded both by the milligas, with the display on each device, and by the software. Using a temperature sensor, the software can provide the volume of methane produced, already normalized to the standard conditions of 0 °C (273.15 Kelvin) and 1013.25 mbar.

5.2.5. *Starting of BMP tests*

The reactors are loaded considering making at least one duplicate for each matrix to be analyzed, so that a reliable result can be obtained from the average value of multiple tests. After loading the reactors, verifying the airtight seals, and connecting the reactors hydraulically and electrically to the other components of the system, it is necessary to perform a flushing with inert gas to remove the oxygen present inside and ensure anaerobic conditions in each reactor. Molecular nitrogen N_2 is blown into each reactor for about 2 minutes through a valve on the lid; this operation also allows the correct hydraulic connections between the reactor, trap, and milligas to be tested.

After this check, all milligas counters are reset, and the BMP test is started from the software. Specifically, the reactors' temperature is set to 37°C to ensure a mesophilic AD process; the stirring time is 5 minutes with a 10 minutes to be continuously repeated at a speed of 10 rpm.

5.2.6. Test monitoring

The test proceeds continuously, and through the software, it is possible to view the graphs of the cumulative volume of methane produced by each reactor, as well as the respective flow rate (Figure 33).

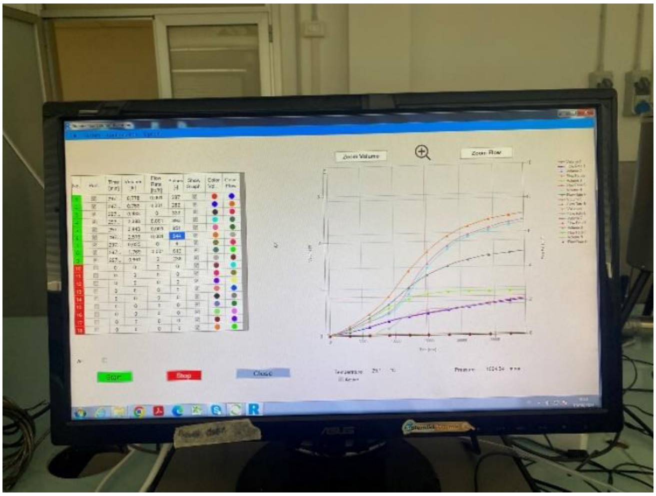

Figure 33 – Management software interface

It is essential to monitor the status of the CO_2 absorbtion bottles by observing the color of the solution to ensure that there is always enough NaOH to capture the CO_2. Additionally, the liquid level in the milligas is monitored to ensure it is always higher than the maximum height of the bascule. Special attention must also be paid to the level of the solution in the trap, as any problems in the reactors could cause the solution to be drawn back into the reactor through suction, compromising the substrate balance.

5.2.7. Gas measurement and BMP calculation

The test is considered finished when, for three consecutive days, each reactor records a methane production less than 1% of the previous day's value. At this point, the test is interrupted, and the data is downloaded from the software.

Due to issues caused by voltage fluctuations, the data recorded by the software often experienced discontinuities. Therefore, for the data analysis of this experimental project, it was decided to use the daily data recorded by the milligas and then to standardize the volumes to temperature and pressure conditions of 273.15 K and 101.325 kPa respectively.

For each test, the data provided by the software and the milligas are compared to ensure the accuracy of the standardization or to highlight any potential issues with the software data acquisition.

The approach used for standardization of biogas volume is the one described by Hafner et al. (2020) in which the standard gas volume is calculated from measured volume in mL (V_{meas}) by correcting for water vapor, temperature, and pressure, applying the following formula:

$$V_{std} = V_{meas} \times \frac{(p_{meas} - p_{H20})}{101.325\ kPa} \times \frac{273.15\ K}{(T_{meas} + 273.15)} \tag{15}$$

Where:

P_{meas}	measured gas pressure (kPa)
T_{meas}	gas temperature at the time of volume measurement (°C)
P_{H20}	water vapor partial pressure (kPa)
273.15 K	standard temperature (0°C)
101.325 kPa	standard pressure (kPa)
V_{std}	standardized gas volume (NmL)

The value of p_{H20} for biogas should be assumed to be the saturation vapor pressure, because biogas is expected to be near equilibrium with anaqueous phase (Hafner et al., 2020); it can be calculated using equation given below.

$$p_{H20} = 0.61094e^{\left(17.625 \times \frac{T_{meas}}{243.04 + T_{meas}}\right)} \tag{16}$$

The measurements recorded by the milligas and the software are cumulative measurements, where the biogas quantity measured at a particular time is the cumulative total, produced in all preceding measurement intervals.

It was therefore possible to determine the trend of the cumulative volume of biogas produced by each reactor. However, it should be considered that, in each reactor, in addition to the substrate to be analyzed, there is also the inoculum, which acts as an activator of the process and contribute with its own rate in the methane production. Therefore, on each test day, for reactors containing only the inoculum, the average volume produced and the daily increase of this value compared to the previous day ($\Delta V_{inoculum}$) are calculated.

The volume of net CH_4 produced by each substrate ($\Delta V_{substrate}$), will then be given by the daily volume recorded by the respective reactor ($\Delta V_{reactor}$), subtracted by the average rate of inoculum production ($\Delta V_{inoculum}$).

$$\mathit{\Delta}V_{substrate} = \Delta \mathrm{V}_{\mathrm{reactor}} - \Delta \mathrm{V}_{\mathrm{inoculum}} \tag{17}$$

It is calculated the average methane production for each substrate and the standard deviations for a complete statistical analysis of data obtained (Angelidaki et al., 2009). The cumulative methane production of each substrate was calculated by adding each daily value of methane production to that produced up to the previous day, thus obtaining the cumulative methane production curve for that specific substrate.

$$V_{i_{substrate}} = V_{i-1_{substrate}} + \Delta \mathrm{V}_{\mathrm{substrate}} \tag{18}$$

The specific methane production is calculated as volume of CH_4 per grams VS (Angelidaki et al., 2009); and so the specific production curve can also be determined. The substrate BMP is considered as the ultimate methane potential given from the ratio of the maximum volume production of CH_4 achieved by that substrate and the grams of volatile solids contained in it.

$$BMP = \frac{V_{CH4}\ (NmL)}{m\ VS\ (g)} \tag{19}$$

The BMP is a distinctive piece of information for a given substrate, so when it is tested in co-digestion with another matrix, to determine the effectiveness of that process, it is possible to compare the methane produced and measured, with the theoretical methane (V_{theor}) that would be obtained by summing the rates produced by the individual matrices as reported in Formula (20).

$$V_{theor} = gVS_1 \times BMP_1 + gVS_2 \times BMP_2 \tag{20}$$

Where gVS_1 e BMP_1 are, respectively, the grams of volatile solids of substrate 1 entered into digestion and the already known BMP of that substrate; the same is true for gVS_2 and BMP_2.

6. RESULTS AND DISCUSSION

In this chapter, the outcomes of a treatability tests conducted at the Environmental Technologies laboratory of the Polytechnic of Bari are presented and discussed in detail.

These tests explored how the yields of digestion processes may differ according to the different organic matrices employed. Specifically, the aim is to evaluate the efficiency and effectiveness of anaerobic co-digestion processes, which involve the simultaneous treatment of different organic waste streams. The primary objective was to determine how different types of waste can be combined in a co-digestion processes to optimize them in terms of increasing methane production. Next, design solutions were hypothesized that would bring together multiple technologies to enhance the joint processes of treating organic waste.

The characterization results of the matrices involved in the experimentation are presented below, followed by the biomethanation tests to which the individual substrates were subjected. Then the co-digestion processes of the OFMSW suspensions from two combined full-scale plants were investigated. For both the matrices of OFMSW from wet-AD plant and from dry-AD plant, co-digestion treatments were tested by BMP tests individually with:

- dewatered sewage sludge (DSS);
- biochar (BC) from sludge pyrolysis;
- hydrochar (HC) from sludge hydrothermal carbonization;
- HTC liquid (HTC-L) from sludge hydrothermal carbonization.

Specifically, 4 scenarios were investigated for the two types of OFMSW (A-B):

Scenario 1: Co-digestion of OFMSW suspension from municipal separate collection then subjected to mechanical pretreatments, with dewatered sludge coming out of WWTPs;

Scenario 2: Co-digestion of OFMSW from municipal separate collection then subjected to mechanical pretreatments, with biochar obtained from drying and pyrolysis process of sludge;

Scenario 3: Co-digestion of OFMSW from municipal separate collection then subjected to mechanical pretreatments, with hydrochar, a solid component from the hydrothermal carbonization process of sludge;
Scenario 4: Co-digestion of OFMSW from municipal separate collection then subjected to mechanical pretreatments, with HTC liquid, a liquid fraction produced as a result of the hydrothermal carbonization process of sludge.

6.1. Materials characterization

This section presents the results of the physico-chemical characterizations of the materials subjected to the BMP tests. Specifically, laboratory analysis for the determination of total solids and volatile solids content were repeated multiple times, not only to obtain accurate information about the material being tested but also to highlight the significant variability and heterogeneity of the product. Despite originating from the same process and the same plant, the material exhibited different characteristics when collected at different times.

6.1.1. Characterization of the pre-treated OFMSW$_A$

The suspension obtained from the pretreatments of the OFMSW at the combined wet AD and composting plant of AMIU Puglia was analyzed. It was sampled at the outlet of the pre-tank, prior to entering the anaerobic digester (see Section 5.1.1); it was subsequently characterized through laboratory tests conducted each time before subjecting the material to BMP tests.

Specifically, the material was analyzed following the methods described in Section 5.2.1 to determine the moisture content of the sample and, in particular, the grams of volatile solids contained in it, as these are responsible for methane production and are necessary for calculating its specific yield.

The results of OFMSW characterization, including the average value and standard deviation, are reported in Table 15.

Table 15 – Results of the laboratory characterizations of $OFMSW_A$

n.	**Total solids** **%**	**Water content** **%**	**Volatile solids** **%dm**	**Volatile solids** **%**	**Ash** **%**
1	1.42	98.58	75.19	1.07	0.35
2	1.73	98.27	81.55	1.41	0.32
3	1.66	98.34	75.66	1.26	0.40
4	1.11	98.89	95.28	1.06	0.05
5	1.16	98.84	87.97	1.02	0.14
Average	1.42	98.58	83.13	1.16	0.25
St. dev.	0.28	0.28	8.55	0.17	0.15

The pretreated $OFMSW_A$ suspension is thus characterized by a very low total solids content, averaging 1.42 percent of which 83 percent are volatile solids, i.e., organic matter.

It is shown that although the material was taken from the same spot in the same plant, it is subject to high variability, mainly due to the heterogeneity of the source material and how it from time to time responds to the physical-mechanical pre-treatments to which it is subjected.

6.1.2. Characterization of the pre-treated $OFMSW_T$

The $OFMSW_T$ suspension, obtained from the combined semi-dry AD and composting plant of TERSAN Puglia company, was also analyzed with laboratory tests conducted to determine the dry matter content, moisture content, and subsequently the ash and volatile solids content.

The material was characterized multiple times based on the tests it was used for, and the results are presented in Table 16. The calculated average values are also reported, which, in this case as well, highlight the high variability of this type of material.

Table 16 – Results of the laboratory characterizations of $OFMSW_T$

n.	Total solids	Water content	Volatile solids	Volatile solids	Ash
	%	%	%dm	%	%
1	14.44	85.56	85.18	12.30	2.14
2	16.41	83.59	90.40	14.83	1.58
3	14.30	85.70	79.20	11.33	2.97
4	8.49	91.51	79.40	6.74	1.75
5	8.50	91.50	81.40	6.92	1.58
Average	12.43	87.57	83.12	10.42	2.00
St. dev.	3.69	3.69	4.73	3.52	0.59

A significantly higher percentage of total solids is observed in the $OFMSW_T$ (12.43%) compared to the TS in the $OFMSW_A$ (1.42%), primarily due to the downstream process being a semi-dry digestion rather than a wet process.

In terms of organic matter, however, the two matrices, $OFMSW_A$ and $OFMSW_T$, exhibit a similar volatile solids content, expressed as a percentage of dry matter, approximately 83% dm.

6.1.3. Inoculum characterization

The inoculum used to start the anaerobic digestion batch tests in the BMP system is a digestate from a full-scale anaerobic digestion plant of olive pomace, from the company Agrolio s.r.l., as described in section 5.1.3. The detailed characterization of this material is given in Table 17.

Table 17 – Physical-chemical characterization of the inoculum

Parameter	Unit	Value	Method
Total solids	%	8.4	DIN EN 12880
Water content	%	91.6	DIN EN 12880
Ash	% dm	20.1	DIN EN 12879
Volatile solids	% dm	79.9	DIN EN 12879
Ammonium_NH4+	mg/L	618.0	MI C03 07 Photometric Method
Ammonium_NH4+-N	mg/L	480.0	MI C03 07 Photometric Method
Acetic Acid	mg/L	38.0	MI C03 09 HPLC for Volatile Fatty Acids
Propionic acid	mg/L	<12	MI C03 09 HPLC for Volatile Fatty Acids

Iso-butyric acid	mg/L	<14	MI C03 09 HPLC for Volatile Fatty Acids
Butyric acid	mg/L	<14	MI C03 09 HPLC for Volatile Fatty Acids
Iso-valeric acid	mg/L	<16	MI C03 09 HPLC for Volatile Fatty Acids
Valeric acid	mg/L	<16	MI C03 09 HPLC for Volatile Fatty Acids
Total VFAs	mg/L	38.0	-
pH	-	7.8	APHA, 20th Edition, 4500-H+ B
Electric conductivity	mS/cm	13.0	APHA, 20th Edition, 2510 B
Redox Potential	mV	-206.0	APHA, 20th Edition, 2580
TAC	mg CaCO3/l	8,320.0	MI C03 11 Titrimetric Method [* FOS-TAC]
FOS	mg HOAC/l	2,190.0	MI C03 11 Titrimetric Method [* FOS-TAC]
FOS/TAC	-	0.26	-

Before using the inoculum for each BMP test, it was re-characterized to determine total solids and volatile solids content, and consequently, the organic matter to be tested. The data from the characterization analyses are presented in Table 18.

Table 18 – Results of the laboratory characterizations of the inoculum

n.	**Total solids**	**Water content**	**Volatile solids**	**Volatile solids**	**Ash**
	%	**%**	**%dm**	**%**	**%**
1	6.07	93.93	81.44	4.94	1.13
2	6.07	93.93	81.86	4.97	1.10
3	5.95	94.05	79.79	4.75	1.20
4	7.47	92.53	94.89	7.09	0.38
5	7.52	92.48	87.41	6.57	0.95
6	5.91	94.09	89.00	5.26	0.65
7	7.85	92.15	96.80	7.60	0.25
8	7.12	92.88	98.20	6.99	0.13
9	8.00	92.00	86.60	6.93	1.07
10	7.22	92.78	85.30	6.16	1.06
11	7.56	92.44	90.60	6.85	0.71
Average	6.98	93.02	88.35	6.16	0.81
St. dev.	0.81	0.81	6.27	1.03	0.38

There is an average total solids content of around 7% with a very small standard deviation; of these total solids, 88% are volatile solids wich means organic matter.

6.1.4. Dewatered sewage sludge characterization

The dewatered sludge used for the BMP tests is a composite mean mix of sludge from wastewater treatment plants in the Apulia region, as described in Section 5.1.4. The results of the characterization performed on this matrix and the resulting average values determined are shown in Table 19.

Table 19 – Results of the laboratory characterizations of dewatered sewage sludge

n.	Total solids	Water content	Volatile solids	Volatile solids	Ash
	%	%	%dm	%	%
1	20.65	79.35	79.93	16.51	4.14
2	21.22	78.78	78.92	16.75	4.47
3	20.60	79.40	72.50	14.94	5.67
Average	20.82	79.18	77.12	16.06	4.76
St. dev.	0.34	0.34	4.03	0.98	0.80

The dewatered sludge is found to have a mean total solids content of 20.82% consistent with the characterizations provided by treatment plant operators and a volatile solids content of 16.06%. This determines, therefore, an ash content of almost 5%, which should be monitored to prevent clogging and accumulation of inert material in the digester which decreases its useful volume, so as to ensure that the process runs properly.

6.1.5. Biochar characterization

The biochar used in the BMP tests came from the pyrolysis process of dewatered and then dried sludge, as described in Section 5.1.5. The material was subjected to chemical and physical analysis (Table 20) to detail its properties for the co-digestion process.

Table 20 - Physical-chemical characterization of the biochar

Parameter	**Unit**	**Value**	**Method**
Total carbon	%	33.6	DIN 51732:2014-07
Higher heating value (HHV)	KJ/kg dm	12,400.0	DIN 51900-3:2005-1
Water content	%	1.7	DIN 51718: 2002-06

Higher Heating Value (HHV)	KJ/kg	12,200.0	DIN 51900-3:2005-1
Lower Heating Value (LHV)	KJ/kg	12,100.0	DIN 51900-3:2005-1
Hydrogen (H)	%	0.6	DIN 51732:2014-07
Ash content (815°C)	%	61.8	DIN 51719: 1997-07
Nitrogen, total (TN)	%	2.4	DIN 51732:2014-07
Total organic carbon (TOC)	%	32.5	DIN EN 15936:2010-11
Volatile matter	%	8.6	DIN 51720: 2001-03

For the pyrolysis process, the physico-chemical properties and yield of biochar are mainly controlled by the feedstock species and thermochemical conditions of the reactions (Ahmad et al., 2014).

The biochar, before being used for the BMP tests under experimentation, was characterized again by performing the tests described in detail in Section 5.2.1, so the results of this characterization are shown in Table 21 with the calculation of the average values and their standard deviation.

Table 21 – Results of the laboratory characterizations of the biochar

n.	Total solids	Water content	Volatile solids	Volatile solids	Ash
	%	%	%dm	%	%
1	93.26	6.74	38.08	35.51	57.75
2	100.00	0.00	39.80	39.80	60.20
3	100.00	0.00	36.40	36.40	63.60
Average	97.75	2.25	38.09	37.24	60.52
St. dev.	3.89	3.89	1.70	2.26	2.94

It can be seen that biochar is a very dry carbonaceous solid having a water content of less than 3 percent. About 38 percent of the dry matter is considered volatile, but the presence of 60 percent ash must also be evaluated.

6.1.6. Hydrochar characterization

The hydrochar used as an additive for OFMSW in the experimental activities was produced through the hydrothermal carbonization of sewage sludge described in section 6.2.5. The solid product resulting from this process, namely hydrochar, was characterized, and the results are reported in Table 22.

For the analyzed parameters are also shown the regulatory limits imposed by the UNI 11853:2022[4] that the material must meet to be considered as a reusable product in the agricultural sector.

Table 22 – Chemical and physical characterization of hydrochar with concentration limits from UNI 11853:2022

Parameter	Unit	Value	Limit value (UNI 11853:2022)
Fixed residue (at 105°C)	%	99.2	
Water content	%	0.8	≤ 10
Fixed residue (at 550 °C)	%	28.8	
Fixed residue (at 550 °C)	%dm	29.0	≤ 35
Volatile solids	%dm	71.0	≤ 70
LHV	kJ/kg	19,150.0	
LHV	kJ/kg dm	19,350.0	≥ 19,000
Carbon	%dm	49.8	
Hydrogen	%dm	8.1	
Total Nitrogen	%dm	2.5	≤ 5
Total Sulfur	%dm	0.7	≤ 1

By comparing the characterization results with the prescribed limits, it is found that the material meets the acceptability criteria for all those shown in the Table, except for volatile solids which are slightly above the limit.

The material was further characterized before its use in the biomethanation tests. The results of these characterizations are presented in Table 23, which also includes the mean values and standard deviations.

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[4] UNI 11853:2022 "Specifics of biochar obtained from hydrothermal carbonization (HTC) treatment of residues from municipal wastewater treatment plants or industrial sludge with organic matrix"

Table 23 – Results of the laboratory characterizations of the hydrochar

n.	Total solids %	Water content %	Volatile solids %dm	Volatile solids %	Ash %
1	88.22	11.78	70.93	62.57	25.65
2	87.61	12.39	74.48	65.25	22.36
3	74.19	25.81	72.50	53.79	20.40
4	88.85	11.15	67.50	59.97	28.88
Average	84.72	15.28	71.35	60.45	24.27
St. dev.	7.04	7.04	2.95	4.90	3.73

The hydrochar is a carbonaceous and porous solid characterized by a very low moisture content and approximately 85% dry matter, of which 70% consists of volatile solids. This material according to its characteristics has many applications, in fact it exhibits a high calorific value, making it suitable for use as a solid fuel in energy production.

If the material does not meet the standards defined by UNI 11853:2022 for application as biolignite, serving as a soil amendment, it can still be further valorized through both thermal and biological processes. Hydrochar stands out as a multi-purpose material with diverse industrial and environmental applications. Indeed, in this experimental activity it is used as an additive to improve microbial activity and biogas yields by enhancing the anaerobic digestion process.

6.1.7. HTC liquid characterization

In the experiment, the liquid fraction derived from the hydrothermal carbonization process of sewage sludge, as described in Section 5.1.6, was also tested as an additive for OFMSW.

The material was characterized in the laboratory prior to being used in the experimental tests. The results of this characterization are presented in Table 24.

Table 24 – Results of the laboratory characterizations of the HTC liquid

n.	**Total solids**	**Water content**	**Volatile solids**	**Volatile solids**	**Ash**
	%	**%**	**%dm**	**%**	**%**
1	1.37	98.63	100.00	1.37	0.00
2	1.53	98.47	92.10	1.41	0.12
3	1.45	98.55	98.90	1.43	0.02
4	1.38	98.62	91.00	1.26	0.12
Average	1.43	98.57	95.50	1.37	0.06
St. dev.	0.07	0.07	4.61	0.08	0.07

This matrix has a very low dry matter content but it is almost all organic matter. In fact this liquid typically contains a high concentration of organic compounds, nutrients (e.g., nitrogen and phosphorus), and soluble intermediates formed during hydrothermal carbonization. The HTC liquid has several potential applications from nutrient recovery to process water recycling, including anaerobic digestion enhancement. The latter assumes that the material is used as a co-substrate or it provides additional nutrients to stimulate microbial activity and improve biogas yields. These properties make the HTC liquid an interesting material for integrated waste valorization strategies and circular economy approaches.

6.1.8. Comparison of substrates characterizations

The results of the laboratory analyses conducted to characterize the various matrices used in the experimentation are compared in Figure 34.

It can be observed that both hydrochar and, even more so, biochar have a high ash content, 24.3% and 60.5%, respectively. As a result, in addition to having these fractions that do not participate in the biological process, they could also cause problems of deposition in the equipment if used in large quantities. However, the advantage lies in their high volatile solids content (60.4% in hydrochar and 37.2% in biochar), which makes these matrices suitable for use as solid additives in the anaerobic digestion of the organic fraction. They can improve buffering capacity and absorb potential process inhibitors; additionally, they contribute to enhancing the structure of the final digestate.

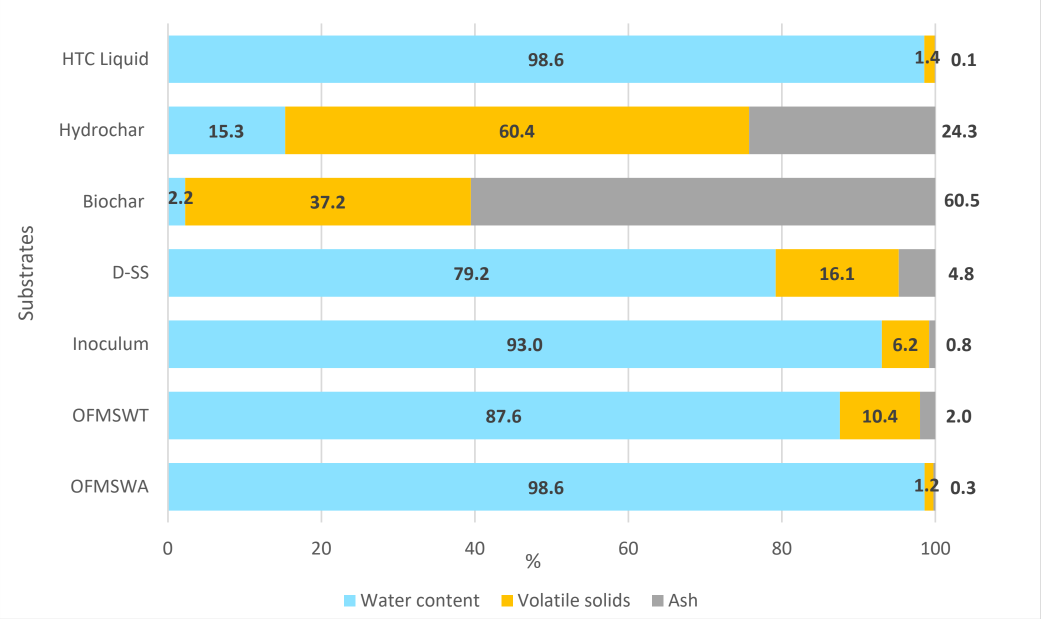

Figure 34 – Comparison of the characterizations of materials under investigation

Biochar, being predominantly composed of ashes, has limited biodegradability. However, it can still be used as an additive because it stabilizes the process by acting as a microbial catalyst and increasing the surface area available for the adhesion of methanogenic bacteria.

The comparison also highlights the similarity between the compositions of $OFMSW_A$ and HTC liquid, both having an almost negligible ash content, a very high water content (98.6%), and a volatile solids content of 1.2-1.4%. HTC liquid could be suitable for co-digestion as it may provide soluble nutrients such as nitrogen, phosphorus, and organic acids, as well as readily degradable substrates to stimulate microbial activity and enhance biogas production.

Dehydrated sewage sludge (DSS), on the other hand, shows good potential for anaerobic digestion due to its relatively high volatile solids content. However, it requires balancing with materials rich in organic content, such as OFMSW, to improve biogas yields.

For these reasons, HTC liquid and DSS are useful additives to optimize microbial nutrition and improve nutrient balance. They are tested at a ratio of 2.3:1.0 (OFMSW:additive) with OFMSW. Substrates like hydrochar and biochar, on the other hand, can be dosed in smaller quantities at a concentration of 13 g/L_{OFMSW}. These materials are used as structural supports and adsorbents to enhance process stability and mitigate potential inhibitions.

6.2. BMP tests results of individual substrates

This chapter presents the results obtained during the biomethanation tests of the individual substrates. The batch reactors, with a capacity of 600 mL, were loaded each time up to a maximum of ¾ of their capacity with inoculum and substrate, ensuring that at least one duplicate reactor was included for each analyzed matrix. An ISR (Inoculum to Substrate Ratio) of 2 was selected and maintained throughout all tests to minimize the risk of inhibition or acidification issues (Holliger et al., 2016).

Therefore, assuming a specific amount of inoculum to be loaded and knowing the dry matter and volatile solids content of both materials, the grams of volatile solids were calculated. Consequently, the total grams of substrate and inoculum to be added to the reactors were also determined. The amount of substrate to be loaded is given by the following formula:

$$m_s = \frac{m_{in} \times TS_{in} \times VS_{in}}{ISR \times TS_s \times VS_s} \tag{21}$$

Where:

- m_{in} Mass of the inoculum (expressed in grams);
- TS_{in} Total solids of the inoculum (expressed as a percentage);
- VS_{in} Volatile solids of the inoculum (expressed as % dry matter);
- m_s Mass of the substrate (expressed in grams);
- TS_s Total solids of the substrate (expressed as a percentage);
- VS_s Volatile solids of the substrate (expressed as % dry matter).

A positive control test was also performed using cellulose, whose BMP was found to be between 345 and 390 mL CH_4/gVS, a value that ensured the reliability and compliance of the experiments (Holliger et al., 2021).

The monitoring of the tests was carried out through daily recording of the data collected from both the milligas counters and the software. It is important to note that the milligas counters provide the CH_4 volume in mL; therefore, data normalization was required (as described in Section 5.2.7) to make the results comparable and evaluate the methane volume produced under standard temperature and pressure conditions (273.15 K and 101.325 kPa, respectively).

By comparing the data provided by the software with the normalized data from the milligas counters, it was confirmed that the normalization process was carried out correctly. In most cases, the normalized data produced a curve that almost always overlaps the one generated by the software. In cases where the curves from the two recordings showed significant discrepancies, this indicated a malfunction of the equipment at the electrical level. For this reason, the milligas data were chosen for manual recording, while the software data were analyzed as a comparative tool.

The tests lasted an average of 33 days and were stopped when a plateau of methane production was reached such that no increases greater than 1 percent were reported, except for special situations described in the following sections.

6.2.1. BMP of pre-treated $OFMSW_A$

The suspension of pretreated $OFMSW_A$ from the AMIU plant was subjected to 3 BMP tests: in one, the methane potential of the substrate alone was determined, while in the other two, methane production from the co-digestion of $OFMSW_A$ with the other substrates was also investigated.

In this section, the monodigestion of $OFMSW_A$ is analyzed and its BMP determined during the T2 test. This trial lasted 42 days and involved the use of an ISR of 2. The average characterization of the substrates used during this trial is shown in Table 25.

Table 25 – Average characterization of the matrices involved in the BMP determination of the substrate $OFMSW_A$

Parameter	Unit	Inoculum	$OFMSW_A$
Total solids	%	5.95	1.42
Water content	%	94.05	98.58
Ash	%	1.20	0.35
Volatile solids	%	4.75	1.07
Volatile solids	%dm	79.79	75.19

In this test, 400 g of inoculum are added to each of the two reactors (R1 and R2) used to represent the "blank"; meanwhile, 100 g of inoculum are added to the two reactors (R8 and R9) also containing the substrate. According to the material characterization, 400 g of inoculum contains 18.99 g of VS, while 100 g contains 4.75 g of VS. To determine the amount of $OFMSW_A$ to be added, the Formula (21) was applied, choosing an ISR value of 2 and knowing the TS (%) and VS (%dm) of both the substrate and the inoculum. Therefore, the quantities reported in Table 26 were loaded into the reactors.

Table 26 – Quantity of inoculum and substrate added to each reactor for the $OFMSW_A$ BMP determination

Reactor	Substrate	Inoculum		$OFMSW_A$	
		g	g VS	g	g VS
R1	Inoculum	400.00	18.99	-	-
R2		400.00	18.99	-	-
R8	Inoculum + $OFMSW_A$	100.00	4.75	222.32	2.37
R9		100.00	4.75	222.32	2.37

Considering that the reactors R1 and R2 contain four times the amount of inoculum compared to that in reactors R8 and R9, to compare the curves and visually represent the production of the $OFMSW_A$, the daily production of reactors R1 and R2 is calculated based on just 100 g of inoculum instead of 400 g. These cumulative production trends, compared with those of reactors R8 and R9, are shown in Figure 35.

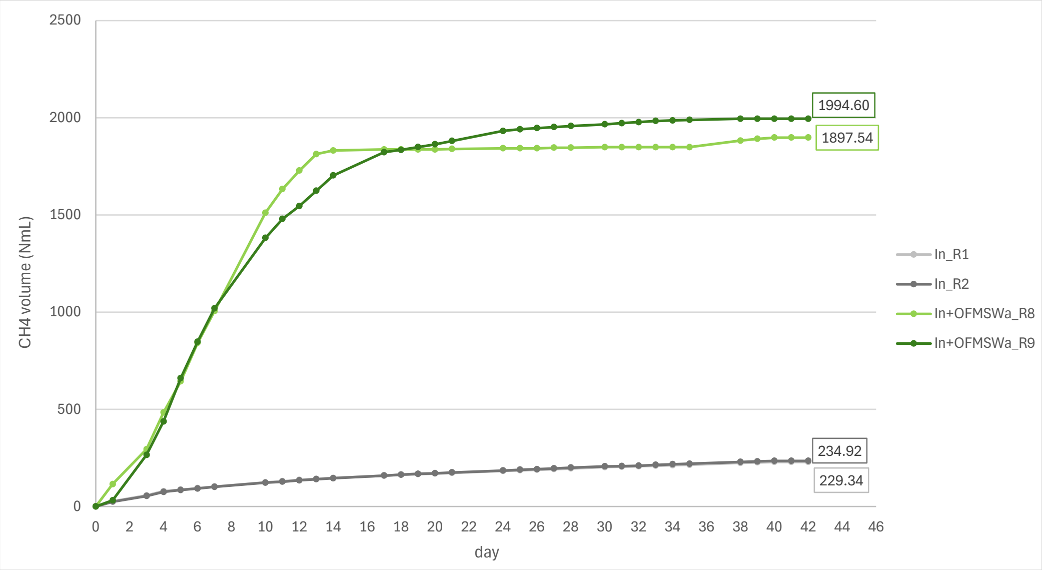

Figure 35 - Gross methane production during 42 days of AD of Inoculum (considering only 100g) and Inoculum with $OFMSW_A$

The graph shows that the two reactors containing inoculum have overlapping production, with an average methane volume of 232.13 NmL.

Regarding the methane production curves of reactors R8 and R9, which contain both inoculum and $OFMSW_A$, it is evident that production in both cases shows rapid growth until the 14th day, after which it begins to stabilize, reaching a production plateau at an average methane volume of 1946.07 NmL. In reactor R8, it seems that some issues occurred, leading to an almost instantaneous stabilization of production, which is therefore unreliable, while the trend observed in reactor R9 is more plausible.

Below, the net methane volume produced by R8 and R9 is calculated by subtracting the daily average production of just the inoculum from the daily increase. The average net methane volume produced by the $OFMSW_A$ on the 42nd day is 1732.81 NmL_{CH4}.

The BMP is calculated by dividing the maximum net methane production by the grams of volatile solids of the substrate; the average value is 731.14 NmL_{CH4}/gVS. The results for each reactor are reported in Table 27.

Table 27 – Summary of the results obtained from the mono-digestion of the pre-treated $OFMSW_A$ suspension in the T2 test

Test	**Reactor**	**Substrate**	**VS** **g**	**Net volume** **NmL_{CH4}**	**BMP** **NmL_{CH4}/gVS**
T2	R1	Inoculum	4.75	229.34	48.28
	R2	Inoculum	4.75	234.92	49.46
	R8	$OFMSW_A$	2.37	1688.40	712.41
	R9	$OFMSW_A$	2.37	1777.21	749.88

Below is the trend of the specific methane production, relating the daily net methane volume produced by $OFMSW_A$ to the grams of volatile solids that generated it.

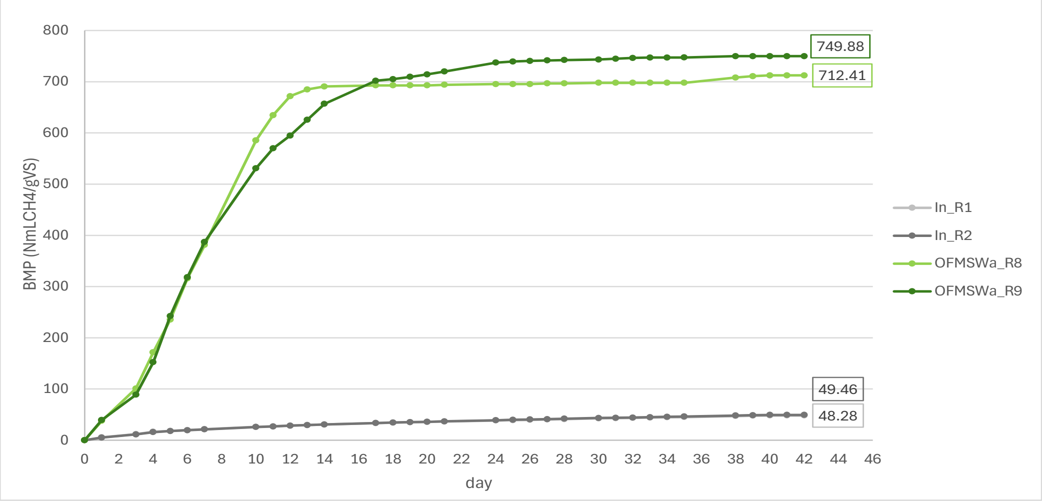

Figure 36 – Trend of BMP during mono-AD of $OFMSW_A$

In the literature is found that food waste determine an high methane production around 300÷600 NmL_{CH4}/gVS (Garcia et al., 2019), the BMP resulting from this test is higher than the classical range defined in the literature; this means that the material is characterized by organic substances that result in a high potential for methanation.

6.2.2. BMP of pre-treated OFMSW$_T$

The suspension of the pre-treated OFMSWT from the TERSAN combined plant was subjected to 4 BMP tests, in which both the methane potential of the substrate alone and the methane production from the co-digestion of the OFMSWT with other substrates were determined. In this section, the BMP of the OFMSWT in mono-digestion, determined in test T7, is analyzed. This test had an ISR of 2 and lasted 36 days. The average characterization of the substrates used is reported in Table 28.

Table 28 – Average characterization of the matrices involved in the BMP determination of the substrate OFMSW$_T$

Parameter	Unit	Inoculum	OFMSW$_T$
Total solids	%	7.61	14.18
Water content	%	92.39	85.82
Ash	%	1.07	2.27
Volatile solids	%	6.54	11.91
Volatile solids	%dm	85.98	84.00

A total of 200 g of inoculum were added to each of the two reactors (R1 and R2), representing the "blank" as well as to the two reactors (R4 and R5) containing the substrate. According to the material characterization, 200 g of inoculum contains 13.09 g of VS. To determine the amount of OFMSW$_T$ to be added, the inverse formula of the ISR (Formula 21) was applied, maintaining an ISR of 2 and knowing the TS (%) and VS (%dm) of both the substrate and the inoculum. Therefore, the quantities reported in Table 29 were loaded into the reactors.

Table 29 – Quantity of inoculum and substrate added to each reactor for the OFMSW$_T$ BMP determination

Reactor	**Substate**	**Inoculum**		**OFMSW$_T$**	
		g	**g VS**	**g**	**g VS**
R1	Inoculum	200.00	13.09	-	-
R2		200.00	13.09	-	-
R4	Inoculum + OFMSW$_T$	200.00	13.09	54.93	6.54
R5		200.00	13.09	54.93	6.54

The methane produced by each reactor was recorded, and the data obtained from the volumetric counters, after being normalized, were used to develop the cumulative CH4 production trends shown in Figure 37.

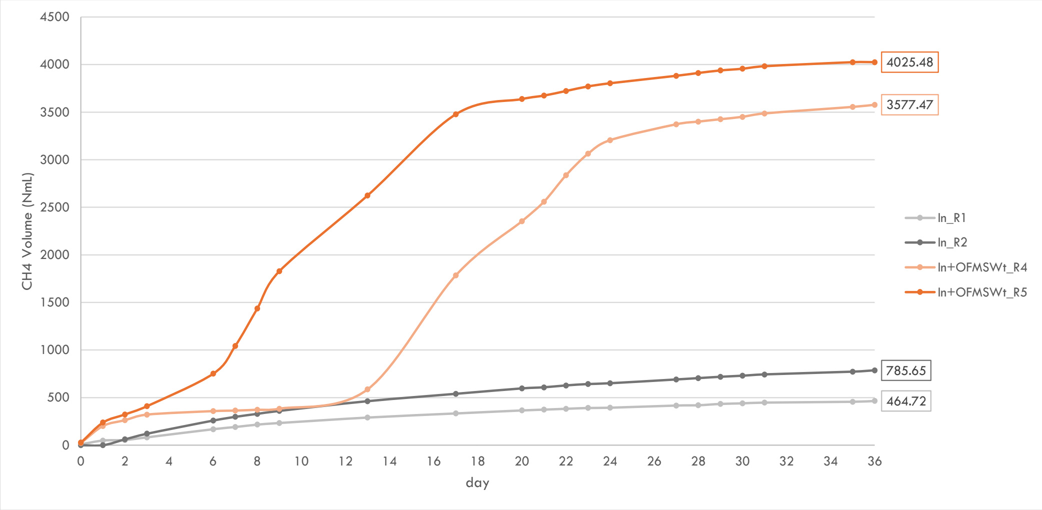

Figure 37 – Gross methane production during 36 days of AD of Inoculum and Inoculum with $OFMSW_T$

The graph shows that the two reactors containing inoculum have a similar methane production trend, with an average final value of 625.19 NmL_{CH4}. Regarding the methane production curves of reactors R4 and R5, which contain both inoculum and $OFMSW_T$, it can be observed that reactor R5 shows rapid growth in methane production, reaching more than 80% of its total production in the first 17 days, followed by a stabilization phase in the subsequent days. Reactor R4, on the other hand, only reaches 500 NmL of methane production in the first 13 days, suggesting that the process was slowed down in its initial phase. After that, the production follows a growth trend similar to that of reactor R5, but shifted by a week. This difference may be due to the inherent heterogeneity of the substrate, which could have caused slower and overall lower methane production in reactor R4 compared to reactor R5. The average methane volume produced by both reactors is 3801.47 NmL. The production plateau is reached by both reactors on the 28th day, with a production increase of less than 1%. The net methane volume produced by R4 and R5 is calculated by subtracting from each reactor's daily production the average daily production of the inoculum (R1 and R2). Table 30 reports the net methane volumes produced by OFMSWT on the 36th day and the calculated BMP. On average, this substrate produced 3323.58 NmL of methane, resulting in an average BMP of 508.19 NmL_{CH4}/gVS.

Table 30 – Summary of the results obtained from the mono-digestion of the pre-treated $OFMSW_T$ suspension in the T7 test

Test	Reactor	Substrate	VS g	Net volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T7	R1	Inoculum	13.09	464.72	35.50
	R2	Inoculum	13.09	785.65	60.02
	R4	$OFMSW_T$	6.54	3231.22	494.07
	R5	$OFMSW_T$	6.54	3415.94	522.32

The trend of specific methane production is shown below, relating the daily net methane volume produced by OFMSWT to the grams of volatile solids that generated it.

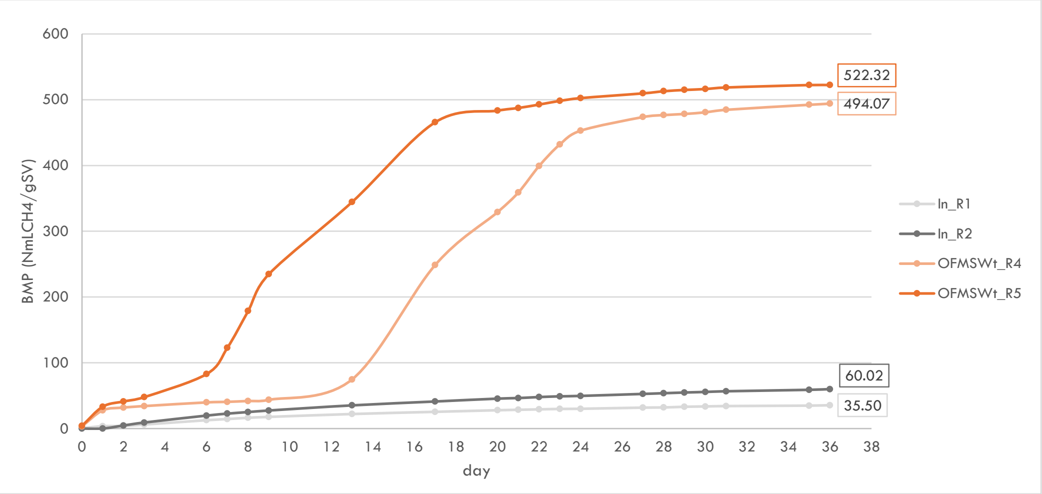

Figure 38 – Trend of BMP during mono-AD of $OFMSW_T$

A similar trend in specific methane production is observed for the two $OFMSW_T$ samples, with an average value of 508.19 NmL_{CH4}/gVS. This result is consistent with literature data, which indicate that food waste produces methane in the range of 300÷600 NmL_{CH4}/gVS (Garcia et al., 2019).

6.2.3. BMP of dewatered sludge

The dewatered sewage sludge (DSS) was subjected to 3 BMP tests, in which the methane potential of the substrate alone and the methane production from the co-digestion of DSS with OFMSW were determined. In this section, the BMP of DSS in mono-digestion, determined in test T2, is analyzed. This test had an ISR of 2 and lasted 42 days. The average characterization of the substrates used is reported in Table 31.

Table 31 – Average characterization of the matrices involved in the BMP determination of the substrate DSS

Parameter	Unit	Inoculum	DSS
Total Solids	%	5.95	20.94
Water content	%	94.05	79.06
Ash	%	1.20	4.31
Volatile Solids	%	4.75	16.63
Volatile Solids	%dm	79.79	79.42

A total of 400 g of inoculum was added to each of the two reactors (R1 and R2), representing the "blank" as well as to the three reactors (R5, R6, and R7) containing the substrate. According to the material characterization, 400 g of inoculum contains 18.99 g of VS. To determine the amount of DSS to be added, Formula (21) was applied, maintaining an ISR of 2 and using the known TS (%) and VS (%dm) values of both the substrate and the inoculum. The quantities loaded into the reactors are reported in Table 32.

Table 32 – Quantity of inoculum and substrate added to each reactor for the DSS BMP determination

Reactor	Substate	Inoculum		DSS	
		g	g VS	g	g VS
R1	Inoculum	400.00	18.99	-	-
R2		400.00	18.99	-	-
R5	Inoculum + DSS	400.00	18.99	57.11	9.50
R6		400.00	18.99	57.11	9.50
R7		400.00	18.99	57.11	9.50

The CH4 volume produced by each reactor was recorded, and the data collected from the volumetric counters, after being normalized, were used to develop the cumulative production trends shown in Figure 39.

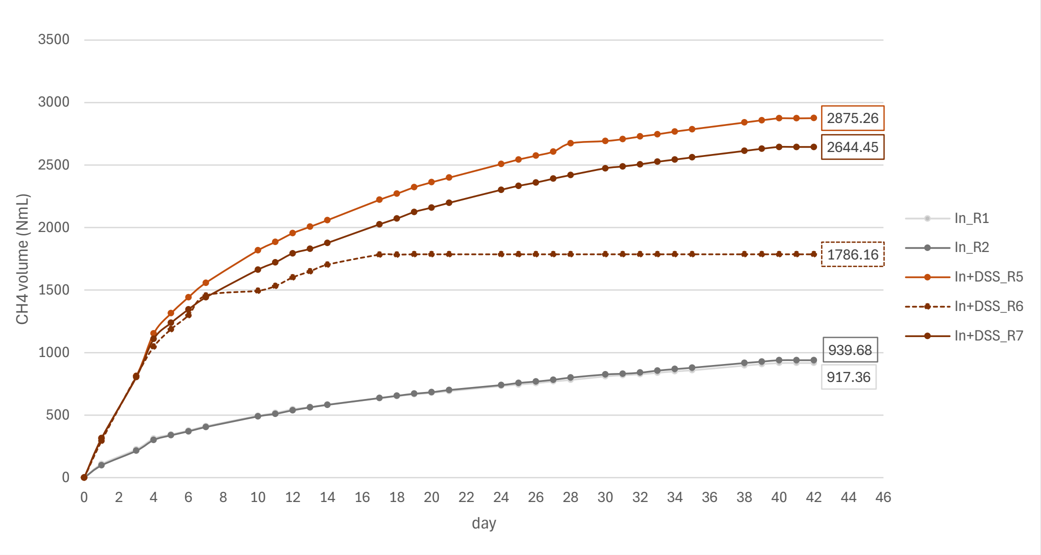

Figure 39 – Gross methane production during 42 days of AD of Inoculum and Inoculum with DSS

The graph shows that the two reactors containing inoculum have overlapping methane production trends, with an average final value of 928.52 NmL_{CH4}.

Regarding the methane production curves of reactors R5, R6, and R7, which contain both inoculum and DSS, it can be observed that during the first 7 days, the methane production of the three reactors is similar, already reaching 1500 NmL, which corresponds to more than half of the final maximum value.

In the following days, the production rate decreases, and in particular, for reactor R6, the cumulative methane volume stops at 1786.16 NmL from the 19th day onward. This curve is represented with a dashed line because, compared to the other two reactors containing the same substrates, its methane production appears to have been interrupted due to factors inhibiting the process. Therefore, the results from this reactor are discarded, and only the outcomes from reactors R5 and R7 are considered valid.

The curves of reactors R5 and R7, on the other hand, show a similar trend, with a difference of about 200 NmL, resulting in an average cumulative methane volume of

2759.85 NmL_{CH4}, with a production plateau reached by both reactors as early as the 25th day.

The net methane volume produced by R5 and R7 is calculated by subtracting the average daily production of the inoculum (R1 and R2) from the daily production of each reactor. Table 33 reports the net methane volumes produced by DSS on the 42nd day, along with the calculated BMP. On average, this substrate produced a net methane volume of 1844.97 NmL, resulting in a mean BMP of 194.21 NmL_{CH4}/gVS.

Table 33 - Summary of the results obtained from the mono-digestion of DSS in the T2 test

Test	**Reactor**	**Substrate**	**VS** **g**	**Net volume** **NmL_{CH4}**	**BMP** **NmL_{CH4}/gVS**
T2	R1	Inoculum	18.99	917.36	48.31
	R2	Inoculum	18.99	939.68	49.48
	R5	DSS	9.50	1973.79	207.77
	R7	DSS	9.50	1716.16	180.65

The specific production trend is shown below by relating the net daily volume of methane produced by DSS to the grams of volatile solids that generated it.

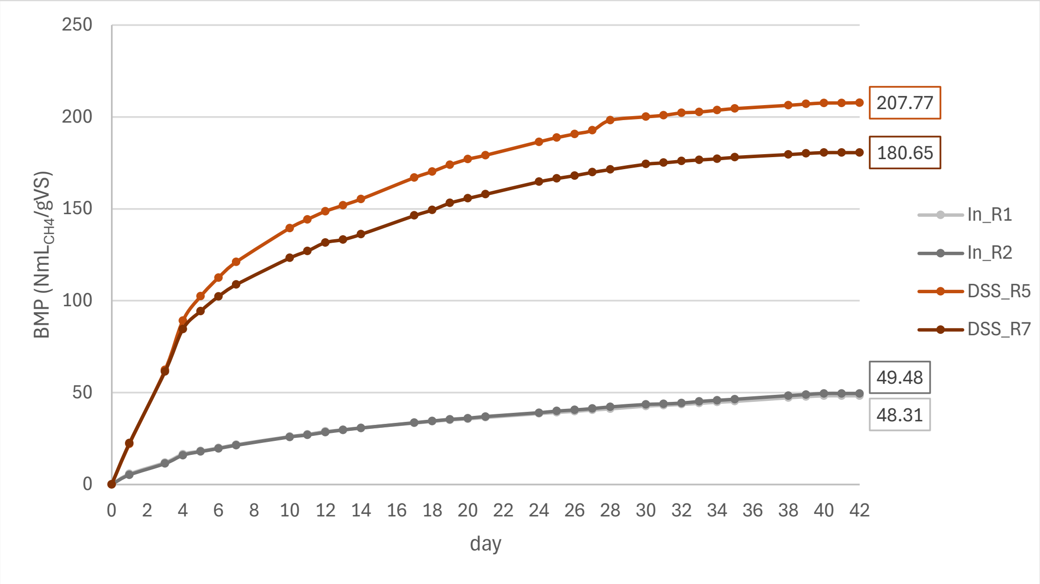

Figure 40 – Trend of BMP during mono-AD of DSS

The average measured BMP of DSS is 194.21 NmL_{CH4}/gVS, a value within the range found in the literature; the SS having a high level of carbohydrates, lipids, and proteins allow a potential methane production ranging from a minimum of 175 L/kgVS to a maximum of 475 L/kgVS (Thorin et al., 2018).

Also Chen et al. (2019) conducted anaerobic fermentation on dewatered SS, obtaining soluble proteins and VFAs as the primary products. In addition, some recalcitrant inhibiting compounds (humic acid-like compounds, melanoidins, nitrogen heterocyclesand phenols) were also found.

6.2.4. BMP of biochar from sludge pyrolysis

Biochar (BC), produced by the pyrolysis process of dewatered sludge, was subjected to 5 BMP trials: in the T6 test, its methanogenic potential was determined, while in the other trials it was used with the two types of OFMSW to test co-digestion and determine its methanation potential. The T6 trial had a duration of 33 days. The average characterization of the substrates used is shown in Table 34.

Table 34 – Average characterization of matrices involved in the BMP determination of the substrate biochar

Parameter	Unit	Inoculum	Biochar
Total Solids	%	7.48	100.00
Water content	%	92.52	0.00
Ash	%	0.18	61.90
Volatile Solids	%	7.30	38.10
Volatile Solids	%dm	97.48	38.10

A total of 150 g of inoculum was added to each of the two reactors (R1 and R2), representing the "blank" as well as to the two reactors (R4 and R5) containing the substrate. According to the material characterization, 150 g of inoculum contains 10.94 g of VS. To determine the amount of biochar to be added, formula (Formula 21) was applied, maintaining an ISR of 2 and using the known TS (%) and VS (%dm) values of both the substrate and the inoculum. Therefore, the quantities loaded into the reactors are reported in Table 35.

Table 35 – Quantity of inoculum and substrate added to each reactor for the biochar BMP determination

Reactor	**Substate**	**Inoculum**		**Biochar**	
		g	**g VS**	**g**	**g VS**
R1	Inoculum	150.00	10.94	-	-
R2		150.00	10.94	-	-
R4	Inoculum + BC	150.00	10.94	14.36	5.47
R5		150.00	10.94	14.36	5.47

The CH4 volume produced by each reactor was recorded, and the data collected from the volumetric counters, after being normalized, were used to develop the cumulative production trends (Figure 41). It is noted that reactors R2 and R4 experienced malfunctions from the early stages, so only the results from reactors R1 and R5 are reported in the analysis.

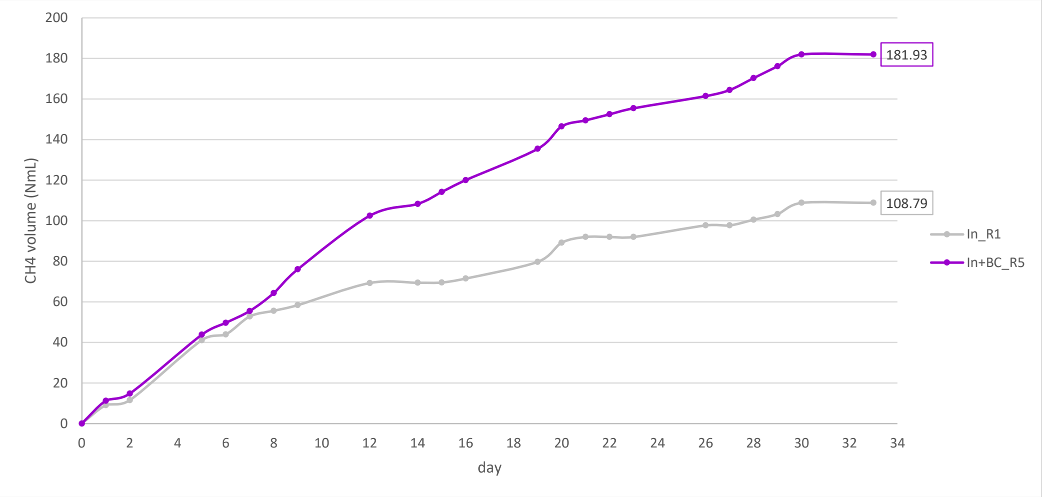

Figure 41 – Gross methane production during 33 days of AD of Inoculum and Inoculum with biochar

The graph highlights that during the initial phase (first 7 days), reactor R5 containing inoculum and biochar, shows a curve similar to that of R1, suggesting a low methane production from the substrate. From day 8 until day 33, the production increases, even if slowly, reaching a gross cumulative methane volume of 181.93 NmL, which is lower than the expected values. Biochar is not considered a material with a high biogas production capacity, but it is used because, with its porous structure and high specific surface area, it can enhance methane production by providing a surface for microorganism adhesion. Therefore, it is tested as an additive to improve the methane production capacity of the main substrate (OFMSW).

The net methane volume produced by the biochar is calculated by subtracting the daily production of reactor R1 from the daily production of reactor R5. Table 36 reports the net methane volumes produced by biochar on day 33, along with the calculated BMP. For this substrate, the methane production is considered to be 128.63 NmL, resulting in a BMP of 23.51 NmL_{CH4}/gVS.

Table 36 - Summary of results obtained from biochar mono-digestion in the T6 trial

Test	Reactor	Substrate	VS g	Net volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T6	R1	Inoculum	10.94	108.79	9.94
	R5	BC	5.47	128.63	23.51

The trend of specific methane production is shown below, relating the daily net volume of CH4 produced by the biochar to the grams of volatile solids that generated it.

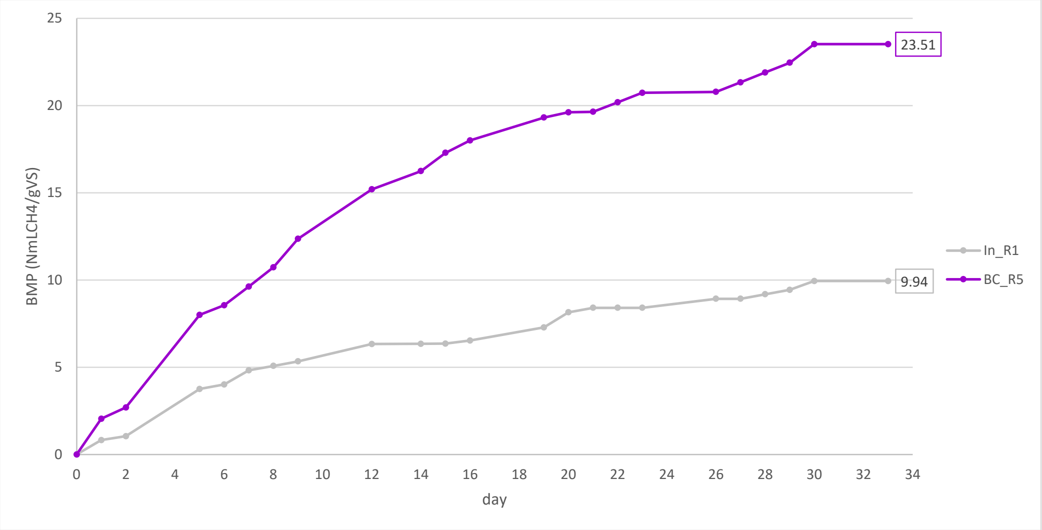

Figure 42 – Trend of BMP during mono-AD of biochar

The BMP of the biochar is quite low, likely due to its high ash content (60%), which results in limited biodegradability.

6.2.5. BMP of hydrochar from hydrothermal carbonization of sludge

The hydrochar (HC), produced from the HTC process of sewage sludge, was subject to 4 BMP trials: in test T6, its methanogenic potential was determined, while in the other trials, it was used with the two types of OFMSW to test co-digestion and assess its methane potential; test T6 lasted 33 days. The average characterization of the substrates used is reported in Table 37.

Table 37 – Average characterization of matrices involved in BMP determination of hydrochar substrate

Parameter	**Unit**	**Inoculum**	**Hydrochar**
Total Solids	%	7.48	81.52
Water content	%	92.52	18.48
Ash	%	0.18	24.63
Volatile Solids	%	7.30	56.89
Volatile Solids	%dm	97.48	69.79

A total of 150 g of inoculum was added to each of the two reactors (R1 and R2), representing the "blank" as well as to the two reactors (R6 and R7) containing the substrate. According to the material characterization, 150 g of inoculum contains 10.94 g of VS. To determine the amount of hydrochar to be added, Formula (21) was applied, maintaining an ISR of 2 and using the known TS (%) and VS (%dm) values of both the substrate and the inoculum. Therefore, the quantities loaded into the reactors are reported in Table 38.

Table 38 – Quantity of inoculum and substrate added to each reactor for the hydrochar BMP determination

Reactor	**Substate**	**Inoculum**		**Hydrochar**	
		g	**g VS**	**g**	**g VS**
R1	Inoculum	150.00	10.94	-	-
R2		150.00	10.94	-	-
R6	Inoculum + HC	150.00	10.94	9.62	5.47
R7		150.00	10.94	9.62	5.47

The CH4 volume produced by each reactor was recorded, and the data collected from the volumetric counters, after being normalized, were used to develop the cumulative production trends presented in Figure 43. It is noted that reactor R2, as mentioned in the previous section, experienced a malfunction from the early stages, so it was excluded from the analysis.

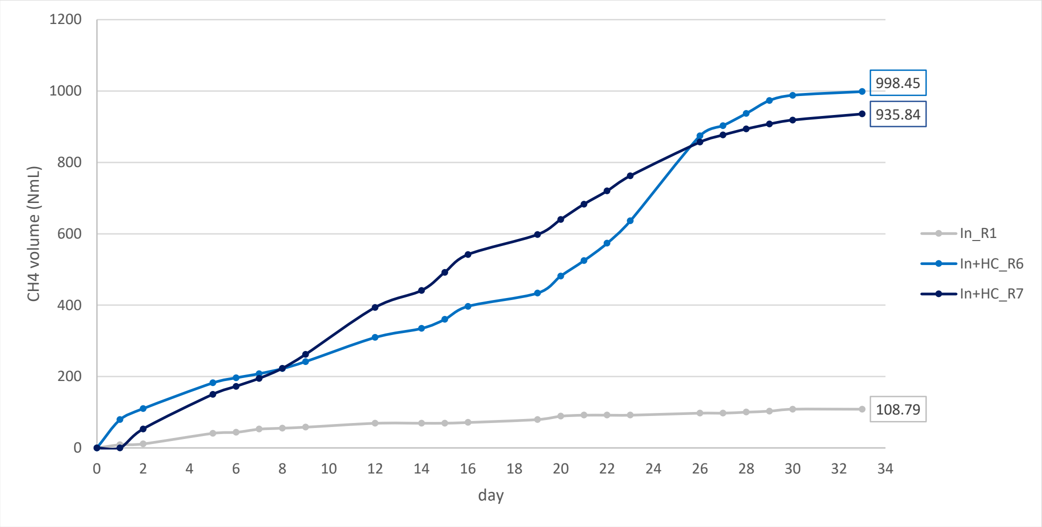

Figure 43 – Gross methane production during 33 days of AD of Inoculum and Inoculum with hydrochar

The graph clearly shows that the methane production in the reactors containing both inoculum and hydrochar deviates significantly from the curve of reactor R1, in contrast to the trend previously observed for the biochar. The two reactors, R6 and R7, record an average cumulative methane production of 967.15 NmL_{CH4}.

The net methane volume produced by R6 and R7 is then calculated by subtracting the daily methane production of the blank from the daily production of each reactor. Table 39 reports the net methane volumes produced by the hydrochar at day 33, along with the BMP calculated.

This substrate produced a mean net methane volume of 862.86 NmL, resulting in an average BMP of 157.74 NmL_{CH4}/gVS.

Table 39 – Summary of the results obtained from the mono-digestion of the hydrochar in the T6 test

Test	Reactor	Substrate	VS g	Net volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T6	R1	Inoculum	10.94	108.79	9.94
	R6	HC	5.47	889.66	162.64
	R7	HC	5.47	836.06	152.85

The specific methane production trend is shown in Figure 44 which relates the daily net CH4 volume produced by the hydrochar to the grams of volatile solids that generated it.

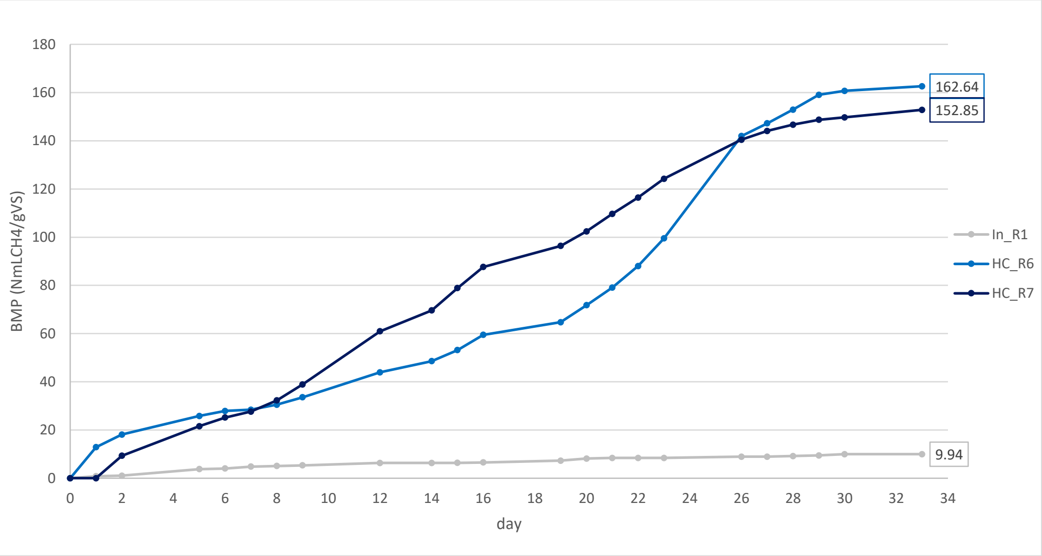

Figure 44 – Trend of BMP during mono-AD of hydrochar

The hydrochar reaches an adequate BMP value, considering that it is a solid matrix containing 24% ash, which can limit its biodegradability. However, this matrix has a methane potential of about 160 NmL_{CH4}/gVS, which could be optimized by combining it with other matrices that are richer in degradable organic substances.

6.2.6. BMP of HTC liquid from hydrothermal sludge carbonization

The HTC liquid (HTC-L) is the liquid phase produced by the hydrothermal carbonization process of sewage sludge. This matrix was subject to 3 BMP tests: in test T8, its methane potential was determined, while in the other tests, it was used in combination with two types of OFMSW to evaluate co-digestion and determine its methane potential. Trial T8 lasted for 37 days. The average characterization of the substrates used is reported in Table 40.

Table 40 – Average characterization of the matrices involved in the BMP determination of the substrate HTC liquid

Parameter	Unit	Inoculum	HTC liquid
Total Solids	%	7.63	1.41
Water content	%	92.37	98.59
Ash	%	0.72	0.07
Volatile Solids	%	6.91	1.34
Volatile Solids	%dm	90.55	94.94

A total of 150 g of inoculum was added to each of the two reactors (R1 and R2), representing the "blank" as well as to the reactors R8 and R9 containing the substrate. According to the material characterization, 150 g of inoculum contains 10.36 g of VS. To determine the amount of HTC liquid to be added, the Formula (21) was applied, maintaining an ISR of 2 and knowing the TS (%) and VS (% dry matter) of both the substrate and the inoculum. The quantities added to the reactors are reported in Table 41.

Table 41 – Quantity of inoculum and substrate added to each reactor for the HTC-L BMP determination

Reactor	**Substate**	**Inoculum**		**HTC liquid**	
		g	**g VS**	**g**	**g VS**
R1	Inoculum	150.00	10.36	-	-
R2		150.00	10.36	-	-
R8	Inoculum + HTC-L	150.00	10.36	385.24	5.18
R9		150.00	10.36	385.24	5.18

The methane volume produced by each reactor was recorded, and the data collected from the volumetric counters were subsequently normalized. These normalized data were used to develop the cumulative production trends (Figure 45). It should be noted that reactors R2 and R8 experienced malfunctions from the initial phase, so only the results from reactors R1 and R9 are included in the analysis.

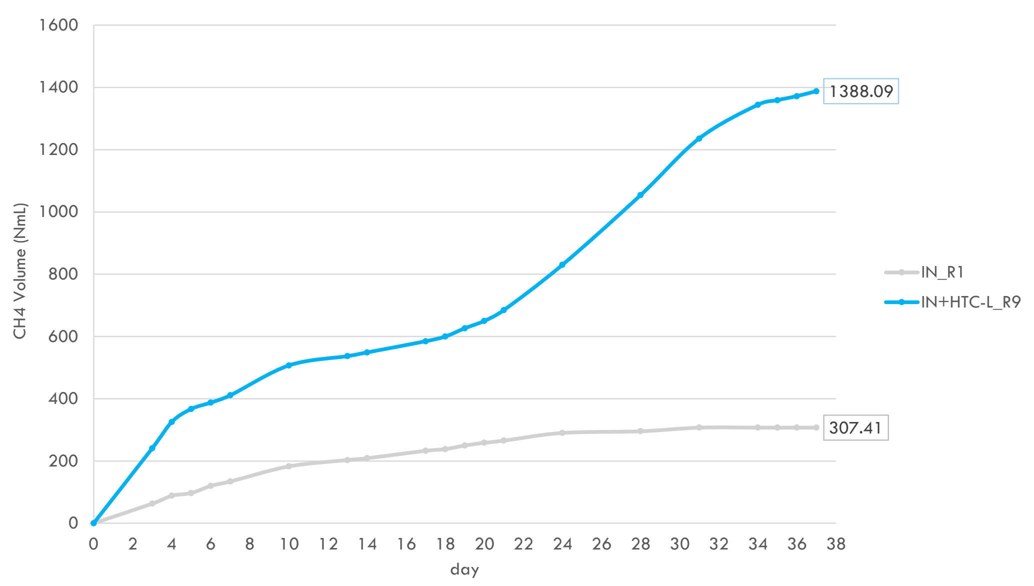

Figure 45 – Gross methane production during 37 days of AD of Inoculum and Inoculum with HTC-L

From the graph, it is evident that the curve of R1 shows a constant growth trend until it stabilizes around day 24. On the other hand, the curve of the cumulative volume produced by R9 shows a noticeable lag phase, which represents the adaptation time needed by the microbiota. From day 16 onwards, the curve accelerates sharply, reaching a gross cumulative methane volume of 1388.09 NmL.

The net methane volume produced by the HTC liquid is then calculated by subtracting the daily production of reactor R1 from the daily increment of reactor R9. In Table 42, the net methane volumes produced by HTC-L on day 37 and the calculated BMP are reported. For this substrate, a net production of 1112.31 NmL of methane is considered, resulting in a BMP of 214.73 NmL_{CH4}/gVS.

Table 42 – Summary of the results obtained from the mono-digestion of HTC-L in the T8 test

Test	Reactor	Substrate	VS g	Net volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T8	R1	Inoculum	10.36	307.41	29.67
	R9	HTC-L	5.18	1112.31	214.73

The trend of specific methane production is presented below, relating the daily net volume of CH4 produced by the HTC liquid to the grams of volatile solids that generated it.

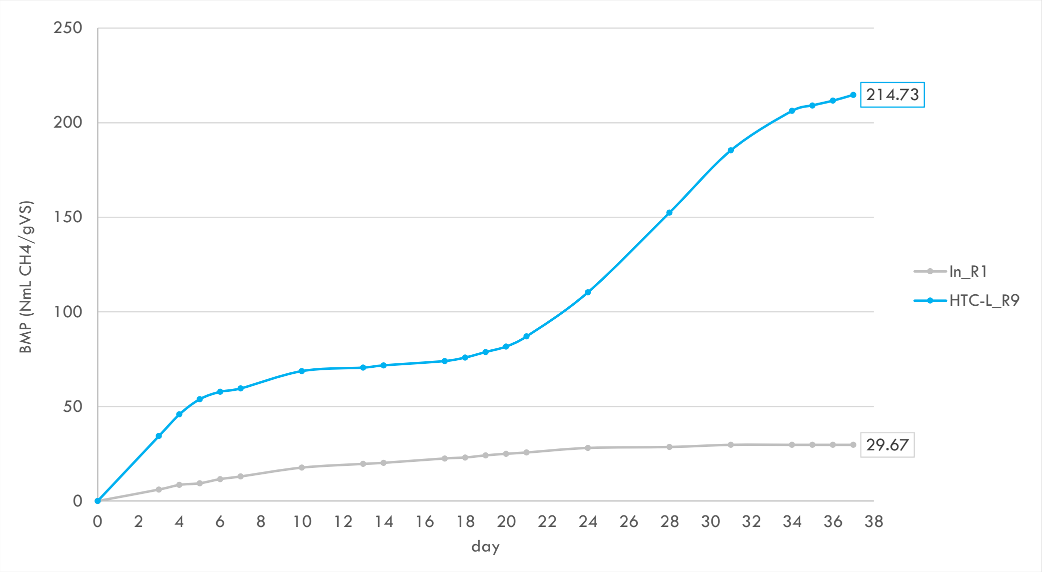

Figure 46 – Trend of BMP during mono-AD of HTC-L

It is noted from the graph that the liquid HTC achieves a high BMP, higher than the hydrochar described in Section 6.2.5. It is believed that after the hydrothermal carbonization process, the nutrients and organics contained in the sludge were predominantly transferred to the liquid phase, making the HTC-L substrate an excellent additive of OMFSW, capable of providing soluble nutrients to the digestion process.

6.2.7. Comparison of individual substrates BMP

To compare the BMP outcomes of each substrate, the average values of specific methane production determined during the individual tests described in the previous sections are shown in Figure 47. The matrices are compared to understand how the specific methane production trends of individual substrates vary over time.

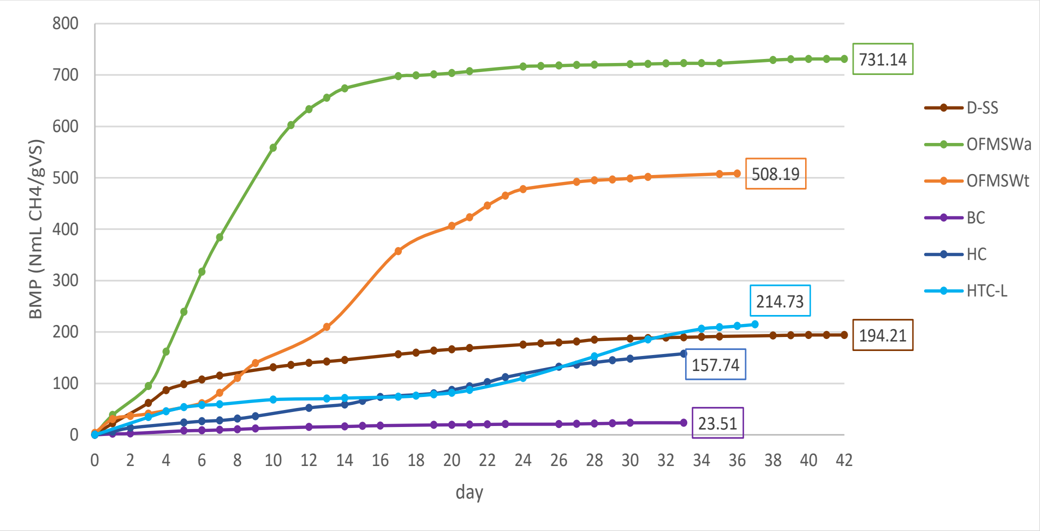

Figure 47 – Comparison of the average biomethanation potential of the tested substrates: $OFMSW_A$, $OFMSW_T$, DSS, BC,HC, HTC liquid

The BMP of dewatered sludge and OFMSWT are in their usual ranges, also attested by scientific literature, while biochar and hydrochar are solid carbonaceous matrices that are not naturally characterized by high methanogenic power. In fact, the BMP of biochar is very low, while the BMP of hydrochar reaches a significant value that is interesting to monitor and compare with the values achieved by the same material in co-digestion with OFMSW. HTC liquid, on the other hand, seems to have a methanation potential comparable to those of sludge, which is, in any case, the starting matrix from which it comes. The results obtained from mono-digestions of these matrices are summarized in Table 43.

Table 43 – Average results of mono-digestion processes of $OFMSW_A$, $OFMSW_T$, DSS, BC, HC and HTC-L

Test	Mono-digestions	VS g	Net volume NmL_{CH4}	Mean BMP NmL_{CH4}/gVS
T2	$OFMSW_A$	2.37	1732.81	731.14
T2	DSS	9.50	1844.97	194.21
T7	$OFMSW_T$	6.54	3323.58	508.19
T6	BIOCHAR	5.47	128.63	23.51
T6	HYDROCHAR	5.47	862.86	157.74
T8	HTC LIQUID	5.18	1112.31	214.73

6.3. Implementation of AD process of $OFMSW_A$ using organic additives

This chapter describes the BMP tests conducted to evaluate the anaerobic co-digestion process of the pre-treated suspension of the organic fraction of municipal solid waste ($OFMSW_A$) derived from a combined wet-digestion and composting plant. The co-digestion trials involved other organic matrices, including dewatered sewage sludge, biochar obtained from sludge pyrolysis, hydrochar, and HTC liquid produced through the hydrothermal carbonization (HTC) process of sludge.

In addition to analyzing the co-digestion processes of $OFMSW_A$ with these matrices, this chapter also explores potential plant layouts (hereafter referred to as Scenario A). These layouts are envisioned within the framework of a biorefinery concept, proposing the establishment of a centralized hub for the integrated management and treatment of organic matrices. The approach involves the sequential use of different technologies to maximize resource recovery, both in terms of material reuse and energy generation.

6.3.1. Scenario A-0: mono-AD of $OFMSW_A$

The baseline scenario, used as a reference for comparison with the outcomes of the co-digestion trials performed in this study, is represented by the most widely adopted technical solution for treating the organic fraction of municipal solid waste: the anaerobic digestion, for the recovery of biogas and digestate. Biogas, due to its high methane content and significant calorific value, can be utilized through combustion to produce energy, which can be employed for external uses or to meet the energy demands of the plant itself. Anaerobic digestion is, in fact, an energy-positive process. The digestate, when combined with lignocellulosic waste, can be valorized through an aerobic composting process to produce compost suitable for agricultural applications.

The process flow diagram, illustrated in Figure 48, depicts the innovative, yet already implemented, combination of anaerobic digestion and composting for the treatment of OFMSW.

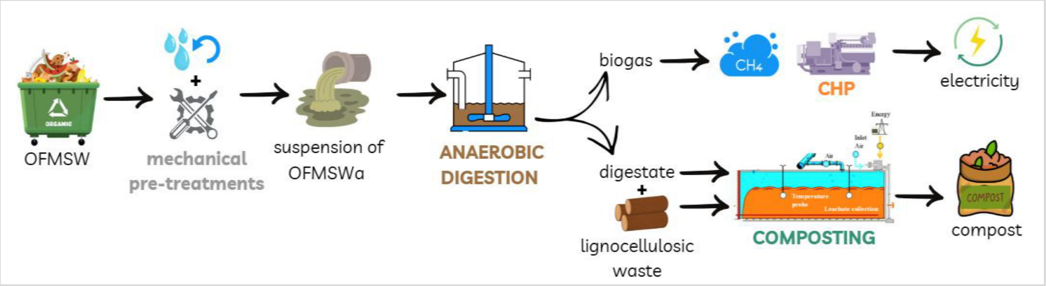

Figure 48 – Scheme of mono-digestion of pre-treated OFMSW$_A$ and composting

In the experimentation, the trial that describes the results produced by the anaerobic digestion of OFMSW$_A$ is test T2. The results of this trial have already been presented in Section 6.2.1 and are summarized in Table 44.

Table 44 – Mono-digestion of OFMSW$_A$

Mono-digestion	**VS** **g**	**Net Volume** **NmL$_{CH4}$**	**BMP** **NmL$_{CH4}$/gVS**
OFMSW$_A$	2.37	1732.81	731.14

In the following sections, a graphical comparison is presented between the mono-digestion of individual substrates and their treatment in co-digestion. This analysis aims to evaluate whether the implementation of this plant solution, investigated step-by-step, can effectively contribute to increasing methane production.

6.3.2. Scenario A-1: co-AD of OFMSW$_A$ and dewatered sewage sludge

The first co-digestion scenario investigated involved the organic matrices OFMSW$_A$ and dewatered sewage sludge (DSS).

These matrices were treated in co-digestion during test T3 to determine the BMP of this new substrate, composed of 70%w by OFMSW$_A$ and 30%w by DSS, and to compare its performance with the yields obtained from mono-digestions. The test lasted 32 days, employing an ISR of 2 in terms of volatile solids. The average characterization of the matrices used is reported in Table 45.

Table 45 – Average characterization of the matrices involved in the co-digestion of OFMSW$_A$ and DSS

Parameter	Unit	Inoculum	OFMSW$_A$	DSS
Total solids	**%**	7.49	1.70	20.94
Water content	**%**	92.51	98.30	79.06
Ash	**%**	0.66	0.36	4.31
Volatile solids	**%**	6.83	1.34	16.63
Volatile solids	**%dm**	91.14	78.66	79.42

A quantity of 400 g of inoculum was added to each of the two reactors (R1 and R2) used as “blanks”. Conversely, a quantity of 250 g of inoculum was added to the two reactors (R8 and R9), which also contained the new substrate under investigation. According to the material characterization, 400 g of inoculum contained 27.32 g of volatile solids, whereas 250 g of inoculum contained 17.07 g of VS. To determine the amount of substrate to be added, Formula (22) was applied. Using an ISR ratio of 2 and knowing the total and volatile solids content of both the inoculum and the two matrices forming the substrate—along with the desired weight ratio between the two matrices—the total mass of substrate to be added to each reactor was calculated.

$$m_s = \frac{m_{in} \times TS_{in} \times VS_{in}}{ISR \times (TS_{s1} \times VS_{s1} \times x_1 + TS_{s2} \times VS_{s2} \times x_2)} \tag{22}$$

Where:

- m_{in} mass of the inoculum (expressed in grams);
- TS_i total solids of the inoculum (expressed as percentage);
- VS_i volatile solids of the inoculum (expressed as percentage of dry matter);
- m_s mass of the substrate (expressed in grams);
- x_i weight percentage of the i-th material in the substrate (expressed as percentage);
- TS_{si} total solids of the i-th material in the substrate (expressed as percentage);
- VS_{si} volatile solids of the i-th material in the substrate (expressed as percentage of dry matter).

Consequently, after determining the total amount of substrate that meets the ISR ratio of 2, the weight percentages of the individual $OFMSW_A$ and DSS to be added were calculated. The amounts loaded into each reactor are reported in Table 46.

Table 46 – Amount of inoculum and substrate added to each reactor for the co-digestion of $OFMSW_A$ and DSS

Reactor	**Matrix**	**Inoculum**		**Substrate**			
				$OFMSW_A$		**DSS**	
		g	**g VS**	**g**	**g VS**	**g**	**g VS**
R1	Inoculum	400.00	27.32	-	-	-	-
R2		400.00	27.32	-	-	-	-
R8	Inoculum + Substrate	250.00	17.07	100.89	1.35	43.24	7.19
R9		250.00	17.07	100.89	1.35	43.24	7.19

Considering that reactors R8 and R9 contain just over half of the inoculum quantity present in reactors R1 and R2, which serve as the reference for the "blank", in order to compare the curves and also provide a graphical representation of the net substrate production, the daily production of reactors R1 and R2 is calculated proportionally as if they had only 250 g of inoculum instead of 400 g. These cumulative methane production trends, compared with those of reactors R8 and R9, are shown in Figure 49.

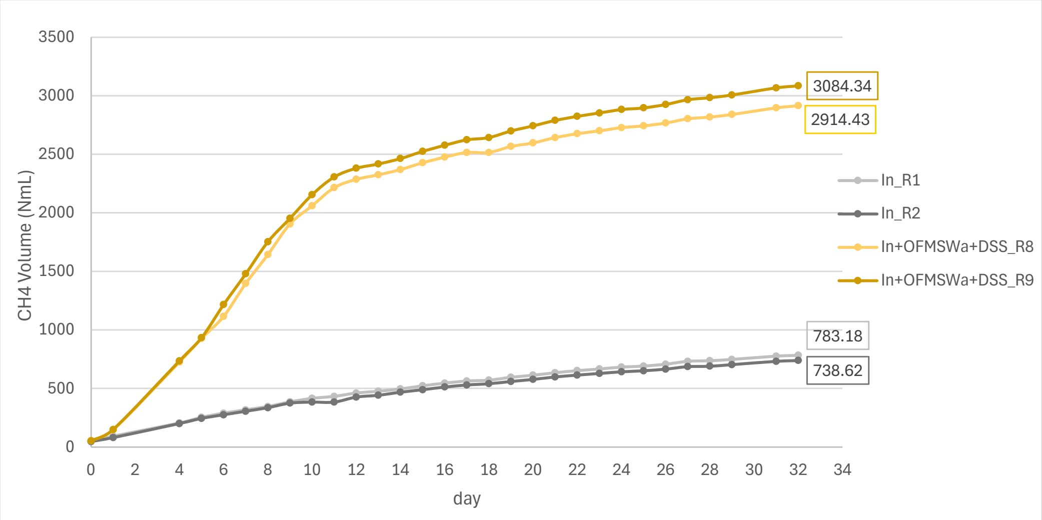

Figure 49 – Gross methane production during 32 days of AD of Inoculum (250g) and Inoculum with the $OFMSW_A$ and DSS substrate mix

The graph shows that the two reactors, R1 and R2, containing inoculum, have a methane production trend that is nearly identical, with a ΔV of less than 50 NmL. Considering, as previously mentioned, the production derived from 250 g of inoculum, the average volume of methane produced by the two reactors is 760.90 NmL_{CH4}.

Regarding the methane production curves of reactors R8 and R9, which contain inoculum and substrate, with the latter consisting of 70%w $OFMSW_A$ and 30%w DSS, it can be observed that these reactors also show a similar cumulative methane production trend, resulting in a final average volume of 2999.38 NmL_{CH4}. It is noTable that in the first 10 days, the substrate already produced 2300 NmL of methane, which is more than 70% of its final production.

Next, the net volume of methane produced by R8 and R9 is calculated by subtracting from the daily increase production of each reactor, the average daily production of the inoculum (R1 and R2). Table 47 shows the net methane volumes produced by the reactors on the 32nd day and the BMP subsequently calculated. The co-digestion of $OFMSW_A$ and DSS produced an average net volume of methane of 2238.48 NmL, resulting in an average BMP for this mix of 262.12 NmL_{CH4}/gVS.

Table 47 – Summary of the results obtained from the co-digestion of $OFMSW_A$ and DSS in test T3

Test	Reactor	Substrate	VS g	Net volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T3	R1	Inoculum	17.07	783.18	45.88
	R2	Inoculum	17.07	738.62	43.27
	R8	$OFMSW_A$ + DSS	8.54	2153.53	252.17
	R9	$OFMSW_A$ + DSS	8.54	2323.44	272.07

Below is represented the trend of the specific production, relating the daily net volume of methane produced from $OFMSW_A$+DSS to the grams of volatile solids that generated it.

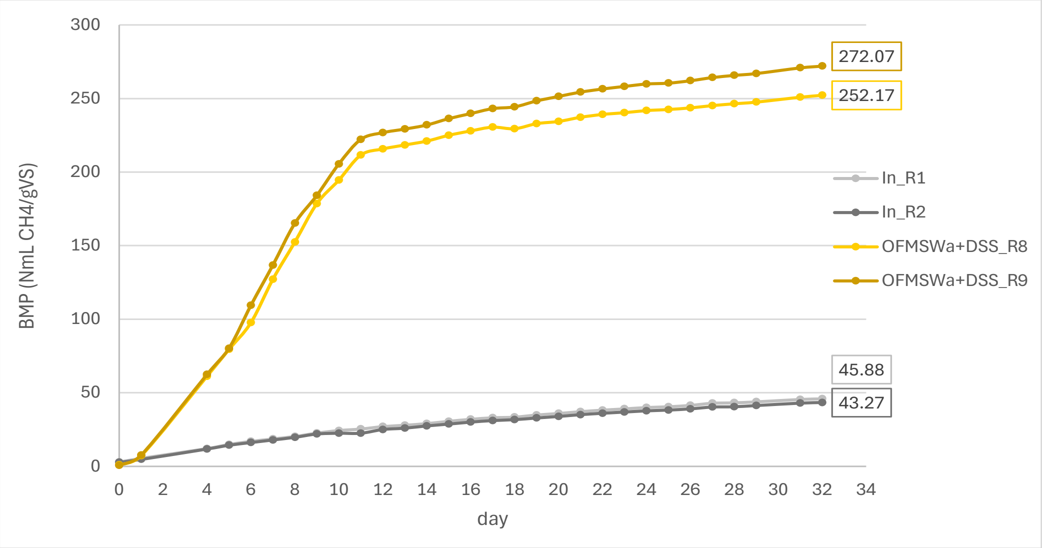

Figure 50 – Trend of BMP during the co-digestion of $OFMSW_A$+DSS

To evaluate if the co-digestion yield of $OFMSW_A$ with dewatered sludge is actually improved, it is necessary to compare the result of this test with the mono-digestion of the individual matrices, determined during test T2. The comparison is shown in Table 48 and graphically in Figure 51, considering the average BMP values for each matrix determined during the trials.

Table 48 – Comparison between the BMP of the substrate mix $OFMSW_A$+DSS and that of the individual substrates

Test	Substrate	VS g	Net Volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T2	$OFMSW_A$	2.37	1732.81	731.14
T2	D-SS	9.50	1844.97	194.21
T3	$OFMSW_A$ +DSS	8.54	2238.48	262.12

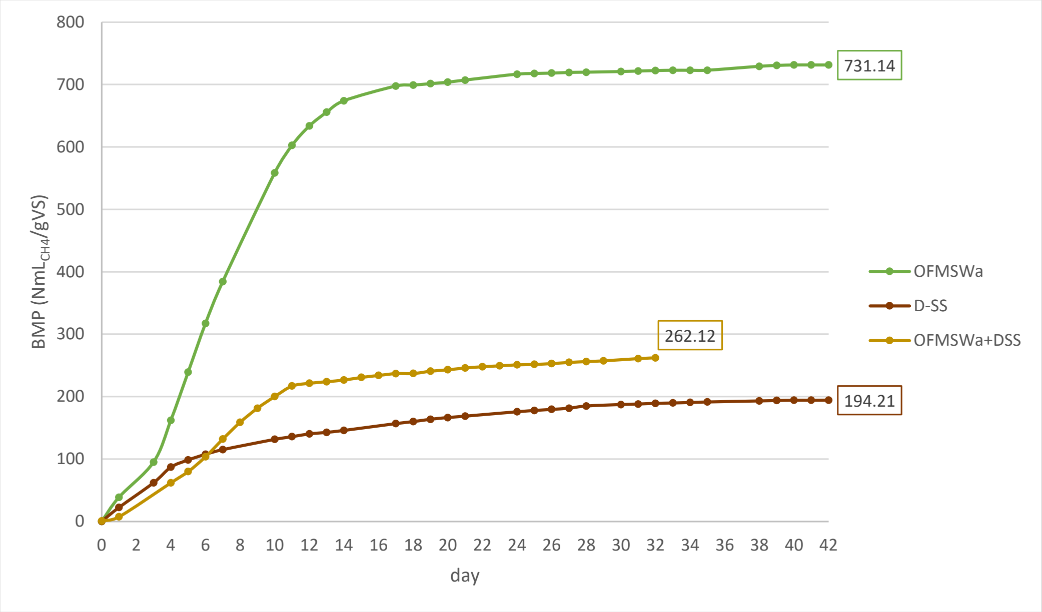

Figure 51 – Comparison of trends in average specific methane production during co-digestion of $OFMSW_A$+DSS and the individual mono-digestions

Therefore, the co-digestion results in a substrate characterized by a biomethanation potential intermediate between those of the starting matrices. For the sludge, the inclusion of OFMSW in co-digestion proves to be beneficial, as reported in the study by Dai et al. (2013), which stated that the addition of FW into the DSS high-solids digestion improved system stability and greatly enhanced volumetric biogas production. However, when considering the $OFMSW_A$ as the starting matrix, the inclusion of DSS in the AD process does not appear equally advantageous, as in the analyzed ratio (30%w DSS, 70%w $OFMSW_A$), it results in a substrate that, with the same amount of volatile solids, produces a smaller amount of methane.

It's important to consider that the outcome of the co-digestion test should be evaluated by comparing the measured methane volume with the theoretical volume, which would be obtained by summing the volumes calculated by multiplying the known BMPs of the individual substrates by the grams of volatile solids added to the co-digestion (as shown in Figure 52).

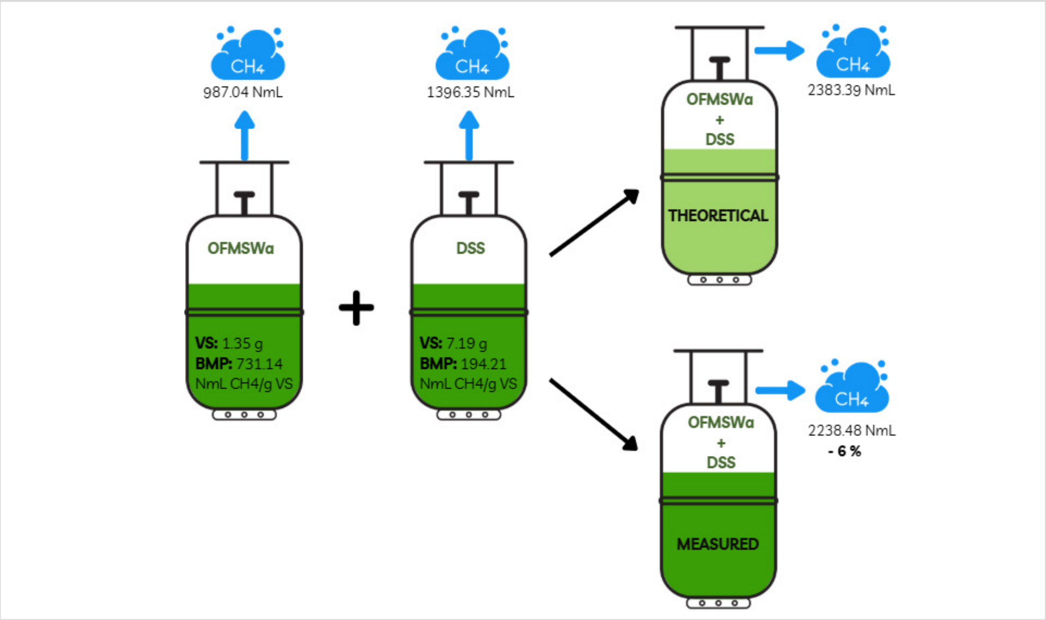

Figure 52 – Comparison between the theoretical methane volume and the measured volume produced from the co-digestion of $OFMSW_A$ and DSS

This comparison shows that 1.35 g of VS of $OFMSW_A$ and 7.19 g of VS of DSS should produce a methane volume of 2383.39 NmL, whereas the measured volume is 2238.48 NmL, resulting in a volume difference of 144.91 NmL_{CH4}. This difference (≈6%) is considered not significant and, therefore, the two matrices treated in co-digestion do not have synergistic effects that improve methane production compared to the digestion of the individual materials. However, the co-digestion treatment is beneficial in terms of waste recovery, as it would allow to DSS, which is a matrix destined for landfill disposal, to be recovered through a biological process, resulting in energy valorization and material recovery through compost production. Figure 53 shows a hypothetical plant scenario for the co-digestion treatment of OFMSW and DSS.

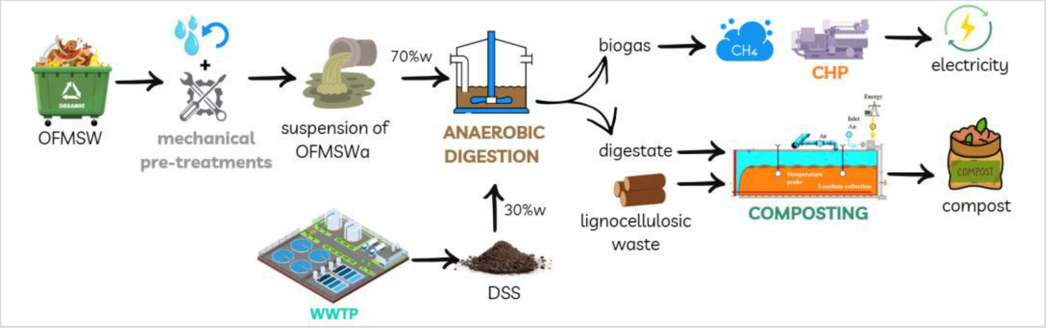

Figure 53 – Layout scenario of a biorefinery for the co-digestion of OFMSW$_A$ and DSS

This process ensures an increase in the organic waste recovery rate and could be implemented by testing the same matrices at different co-digestion ratios. As reported by Lijó et al. (2017), the co-treatment of FW and wastewater sludge would be more environmentally friendly than their separate treatments, but its economic feasibility strongly depends on the ratio between the management costs of FW and SS. Moreover would be better to test the primary sludge in a wet co-digestion with OFMSW$_A$ before it is dewatered. In fact, based on BMP tests presented by Xie et al. (2017) is determined that the co-digestion of primary sludge and food waste in a 1.0:1.0 ratio (VS basis) has a specific methane yields of 799 mL/gVS, higher then single materials BMP, with food waste of 17.4% TS and primary sludge of 1.3% TS.

6.3.3. Scenario A-2: co-AD of OFMSW$_A$ and biochar

The co-digestion of OFMSW$_A$ with biochar was tested in the T4 test. This material was added to the reactors at a concentration of 10 g/L. Specifically, the additive was present at a concentration of 13 g/L relative to the OFMSW$_A$. The trial lasted 25 days, and to determine the amount of OFMSW$_A$ to be treated, an ISR of 2 was used. The average characterization of the matrices used during the trial is reported in Table 49.

Table 49 – Average characterization of the matrices involved in the co-digestion of $OFMSW_A$ and BC

Parameter	Unit	Inoculum	$OFMSW_A$	Biochar
Total solids	%	7.49	1.13	96.43
Water content	%	92.51	98.87	3.57
Ash	%	0.66	0.10	47.72
Volatile solids	%	6.83	1.04	48.71
Volatile solids	%dm	91.14	91.56	50.52

A total of 400 g of inoculum was added to each of the two reactors (R1 and R2) used to represent the "blank"; instead, 50 g of inoculum was added to the reactors (R4 and R5) containing also the new mix to be investigated. According to the material characterization, 400 g of inoculum contains 27.32 g of VS, while 50 g contains 3.41 g of VS. The amount of $OFMSW_A$ to be added was determined by choosing an ISR of 2 and knowing the volatile and total solids of both the inoculum and the $OFMSW_A$; the biochar to be added was instead introduced at a concentration of 13 g/L_{OFMSW}. The amounts loaded into each reactor are reported in Table 50.

Table 50 – Amount of inoculum and substrate added to each reactor for the co-digestion of $OFMSW_A$ and BC

Reactor	Matrix	Inoculum		Substrate			
				$OFMSW_A$		BIOCHAR	
		g	g VS	g	g VS	g	g VS
R1	Inoculum	400.00	27.32	-	-	-	-
R2		400.00	27.32	-	-	-	-
R4	Inoculum + Substrate	50.00	3.41	164.52	1.71	2.15	1.05
R5		50.00	3.41	164.52	1.71	2.15	1.05

Considering that reactors R4 and R5 contain 1/8 of the inoculum amount present in reactors R1 and R2, which serve as the reference for the "blank", in order to compare the curves and also provide a graphical representation of the net substrate production, the daily production of reactors R1 and R2 was proportionally calculated as if they had only 50 g of inoculum instead of 400 g. These cumulative methane production trends, compared with those of reactors R4 and R5, are shown in Figure 54.

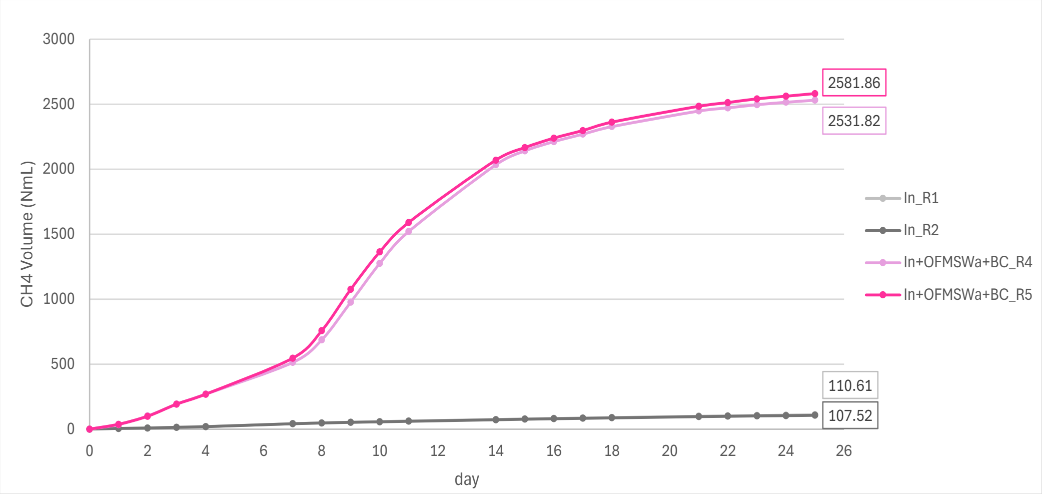

Figure 54 – Gross methane production during 25 days of AD of Inoculum (50g) and Inoculum with the OFMSW$_A$ and BC substrate mix

The graph shows that the two reactors, R1 and R2, containing inoculum, have a methane production trend that is nearly identical. Considering, as previously mentioned, the production obtained from 50 g of inoculum, the average volume of methane produced by the two reactors is 109.06 NmL.

Regarding the methane production curves of reactors R4 and R5, which contain both inoculum and substrate, it can be observed that the methane production had an initial phase (the first week) of moderate growth, followed by an increase in the production rate during the second week. From day 14 onwards, the curves continued to grow but at a slower rate, until reaching a plateau with a final average methane production of 2556.84 NmL.

Next, the net methane volume produced by R4 and R5 is calculated by subtracting the average daily production of the inoculum (R1 and R2) from the daily production increase of each reactor. Table 51 shows the net methane volumes produced by the reactors on the 25th day and the BMP subsequently calculated. The co-digestion of

$OFMSW_A$ and BC produced an average net methane volume of 2447.78 NmL, resulting in an average BMP for this mix of 886.88 NmL_{CH4}/gVS.

Table 51 – Summary of the results obtained from the co-digestion of $OFMSW_A$ and BC in test T4

Trial	Reactor	Substrate	VS g	Net volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T4	R1	Inoculum	3.41	110.61	32.39
	R2	Inoculum	3.41	107.52	31.48
	R4	$OFMSW_A$ + BC	2.76	2422.75	877.81
	R5	$OFMSW_A$ + BC	2.76	2472.80	895.94

Below is represented the trend of specific methane production, relating the daily net volume produced by $OFMSW_A$ + BC to the grams of volatile solids that generated it.

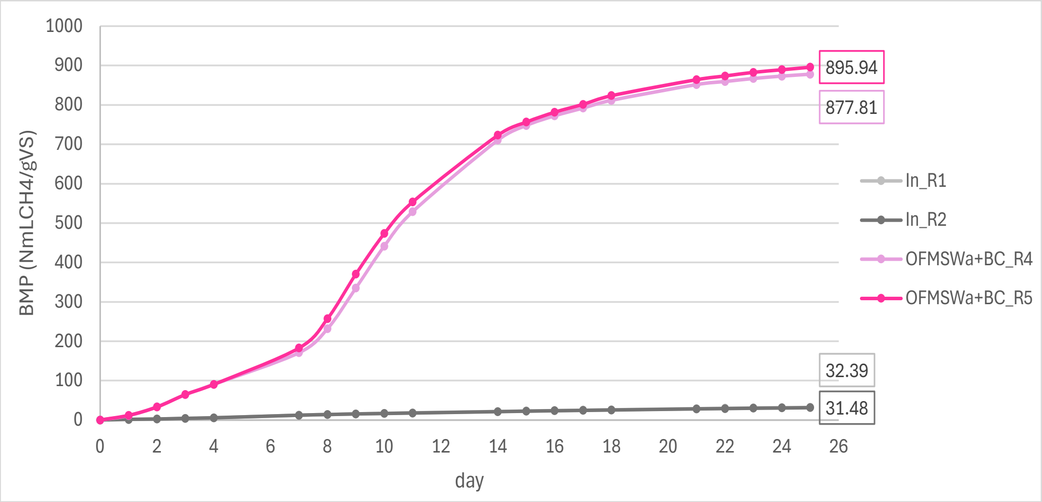

Figure 55 – Trend of BMP during the co-digestion of $OFMSW_A$ + BC

It can be observed that the BMP achieved by this substrate is very high, indicating that the co-digestion treatment has a positive outcome, showing a significant increase in methane production. However, to assess if the co-digestion yield is truly improved, the result of this test needs to be compared with the mono-digestions of the individual matrices, determined during tests T2 and T6. For each matrix, the average values reported in Table 52 were considered.

Table 52 – Comparison between the BMP of the substrate mix $OFMSW_A$+BC and that of the individual substrates

Test	Substrate	VS g	Net Volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T2	$OFMSW_A$	2.37	1732.81	731.14
T6	BC	5.47	128.63	23.51
T4	$OFMSW_A$ +BC	2.76	2447.78	886.88

These values were graphically represented in Figure 56, from which it can be observed that biochar, when analyzed individually, has a very low methanogenic potential. However, by using even a small amount of this material as an additive to the AD treatment of $OFMSW_A$, a substrate mix is obtained with a BMP of about 890 NmL_{CH4}/gVS. The methane production from this mix is initially slow, with production lower than that of the single $OFMSW_A$, while from the second week onwards, the growth rate increases and surpasses the BMP of $OFMSW_A$.

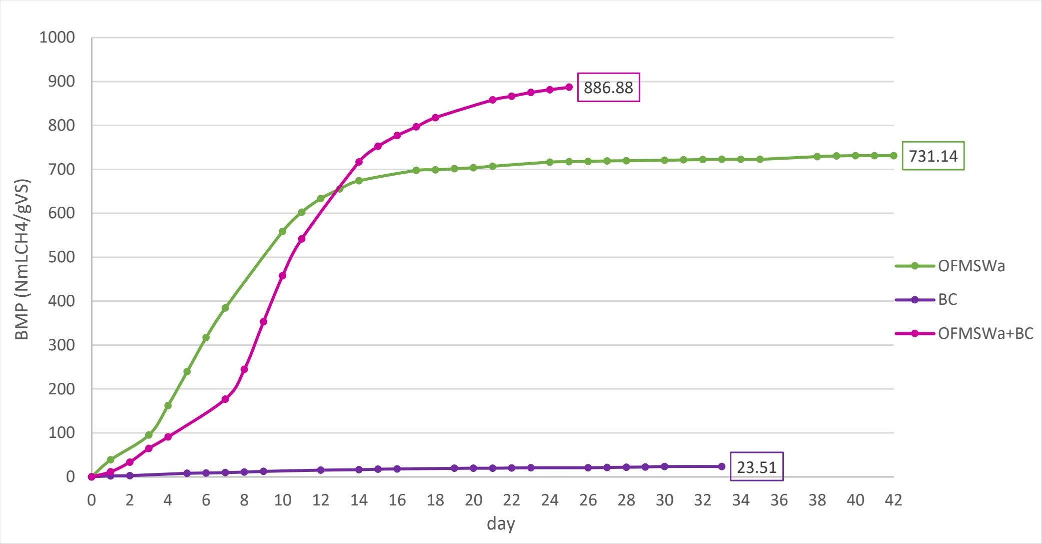

Figure 56 – Comparison of trends in average specific methane production during co-digestion of $OFMSW_A$+BC and the individual mono-digestions

However, the outcome of the co-digestion trial must be evaluated by comparing the measured methane volume with the theoretical volume; the latter is obtained summing the volumes derived from multiplying the known BMPs of the individual substrates by the grams of volatile solids added to the co-digestion (as shown in Figure 57).

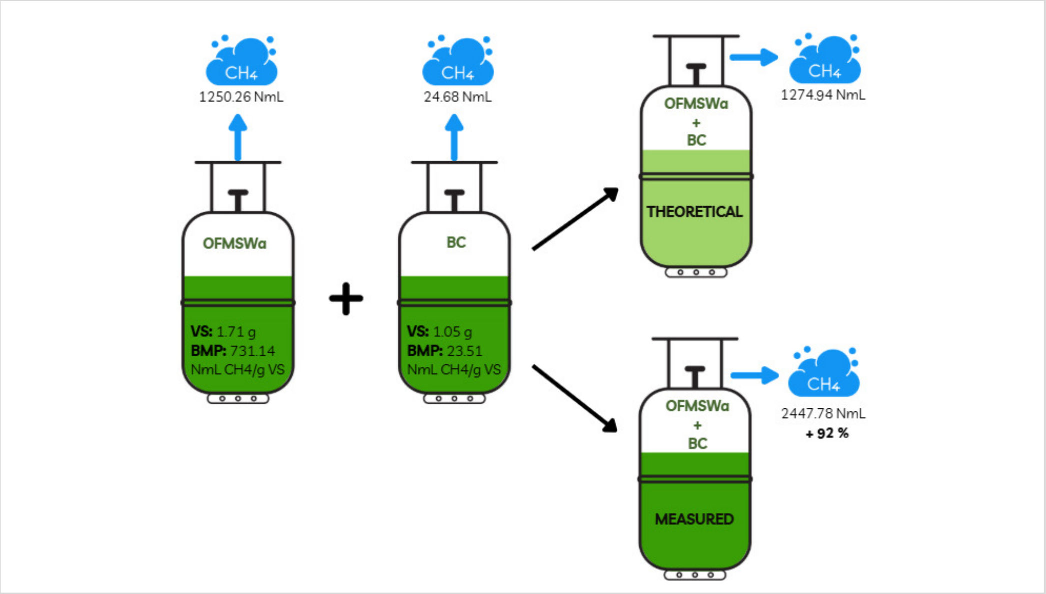

Figure 57 - Comparison between the theoretical methane volume and the measured volume produced from the co-digestion of $OFMSW_A$ and BC

This comparison shows that 1.71 g of VS from $OFMSW_A$ and 1.05 g of BC should produce 1274.94 NmL_{CH4}, while the measured volume is 2447.78 NmL_{CH4}. Therefore, the co-digestion of these two matrices results in a substantial improvement in methane production, with a +92% increase compared to the materials treated in mono-digestion. The BMP of this new substrate is 886.88 NmL_{CH4}/gVS, higher than that of the individual matrices. Thus, the results of this trial demonstrate the significant effectiveness of this combined treatment using biochar at the tested concentration of 13 g/L of $OFMSW_A$. As reported by Qiu et al. (2019), the porous structure of biochar favors the colonization of methanogenic archaea, which facilitates the total organic carbon removal as well as the reaction rate in AD. The implementation, at the industrial level, of this solution, which leads to an improvement in the anaerobic digestion yields of OFMSW in terms of methane production, is shown in Figure 58.

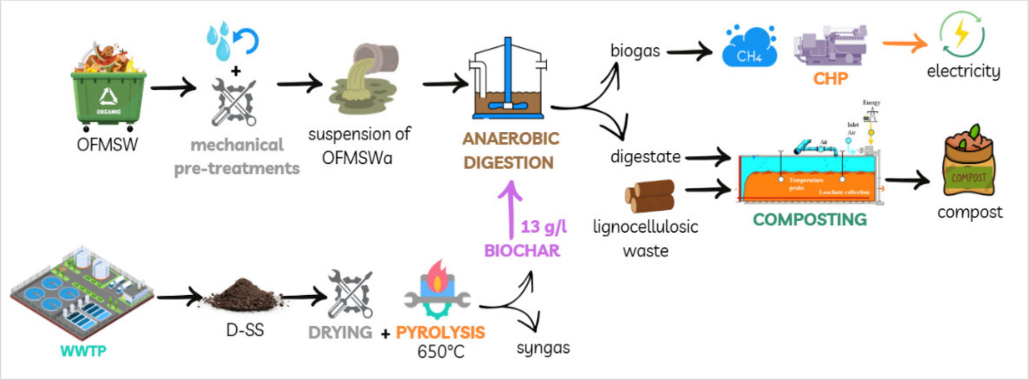

Figure 58 – Layout scenario of a biorefinery for the co-digestion of $OFMSW_A$ and biochar

It would therefore be possible to hypothesize a treatment hub for organic matrices, which envisions that the sewage sludge from treatment plants is pre-treated through a drying process and then subjected to pyrolysis. The outputs of this technology result in both a gas (syngas) with high calorific value, which can be converted into electricity and thermal energy via CHP, and biochar, which could be partially used in co-digestion with OFMSW and, if it meets regulatory limits, potentially also as a fertilizer in agriculture due to its high nutrient content. In addition, biochar can also be used as bulking agent during the composting of nitrogen-rich materials, because is known that through its introduction, emissions from the natural decomposition of organic waste and crop residues in soil could be reduced and even prevented (Zhang et al., 2019).

6.3.4. *Scenario A-3: co-AD of $OFMSW_A$ and hydrochar*

Another scenario presented in this thesis is the co-digestion of $OFMSW_A$ with the hydrochar produced from the hydrothermal carbonization process described in section 5.1.6. This alternative was investigated in test T4. It was decided to add the hydrochar to the $OFMSW_A$ at the same concentration tested for biochar, i.e. 13 g/L relative to the amount of $OFMSW_A$ added to the reactor.

The trial lasted 25 days, and to determine the amount of $OFMSW_A$ to treat, an ISR of 2 was adopted. The average characterization of the matrices used is shown in Table 53.

Table 53 – Average characterization of the matrices involved in the co-digestion of $OFMSW_A$ and HC

Parameter	Unit	Inoculum	$OFMSW_A$	Hydrochar
Total solids	%	7.49	1.13	87.91
Water content	%	92.51	98.87	12.09
Ash	%	0.66	0.10	24.00
Volatile solids	%	6.83	1.04	63.91
Volatile solids	%dm	91.14	91.56	72.70

A total of 400 g of inoculum was added to each of the two reactors (R1 and R2) used to represent the “blank”; whereas 50 g of inoculum was added to the two reactors (R6 and R7) containing also the new mix to be investigated. According to the material characterization, 400 g of inoculum contains 27.32 g of VS, while 50 g contains 3.41 g of VS.

The amount of $OFMSW_A$ to be added was determined by selecting an ISR of 2 and knowing the volatile and total solids of both the inoculum and the $OFMSW_A$. The hydrochar to be added was loaded at a concentration of 13 g/L_{OFMSW}. The quantities loaded into each reactor are shown in Table 54.

Table 54 – Amount of inoculum and substrate added to each reactor for the co-digestion of $OFMSW_A$ and HC

Reactor	Matrix	Inoculum		Substrate			
				$OFMSW_A$		HYDROCHAR	
		g	g VS	g	g VS	g	g VS
R1	Inoculum	400.00	27.32	-	-	-	-
R2		400.00	27.32	-	-	-	-
R6	Inoculum + Substrate	50.00	3.41	164.50	1.71	2.15	1.37
R7		50.00	3.41	164.50	1.71	2.15	1.37

Considering that reactors R6 and R7 contain 1/8 of the amount of inoculum present in reactors R1 and R2, the daily production of the reactors R1 and R2 was proportionally calculated based on the amount of 50 g of inoculum instead of 400 g. These cumulative methane production trends, compared to those of reactors R6 and R7, are shown in Figure 59.

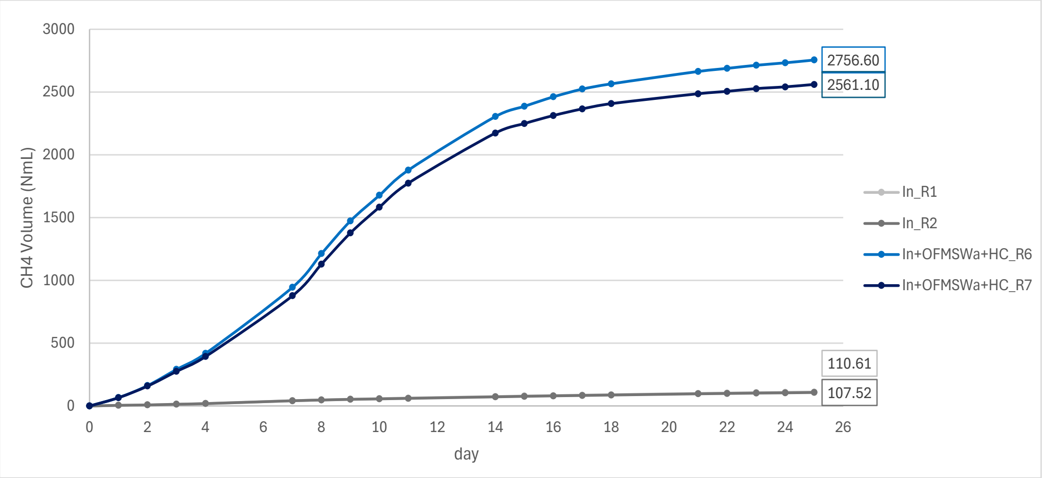

Figure 59 – Gross methane production during 25 days of AD of Inoculum (50g) and Inoculum with the $OFMSW_A$ and HC substrate mix

As already shown for the co-digestion of $OFMSW_A$ and BC (it’s the same test T4), the reactors R1 and R2 containing 50 g of inoculum have a methane production trend that is almost identical, with an average volume of 109.06 NmL_{CH4}. Regarding the methane production curves from reactors R6 and R7 containing both inoculum and substrate, it can be observed that the production shows a gradual increase until it reaches a plateau, with a final average methane production of 2658.85 NmL. The net methane volume produced by R6 and R7 is calculated by subtracting the average daily production of the inoculum (R1 and R2) from the daily production increment of each reactor. Table 55 shows the net methane volumes produced by the reactors on the 25th day and the BMP calculated. The co-digestion of $OFMSW_A$ and HC produced an average net methane volume of 2549.79 NmL, resulting in an average BMP for this mix of 827.85 NmL_{CH4}/gVS.

Table 55 – Summary of the results obtained from the co-digestion of $OFMSW_A$ and HC in test T4

Test	Reactor	Substrate	VS g	Net volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T4	R1	Inoculum	3.41	110.61	32.39
	R2	Inoculum	3.41	107.52	31.48
	R6	$OFMSW_A$ + HC	3.08	2647.54	859.59
	R7	$OFMSW_A$ + HC	3.08	2452.04	796.12

In Figure 60 is shown the trend of specific methane production, relating the daily net volume of methane produced by $OFMSW_A$ + HC to the grams of volatile solids that generated it.

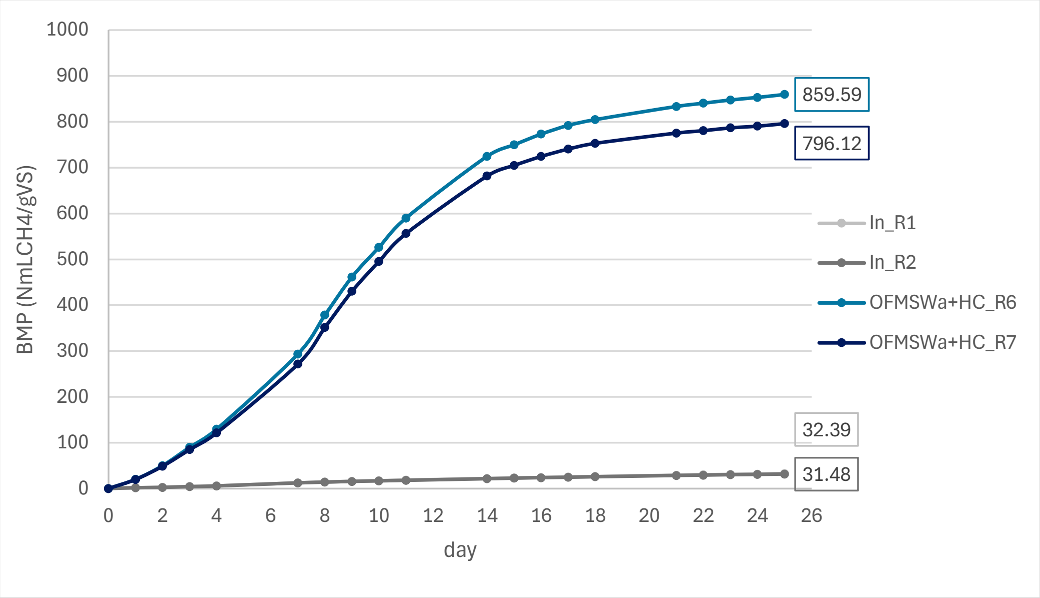

Figure 60 – Trend of BMP during the co-digestion of $OFMSW_A$+ HC

It can be observed that the BMP achieved by this substrate is very high, so the co-digestion treatment seems to have had a positive outcome in terms of increasing methane production. However, to evaluate if the co-digestion yield is actually improved, the result of this test needs to be compared with the monodigestions of the individual matrices, determined during the T2 and T6 tests. The comparison is shown in Table 56 and graphically in Figure 61, considering the average BMP values determined for each matrix during the tests.

Table 56 - Comparison between the BMP of the substrate mix $OFMSW_A$+HC and that of the individual substrates

Test	**Substrate**	**VS** **g**	**Net Volume** **NmL_{CH4}**	**BMP** **NmL_{CH4}/gVS**
T2	$OFMSW_A$	2.37	1732.81	731.14
T6	HC	5.47	862.86	157.74

T4	OFMSW$_A$ +HC	3.08	2549.79	827.85

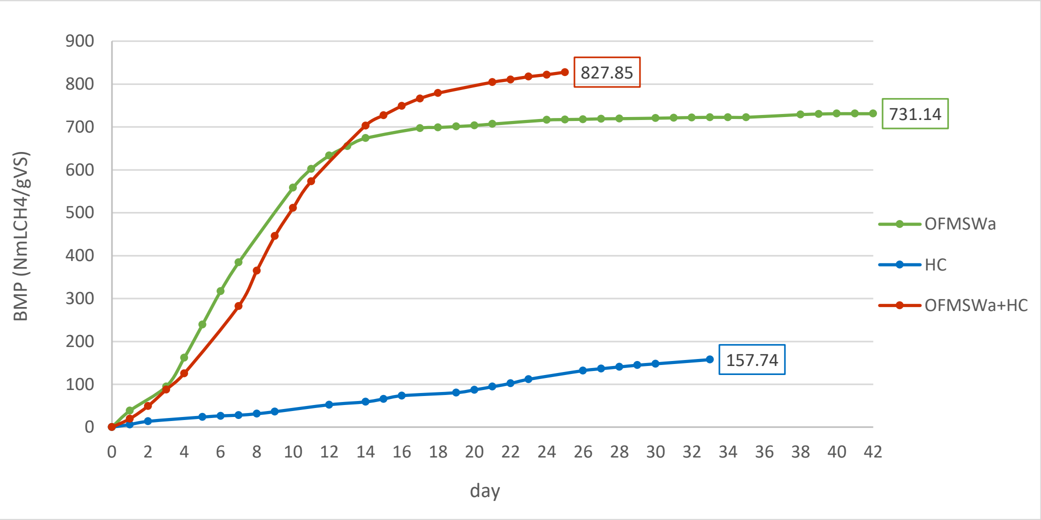

Figure 61 – Comparison of trends in average specific methane production during the co-digestion of OFMSW$_A$+HC and the individual mono-digestions

It can be noted that hydrochar has a relatively low methanogenic potential by itself; however, from this experiment, it can be seen that using even a small amount of this material (2.15 g) as additive in the AD treatment of OFMSW$_A$ results in a new substrate characterized by a BMP of approximately 830 NmL$_{CH4}$/gVS. The methane production from this mix shows a high growth rate, so it’s possible to see a curve characterized by a steeper then that of OFMSW$_A$.

The outcome of the co-digestion test, however, needs to be evaluated by comparing the measured methane volume with the theoretical volume, obtained by summing the volumes derived from multiplying the known BMPs of the individual substrates by the grams of volatile solids added in co-digestion (as shown in Figure 62).

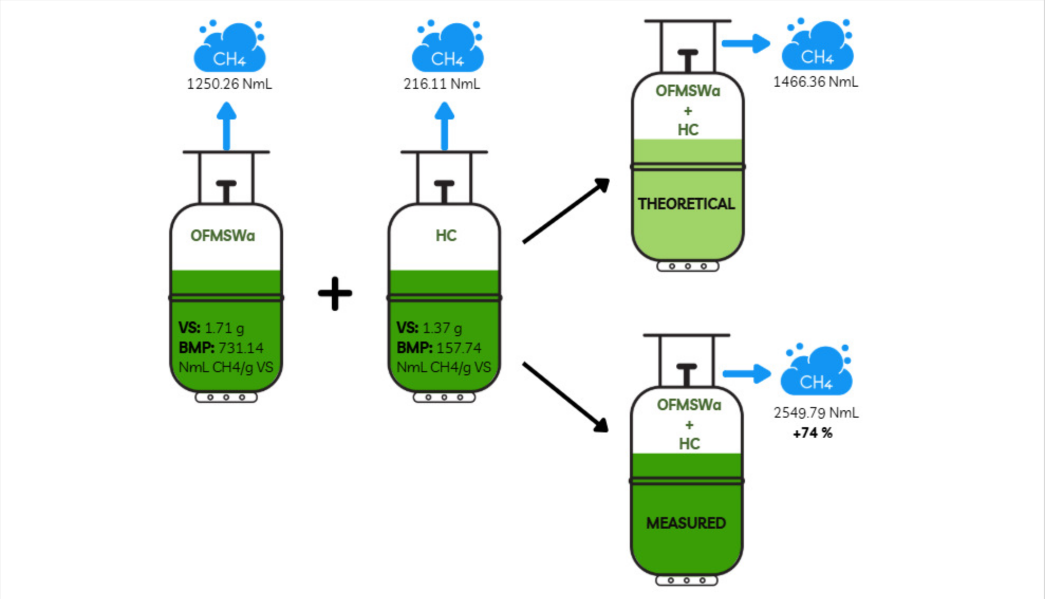

Figure 62 – Comparison between the theoretical methane volume and the measured volume produced from the co-digestion of $OFMSW_A$ and HC

From the analysis carried out, it can be observed that the volume of methane that 1.71 g of VS from $OFMSW_A$ and 1.37 g of HC should produce - without any synergically effect - is 1466.36 NmL_{CH4}, whereas the measured value during the trial is 2549.79 NmL_{CH4}. Therefore, the co-digestion of these two matrices results in a substantial improvement in methane production with an increase of 74% compared to the materials treated in mono-digestion. The BMP of this new substrate is 827.85 NmL_{CH4}/gVS, higher than that of the individual matrices. This trial demonstrates the noTable effectiveness of this joint treatment with the use of hydrochar at the tested concentration of 13 g/L_{OFMSW}.

A possible implementation of this solution, which results in an improvement of the anaerobic digestion performance of OFMSW in terms of methane production, is shown in Figure 63.

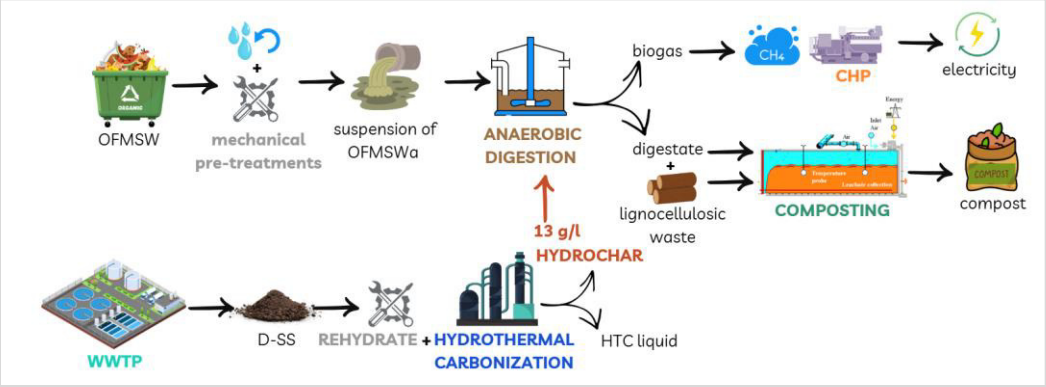

Figure 63 – Layout scenario of a biorefinery for the co-digestion of $OFMSW_A$ and hydrochar

It would therefore be possible to hypothesize an organic waste treatment hub, where the sewage sludge exiting the plants is pre-treated and then subjected to hydrothermal carbonization. The output of this technology results in the production of both a liquid by-product, which can be further valorized through biological processes, and a solid by-product: the hydrochar, which could be used in co-digestion with OFMSW, leading to an increase in methane production as well as energy valorization.

6.3.5. Scenario A-4: co-AD of $OFMSW_A$ and HTC liquid

The co-digestion of $OFMSW_A$ with the HTC liquid produced by the hydrothermal carbonization process described in section 5.1.6 has also been investigated. These matrices were treated in co-digestion during test T4, to determine the BMP of this new substrate – which consists of 70%w $OFMSW_A$ and 30%w HTC-L – and compare it with the yields obtained from the mono-digestion tests. The trial lasted for 25 days, with an inoculum-to-substrate ratio of 2 in terms of volatile solids, and the average characterization of the matrices used is reported in Table 57.

Table 57 – Average characterization of the matrices involved in the co-digestion of $OFMSW_A$ and HTC-L

Parameter	**Unit**	**Inoculum**	**$OFMSW_A$**	**HTC-L**
Total solids	%	7.49	1.13	1.45
Water content	%	92.51	98.87	98.55
Ash	%	0.66	0.10	0.06
Volatile solids	%	6.83	1.04	1.39
Volatile solids	%dm	91.14	91.56	95.84

A quantity of 400 g of inoculum was added to each of the two reactors (R1 and R2) used to represent the "blank"; instead, a quantity of 50 g of inoculum was added to the two reactors (R8 and R9) containing the new mix under investigation. According to the material characterization, 400 g of inoculum contain 27.32 g of VS, while 50 g contain 3.41 g of VS.

The amount of substrate to be added was determined using Formula (22). Given the choice to use an ISR of 2, and knowing the volatile and total solids of both the inoculum and the two components of the substrate, as well as the desired weight percentage of each component, the total mass of substrate required for each reactor was calculated.

Subsequently, after determining the total substrate quantity that meets the selected ISR, the weight percentages of individual $OFMSW_A$ and HTC-L to be added were calculated. The quantities loaded into each reactor are reported in Table 58.

Table 58 – Amount of inoculum and substrate added to each reactor for the co-digestion of $OFMSW_A$ and HTC-L

Reactor	**Matrix**	**Inoculum**		**Substrate**			
				$OFMSW_A$		**HTC Liquid**	
		g	**g VS**	**g**	**g VS**	**g**	**g VS**
R1	Inoculum	400.00	27.32	-	-	-	-
R2		400.00	27.32	-	-	-	-
R8	Inoculum + Substrate	50.00	3.41	104.50	1.08	44.79	0.62
R9		50.00	3.41	104.50	1.08	44.79	0.62

Considering that reactors R8 and R9 contain 1/8 of the amount of inoculum in reactors R1 and R2, which represent the "blank" reference, the daily production of reactors R1 and R2 was proportionally calculated to 50 g of inoculum instead of 400 g.

This proportional adjustment allows for the comparison of curves and the graphical representation of the net methane production from the substrate. These cumulative methane production trends, compared with those of reactors R8 and R9, are shown in Figure 64.

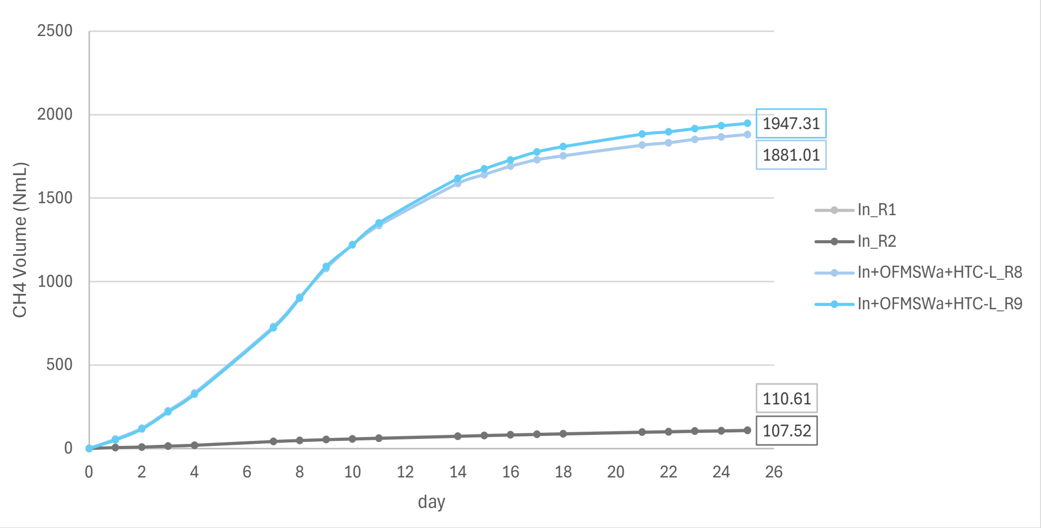

Figure 64 – Gross methane production during 25 days of AD of Inoculum (50g) and Inoculum with the $OFMSW_A$ and HTC-L substrate mix

As already shown in the previous sections, in trial T4 the methane production trend of reactors R1 and R2 is comparable. By analyzing the simplified condition in which these reactors contain only 50 g of inoculum, an average methane production of 109.06 NmL_{CH4} is determined over the 25-day trial period.

Regarding the methane production curves of reactors R8 and R9, which contain inoculum and substrate, it can be observed that the production grows gradually until reaching a plateau, with a final average methane production of 1914.16 NmL.

Subsequently, the net methane volume produced by R8 and R9 is calculated by subtracting the average daily production of the two inoculum-only reactors (R1 and R2)

from the daily production of each reactor. Table 59 reports the net methane volumes produced by the reactors on the 25th day and the BMP subsequently calculated.
The co-digestion of $OFMSW_A$ and HTC-L produced an average net methane volume of 1805.10 NmL, resulting in an average BMP of this mix equal to 1061.82 NmL_{CH4}/gVS.

Table 59 – Summary of the results obtained from the co-digestion of $OFMSW_A$ and HTC-L in trial T4

Test	Reactor	Substrate	VS g	Net volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T4	R1	Inoculum	3.41	110.61	32.39
	R2	Inoculum	3.41	107.52	31.48
	R8	OFMSWA + HTC-L	1.71	1771.94	1042.32
	R9	OFMSWA + HTC-L	1.71	1838.25	1081.32

The specific methane production trend is shown below, relating the net daily volume produced by $OFMSW_A$ + HTC-L to the grams of volatile solids that generated it.

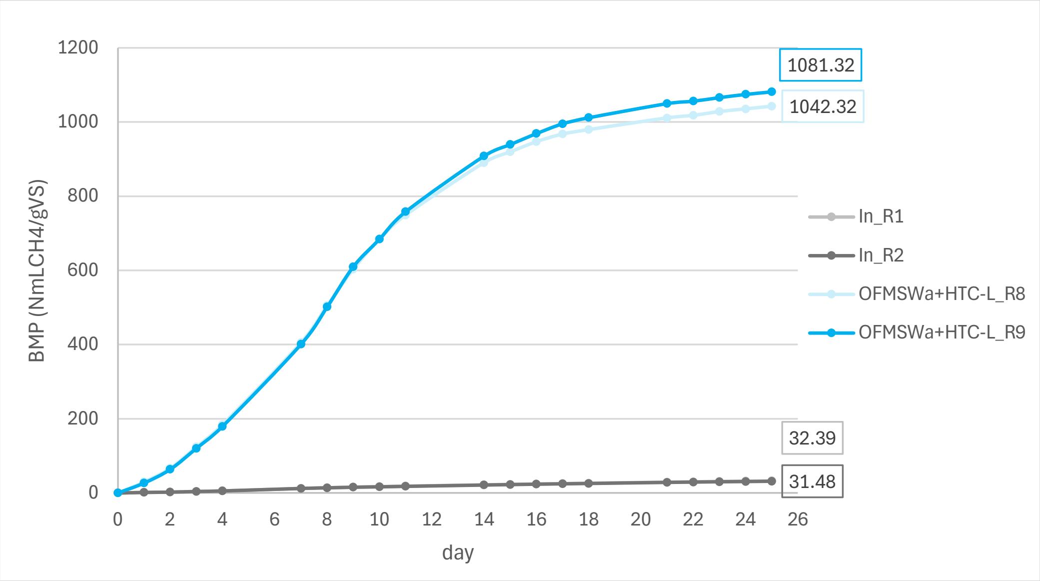

Figure 65 – Trend of BMP during the co-digestion of $OFMSW_A$ + HTC-L

It can be observed that the BMP achieved by this substrate has a very high value, which demonstrates how the co-digestion treatment of $OFMSW_A$ and HTC liquid is effective in enhancing methane production. However, to assess whether the performance in co-digestion is actually improved, it is necessary to compare the result of this test with the mono-digestions of the individual matrices, determined during tests T2 and T8. For each matrix, the average values reported in Table 60 were considered.

Table 60 – Comparison between the BMP of the substrate mix OFMSW$_A$+ HTC-L and that of the individual substrates

Test	**Substrate**	**VS** **g**	**Net Volume** **NmL$_{CH4}$**	**BMP** **NmL$_{CH4}$/gVS**
T2	OFMSW$_A$	2.37	1732.81	731.14
T8	HTC-L	5.18	1112.31	214.73
T4	OFMSW$_A$ +HTC-L	1.70	1805.10	1061.82

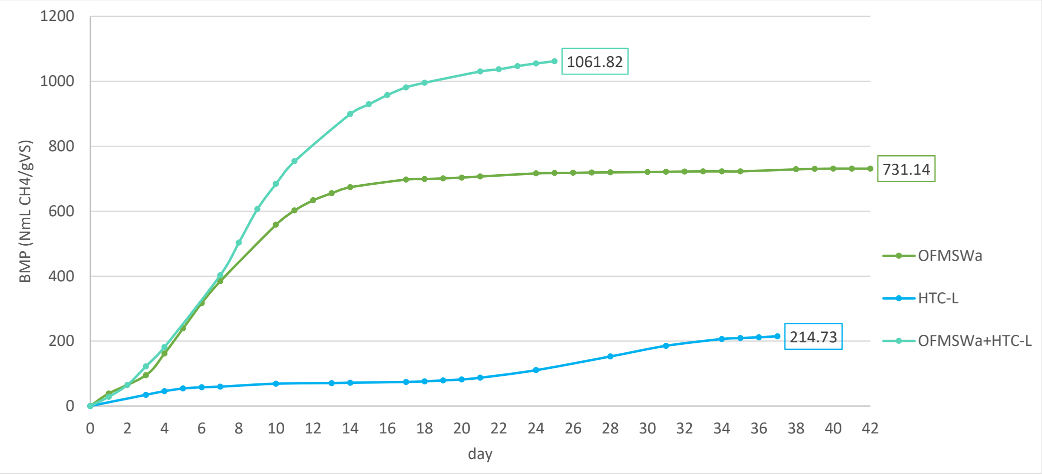

Figure 66 – Comparison of trends in average specific methane production during co-digestion of OFMSW$_A$ + HTC-L and individual mono-digestions

It can be observed that by introducing OFMSW$_A$ and HTC-L into anaerobic co-digestion at a ratio of 2.3:1.0 (in terms of the weight of the raw materials), the mixture obtained is characterized by a biomethanation potential of 1061.82 NmL$_{CH4}$/gVS, which is 45% higher than the BMP of OFMSW$_A$ alone.

However, the outcome of the co-digestion test must be evaluated by comparing the measured methane volume with the theoretical volume; the latter is obtained from the sum of the volumes calculated by multiplying the known BMPs of the individual substrates by the grams of volatile solids introduced into co-digestion (as shown in Figure 67).

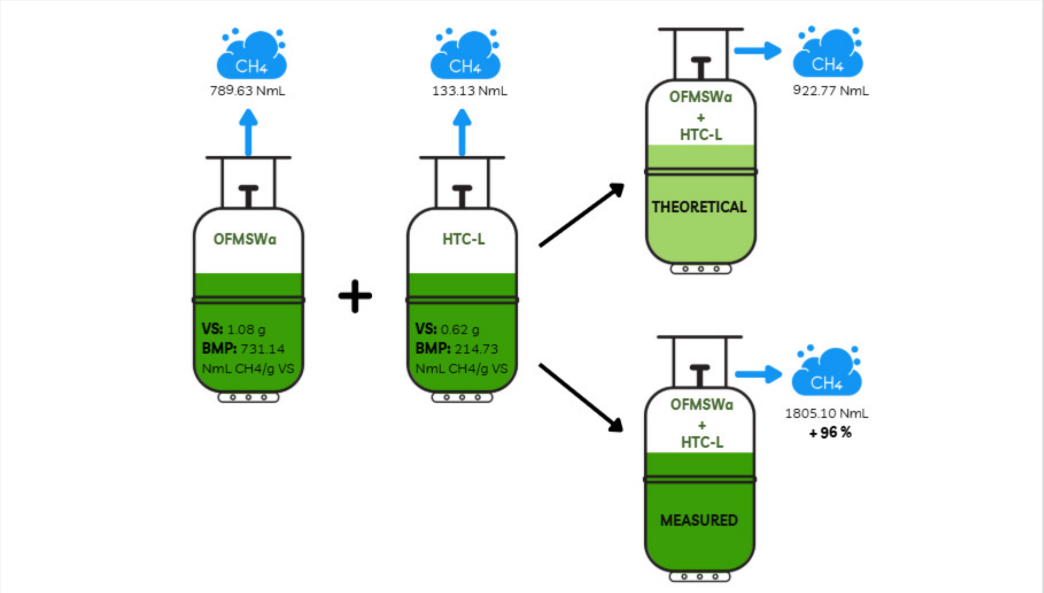

Figure 67 - Comparison between the theoretical methane volume and the measured volume produced from the co-digestion of $OFMSW_A$ and HTC-L

From the analysis conducted, it can be observed that the volume of methane that 1.08 g of VS of $OFMSW_A$ and 0.62 g of HTC-L should produce is equal to 922.77 NmL_{CH4}, while the measured value is 1805.10 NmL_{CH4}. This indicates that the co-digestion of these two matrices leads to a substantial improvement in methane production, with a 96% increase compared to what would be obtained with the same materials treated in mono-digestion. The BMP of this new substrate is 1061.82 NmL_{CH4}/gVS, which is higher than that of the individual matrices.

Therefore, this test highlights the remarkable effectiveness of this combined treatment using HTC liquid. Initially considered a waste product of the hydrothermal carbonization process, HTC-L proves to be a valuable substrate due to its nutrient content, promoting methanization and enhancing methane production through the biological process of anaerobic digestion.

A possible implementation at the industrial level, which improves the yields of anaerobic digestion of OFMSW in terms of methane production, is shown in Figure 68.

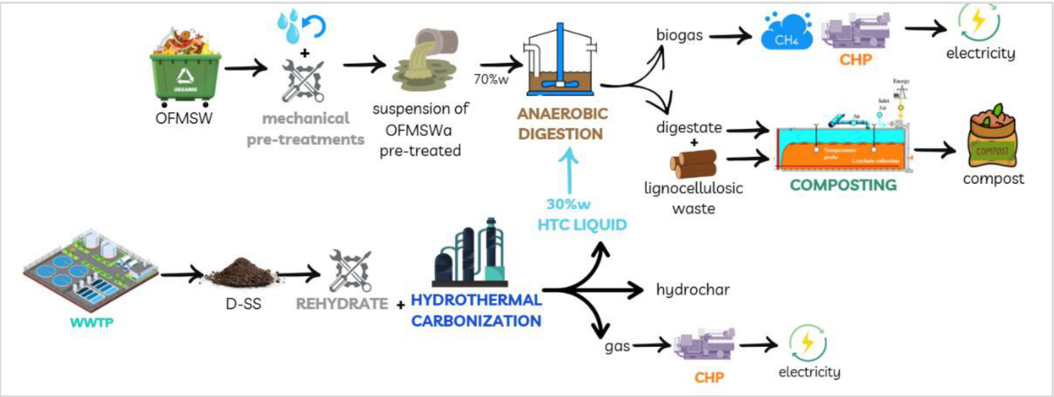

Figure 68 – Layout scenario of a biorefinery for the co-digestion of $OFMSW_A$ and HTC-liquid

It would therefore be possible to hypothesize an organic matrices treatment hub whereby sewage sludge leaving the WWTP is pretreated and then subjected to HTC. The output of this technology results in the production of both a solid and a liquid contribution both of which can still be enhanced by biological processes in co-digestion with OFMSW, leading to increased methane production as tested in this study.

6.3.6. Comparison of A-scenarios

The scenarios presented in the previous sections define the biomethanation potential of substrates composed of $OFMSW_A$ co-digested with different organic matrices. The BMP values of the investigated co-digestions, calculated from the volume of biomethane produced by each substrate relative to the unit mass of volatile solids that generated it, were compared to determine the most effective solutions. In Figure 69 is illustrated the specific methane production trend of the analyzed substrates over the duration of the test. It can be observed that the substrate with the highest biomethanation capacity is the one containing $OFMSW_A$ and HTC liquid in a 2.3:1.0 ratio.

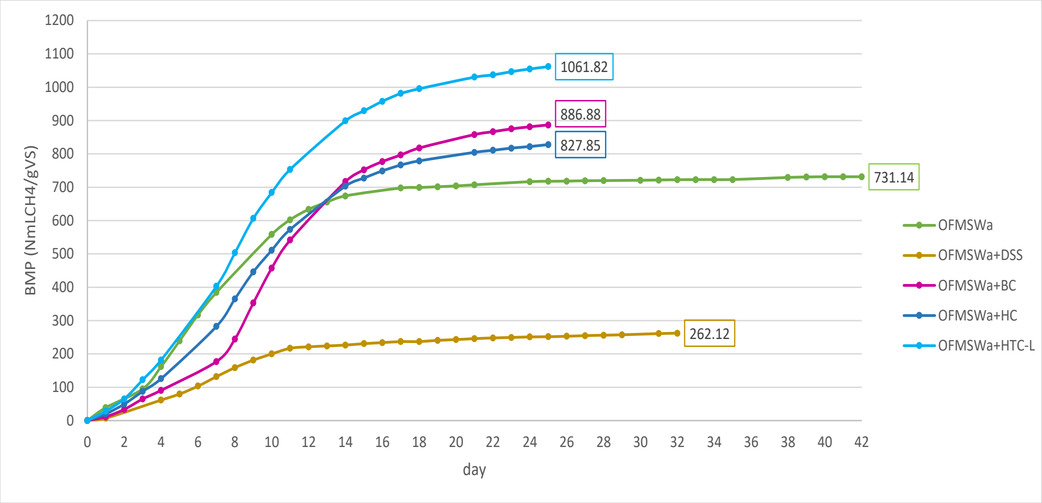

Figure 69 – Comparison of co-digestions tested with the OFMSW$_A$ matrix

The BMP of the OFMSW$_A$+HTC-L mix is higher probably as a result of the composition of the HTC liquid, which may have determined optimal conditions for the development of metabolic activities by the microorganisms: this is due to the nutrients, initially contained in the sludge, with hydrothermal carbonization have been transferred to the liquid component in solubilized form and thus appear to be more readily utilized by the microorganisms.

A summary of the results obtained from the different OFMSW$_A$ co-digestion A scenarios is shown in Table 61.

Table 61 – Comparison of substrate mix BMP derived in scenarios A

Scenario	**Test**	**Substrate**	**VS g**	**Net Volume NmL$_{CH4}$**	**BMP NmL$_{CH4}$/gVS**	**BMP variation**
A-0	T2	OFMSW$_A$	2.37	1732.81	731.14	0%
A-1	T3	OFMSW$_A$ +DSS	8.54	2238.48	262.12	- 64%
A-2	T4	OFMSW$_A$ +BC	2.76	2447.78	886.88	+ 21%
A-3	T4	OFMSW$_A$ +HC	3.08	2549.79	827.85	+ 13%
A-4	T4	OFMSW$_A$ +HTC-L	1.70	1805.10	1061.82	+ 45%

The BMP values obtained in the various co-digestion scenarios indicate that, for the same amount of volatile solids, the OFMSW$_A$ +HTC-L mix, prepared with a weight ratio of 2.3:1.0, achieves the highest methane production, with a BMP of 1061.82 NmL_{CH4}/gVS. This corresponds to a 45% increase compared to the mono-digestion of $OFMSW_A$.

Additionally, scenarios A-2 and A-3, which involve the co-digestion of $OFMSW_A$ with biochar and hydrochar, show mixes characterized by BMP values higher than that of $OFMSW_A$ alone. Specifically, these scenarios demonstrate a 21% and 13% advantage, respectively, in methane production. This improvement allows for the generation of approximately 800 NmL of methane per gram of volatile solids in the reactor, compared to 730 NmL_{CH4} for $OFMSW_A$ alone.

In contrast, the co-digestion of $OFMSW_A$ with dewatered sludge resulted in a 64% riduction in BMP compared to the biomethanation capacity of $OFMSW_A$ in scenario A-0.

It should be considered, however, that in order to obtain a more meaningful comparison of the advantage or disadvantage gained from co-digestion, the new mix tested in the various scenarios should be compared in terms of the volume of methane produced, with the volume that would be produced from the individual digestions of the starting matrices, as presented in the preceding paragraphs and shown briefly in Figure 70.

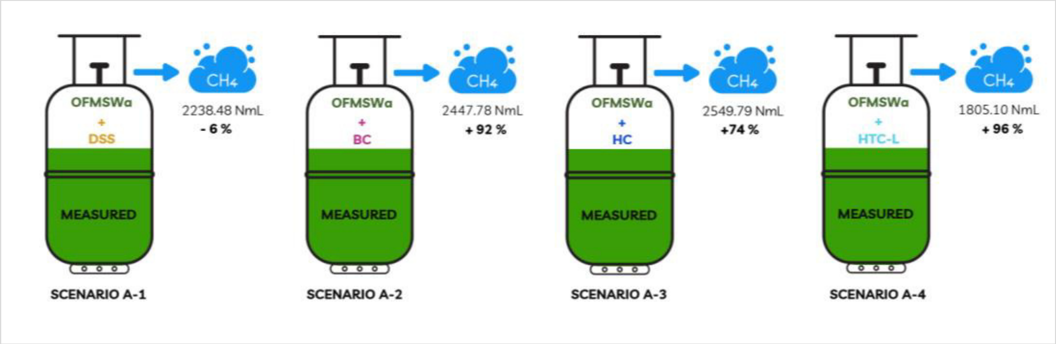

Figure 70 – Comparison of type A scenarios based on theoretical and measured methane volume

Figure 70 presents the results in terms of methane volume produced, as discussed in the paragraphs of the individual scenarios and are summarized in Table 62.

Table 62 – Summary of the comparison of A-scenarios

scenario	**Co-digestion with OFMSW_A**	**BMP sub 1 NmL/gVS**	**BMP sub 2 NmL/gVS**	**gVS sub 1**	**gVS sub 2**	**V sub 1 NmL_{CH4}**	**V sub 2 NmL_{CH4}**	**V co-dig calculated NmL**	**V co-dig measured NmL**	**ΔV NmL**	**ΔV %**
A-1	sub 1: OFMSW_A sub 2: **D-SS**	731.14	194.21	1.35	7.19	987.04	1396.35	2383.39	2238.48	-144.91	-6%
A-2	sub 1: OFMSW_A sub 2: **BC**	731.14	23.51	1.71	1.05	1250.26	24.68	1274.94	2447.78	1172.84	92%
A-3	sub 1: OFMSW_A sub 2: **HC**	731.14	157.74	1.71	1.37	1250.26	216.11	1466.36	2549.79	1083.43	74%
A-4	sub 1: OFMSW_A sub 2: **HTC-L**	731.14	214.73	1.08	0.62	789.63	133.13	789.63	1805.10	882.33	96%

From this comparison, similarly to the previous analysis, it emerges that BC and HC are advantageous when used in co-digestion with OFMSW_A at concentration of 13 $\text{g/L}_{\text{OFMSW.}}$ Instead, the co-digestion of OFMSW_A with DSS at a ratio of 1.0:2.3 results in a minimum reduction (of 6%) in methane production compared to what would be obtained from the digestion of the individual matrices. This means that during the co-digestion, matrices show a neutral behavior producing approximately the same volume as they would if treated with mono-digestion. This suggests the need to test additional combination ratios to discover synergistic actions between these materials.

In contrast, the same ratio of 1.0:2.3 was tested for the co-digestion with HTC-L, resulting in a methane production that is 96% higher than the theoretical volume that the two matrices would produced, without any synergistic action, based on the volatile solids added and their respective BMP. This specific substrate mix allows the materials to work synergistically, leading to a greater yield in terms of methane production capacity.

6.4. Implementation of AD process of OFMSW$_T$ using organic additives

This chapter describes the BMP tests of the anaerobic co-digestion process of the pre-treated suspension of OFMSW from a combined AD semi-dry and composting plant with other organic matrices, such as dewatered sewage sludge, biochar from sludge pyrolysis, hydrochar and HTC liquid produced by the sludge HTC process. In this chapter, in addition to analyze OFMSW$_T$ co-digestion processes with the aforementioned matrices, we also hypothesize plant scenarios (identified below as Scenario B) suitable to allow, in the logic of biorefinery, the realization of a hub for the centralized and joint management of organic matrices, through the joint use of different technologies for the treatment with the aim of maximizing the recovery.

6.4.1. Scenario B-0: mono-AD of OFMSW$_T$

Also for OFMSW$_T$ coming from the combined plant of TERSAN Puglia, the starting scenario given by the mono-digestion of this matrix was analyzed in order to compare it with the outcomes of the co-digestion tests carried out in the experimentation.

The process scheme is depicted in Figure 71 and involves an initial solid/liquid separation using a press that allows only the liquid component to proceed to anaerobic digestion, as the solid component is already sent along with the lignocellulosic waste and dry digestate, to composting. The liquid suspension sent to digestion is the subject of the present analysis to monitor the methane yield of mono-digestion of this matrix but also the yields of co-digestions with the other organic matrices already described.

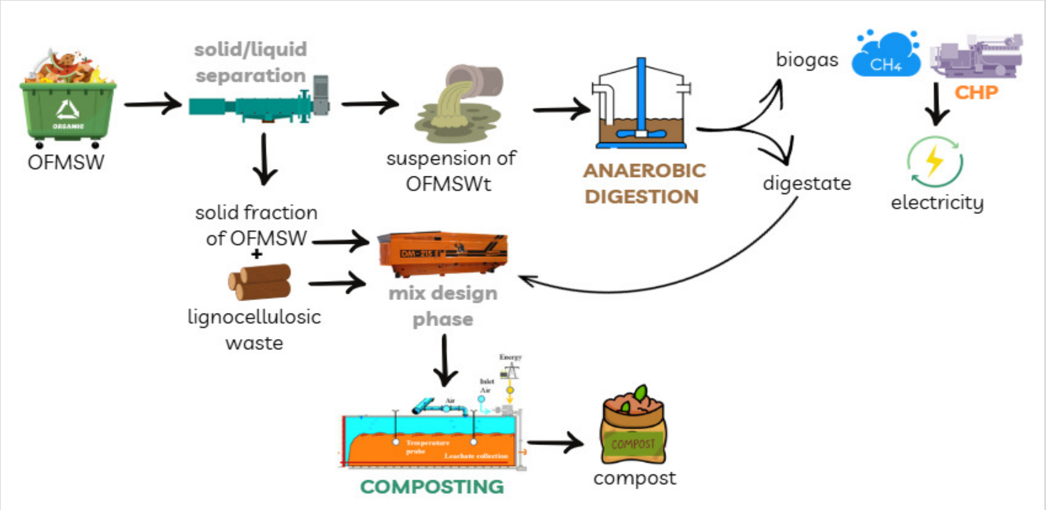

Figure 71 – Scheme of mono-digestion of pre-treated OFMSW$_T$ and composting

At the experimental level, the test that describes the results produced by the anaerobic digestion of OFMSW$_T$ is the T7 test, its results have already been presented in Section 6.2.2. and are summarized in Table 63.

Table 63 – Mono-digestion of OFMSW$_T$

Mono-digestion	**VS**	**Net volume**	**BMP**
	g	**NmL$_{CH4}$**	**NmL$_{CH4}$/gVS**
OFMSW$_T$	6.54	3323.58	508.19

In the following paragraphs, a graphical comparison between the mono-digestions of individual substrates and their co-digestion treatment is presented so it's possible to evaluate how implementations of this plant solution may or may not be useful in increasing methane production.

6.4.2. Scenario B-1: co-AD of OFMSW$_T$ and dewatered sludge

The first co-digestion scenario investigated involved the organic matrices of OFMSW$_T$ and dewatered sewage sludge. These matrices were treated in co-digestion in the T6 test to determine the BMP of this new substrate consisting of 700%w OFMSW$_T$ and

30%w DSS; then the BMP of the co-digestion was compared with the yields obtained for mono-digestions.

The test lasted 33 days with ISR of 2; the average characterization of the matrices used is shown in Table 64.

Table 64 – Average characterization of the matrices involved in the co-digestion of $OFMSW_T$ and DSS

Parameter	Unit	Inoculum	$OFMSW_T$	DSS
Total Solids	%	7.48	15.35	20.60
Water content	%	92.52	84.65	79.40
Ash	%	0.18	2.27	5.66
Volatile Solids	%	7.30	13.08	14.94
Volatile Solids	%dm	97.48	85.17	72.53

It was decided to add a quantity of 150 g of inoculum both to reactors (R1 and R2) used to represent the “blank” and to the reactors R8 and R9, which contain also the substrate to be tested. According to the characterization of the material, 150 g of inoculum contains 10.94 g of VS. The amount of substrate to be added was determined using Formula (22), where with an ISR of 2 and knowing the volatile and total solids of both the inoculum and the two matrices making up the substrate, and the respective weight percentage to be used, the total mass of substrate to be added to each reactor was calculated as 40.13 g. The amounts loaded into each reactor are shown in Table 65.

Table 65 – Amount of inoculum and substrate added to each reactor for the co-digestion of $OFMSW_T$ e DSS

Reactor	Matrix	Inoculum		Substrate			
				$OFMSW_T$		DSS	
		g	g VS	g	g VS	g	g VS
R1	Inoculum	150.00	10.94	-	-	-	-
R2		150.00	10.94	-	-	-	-
R8	Inoculum + Substrate	150.00	10.94	28.09	3.67	12.04	1.80
R9		150.00	10.94	28.09	3.67	12.04	1.80

The volume of CH4 produced by each reactor was recorded, and the data obtained from the milligas counters were subsequently normalized. These normalized data were used to elaborate the cumulative production trends shown in Figure 72. It is specified that reactor R2, as mentioned in section 6.3.3., had some malfunctions from the early stages and was therefore excluded from the analysis.

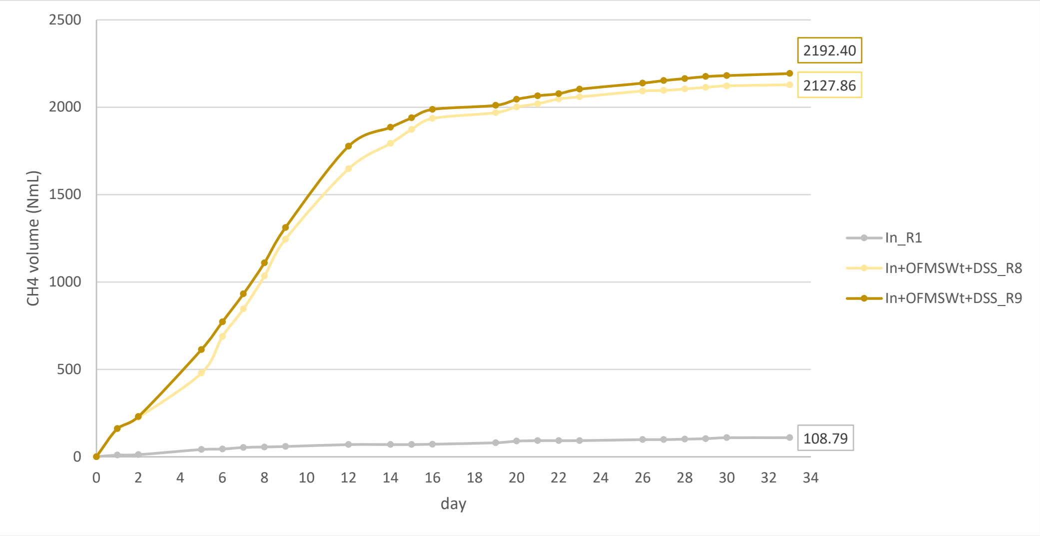

Figure 72 – Gross methane production during 33 days of AD of Inoculum and Inoculum with the $OFMSW_T$ and DSS substrate mix

In Figure 72, the methane production by reactors R8 and R9 define a similar trand resulting in a final average volume of 2160.13 NmL_{CH4}. It is highlighted that during the first 16 days of the test, reactors R8 and R9 produced about 2000 NmL of methane, which is more than 90% of the final production. In the remaining two weeks, the production rate decreases, and the cumulative methane curve levels off, forming a plateau.

Next, the net methane volume produced by R8 and R9 is calculated by subtracting the daily production increase of each reactor by the daily production of the inoculum in R1. Table 66 shows the net methane volumes produced by the reactors on day 33 and the BMP subsequently calculated. The co-digestion of $OFMSW_T$ and DSS produced an average net methane volume of 2051.35 NmL, resulting in an average BMP for this mix of 375.02 NmL_{CH4}/gVS.

Table 66 – Summary of the results obtained from the co-digestion of $OFMSW_T$ and DSS in trial T6

Test	**Reactor**	**Substrate**	**VS g**	**Net volume NmL_{CH4}**	**BMP NmL_{CH4}/gVS**
	R1	Inoculum	10.94	108.79	9.94
T6	R8	$OFMSW_T$ + DSS	5.47	2019.07	369.12
	R9	$OFMSW_T$ + DSS	5.47	2083.62	380.92

The trend of specific production is shown below, relating the daily net methane volume produced by $OFMSW_T$ + DSS to the grams of volatile solids that generated it.

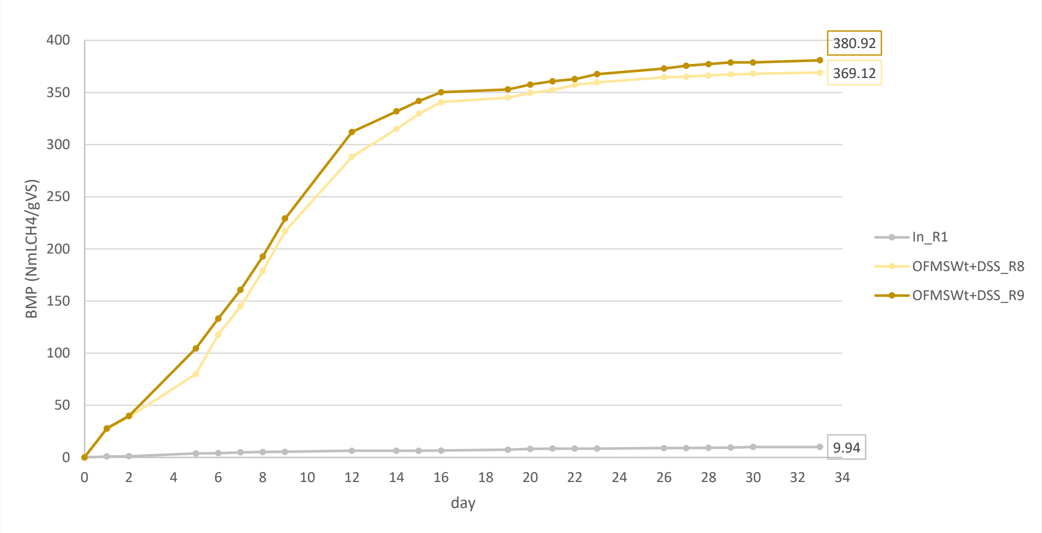

Figure 73 – Trend of BMP during the co-digestion of $OFMSW_T$ + DSS

To evaluate if the yield in co-digestion is improved compared to the individual mono-digestions, the results of this test were compared with the mono-digestions of the individual matrices, determined during tests T2 and T7. For each matrix, the average values obtained during the tests were considered and compared in Table 67 and Figure 74.

Table 67 – Comparison between the BMP of the substrate mix OFMSW$_T$+DSS and that of the individual substrates

Test	Substrate	VS g	Net Volume NmL$_{CH4}$	BMP NmL$_{CH4}$/gVS
T7	OFMSW$_T$	6.54	3323.58	508.19
T2	D-SS	9.50	1844.97	194.21
T6	OFMSW$_T$+DSS	5.47	2051.35	375.02

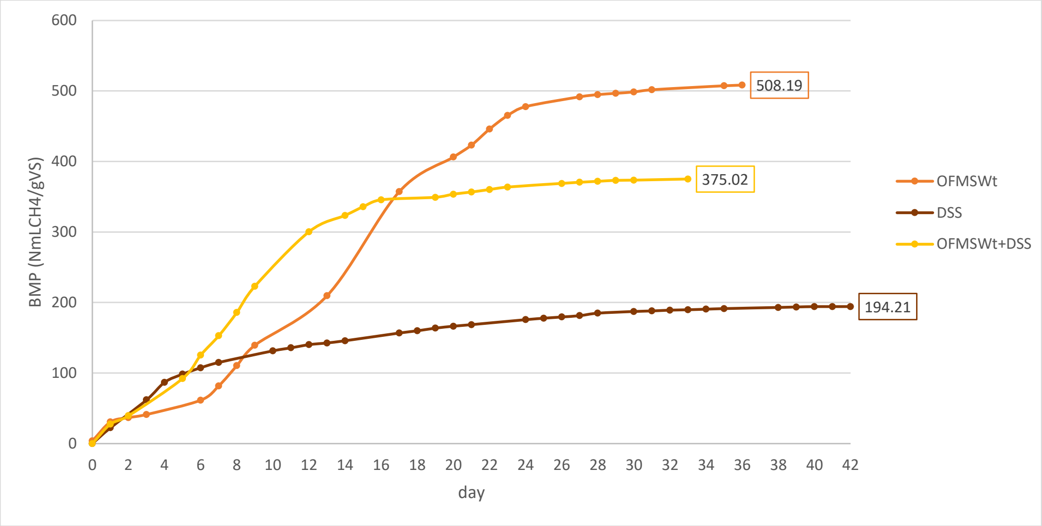

Figure 74 – Comparison between the trends of specific methane production in the co-digestion of OFMSW$_T$+DSS and the individual mono-digestions

Co-digestion thus produces a substrate characterized by a BMP intermediate between those of the starting matrices. For sludge, the addition of FW into the DSS high-solids digestion improved system stability and enhanced volumetric biogas production (Dai et al., 2013). However, considering OFMSW as the starting matrix, it does not turn out to be equally advantageous to include DSS in the AD process because, in the ratio analyzed (30%w DSS, 70%w OFMSW$_T$) it results in a substrate mix characterized by a lower BMP, so for the same amount of volatile solids fed into the reactor, less methane is obtained.

The outcome of the co-digestion test, however, must be evaluated by comparing the measured volume of methane with the theoretical volume; the latter is the sum of volumes obtained by multiplying the grams of volatile solids inserted in co-digestion by their specific BMP (as shown in Figure 75).

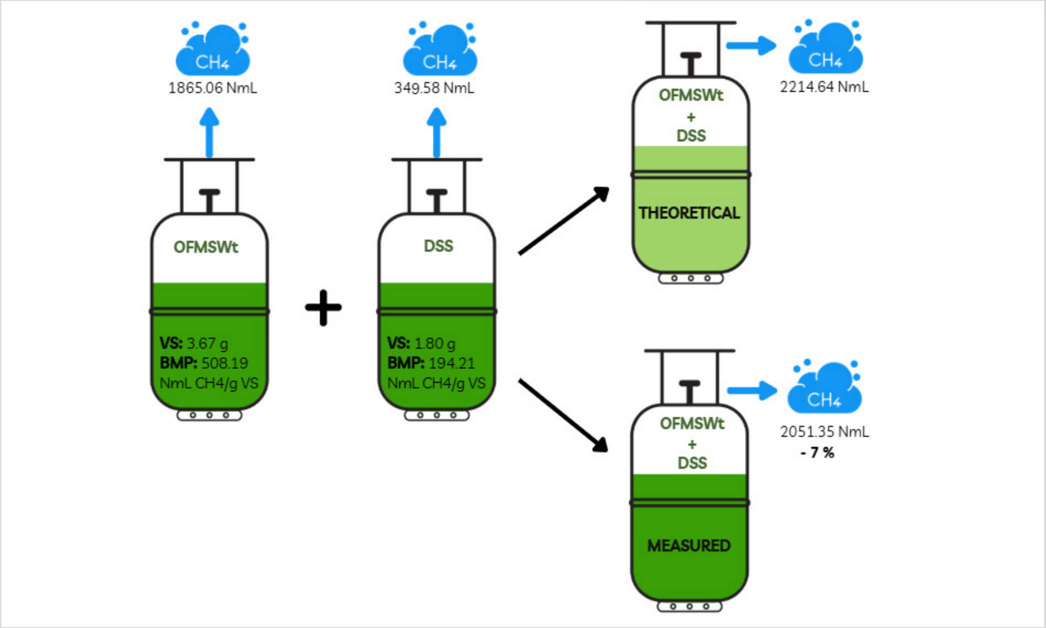

Figure 75 – Comparison between the theoretical methane volume and the measured volume produced from the co-digestion of $OFMSW_T$ e DSS

The analysis reveals that the theoretical methane volume that the quantities of $OFMSW_T$ and DSS loaded into reactors R8 and R9 should produce is slightly higher than the actual volume produced during test T6, with a difference of 7%. This situation is similar to what was observed in scenario A-1 for the co-digestion treatment of $OFMSW_A$ + DSS. Since is a difference of less than 10%, it can be concluded that in the ratio of 2.3:1.0 ($OFMSW_T$ and DSS), this new mix does not result in a significant change in the efficiency of the anaerobic digestion process. Therefore, it is concluded that the two matrices treated in co-digestion do not have synergistic effects to improve the digestion of the individual materials. However, although the co-digestion treatment is not advantageous in terms of methane production, it is beneficial in terms of waste recovery, as it would allow a matrix intended for disposal in landfills (DSS) to be recovered through a biological process, with subsequent energy recovery and material recovery through compost production. Figure 76 shows a hypothetical plant scenario that involves the co-digestion treatment of OFMSW and DSS.

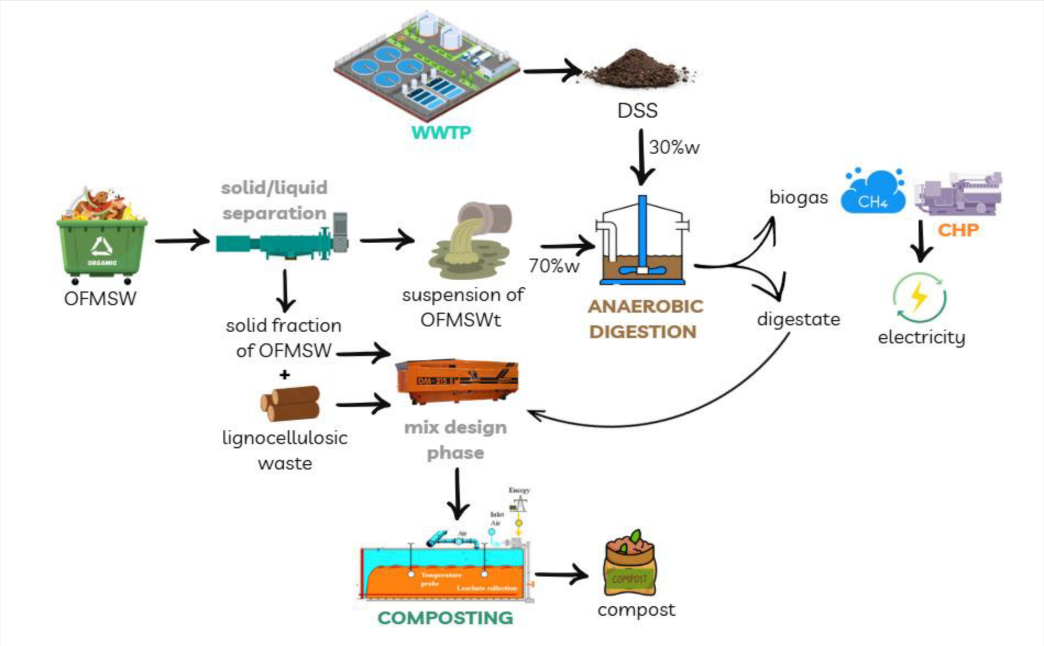

Figure 76 – Layout scenario of a biorefinery for the co-digestion of $OFMSW_T$ and dewatered sewage sludge

6.4.3. Scenario B-2: co-AD of $OFMSW_T$ and biochar

The $OFMSW_T$ matrix was also tested in co-digestion with biochar in test T5. This material was added to the reactors at a concentration of 13 g/L_{OFMSW}. The test lasted 26 days, and to determine the amount of $OFMSW_T$ to treat, an ISR of 2 was adopted. Based on the weight of $OFMSW_T$ and knowing its density, 13 g/L of biochar was added. Table 68 shows the average characterization of the matrices used.

Table 68 – Average characterization of the matrices involved in the co-digestion of $OFMSW_T$ and BC

Parameter	Unit	Inoculum	$OFMSW_T$	Biochar
Total solids	**%**	5.91	14.44	96.43
Water content	**%**	94.09	85.56	3.57
Ash	**%**	0.65	2.14	47.72
Volatile solids	**%**	5.26	12.30	48.71
Volatile solids	**%dm**	89.00	85.18	50.52

A quantity of 150 g of inoculum was added to both reactors R1 and R2, used to represent the "blank" as well as to reactors R6 and R7, which also contained the new mix under investigation. According to the material characterization, 150 g of inoculum contained 7.89 g of volatile solids.

The amount of $OFMSW_T$ to be added was determined by selecting an ISR of 2 and taking into account the volatile and total solids content of both the inoculum and the $OFMSW_T$. The biochar, on the other hand, was added at a concentration of 13 g/L_{OFMSW}. The quantities loaded into each reactor are summarized in Table 69.

Table 69 – Amount of inoculum and substrate added to each reactor for the co-digestion of $OFMSW_T$ e BC

Reactor	**Matrix**	**Inoculum**		**Substrate**			
				$OFMSW_T$		**BIOCHAR**	
		g	**g VS**	**g**	**g VS**	**g**	**g VS**
R1	Inoculum	150.00	7.89	-	-	-	-
R2		150.00	7.89	-	-	-	-
R6	Inoculum + Substrate	150.00	7.89	32.07	3.95	0.38	0.18
R7		150.00	7.89	32.07	3.95	0.38	0.18

The volume of CH4 produced by each reactor was recorded, and the data collected in this case by the software were used to develop the cumulative production trends shown in Figure 77. It is important to note that reactor R7 experienced malfunctions starting from the fifth day of testing; for this reason, its results were excluded from the analysis.

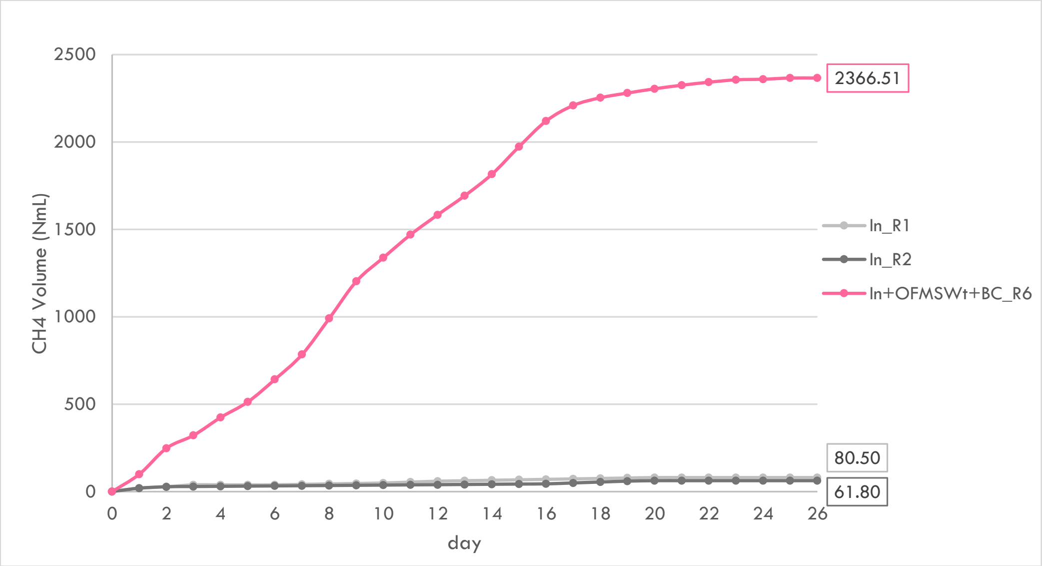

Figure 77 – Gross methane production during 26 days of AD of Inoculum and Inoculum with the OFMSW$_T$ and BC substrate mix

The graph shows that the two reactors, R1 and R2, containing only inoculum, exhibit overlapping methane production trends, with an average methane volume of 71.15 NmL. Reactor R6, which contains inoculum and substrate, achieves a methane production of 2366.51 NmL by the 26th day.

The net methane volume produced by this reactor is calculated by subtracting the average daily production of the two inoculum-only reactors (R1 and R2) from R6 daily production increment. Table 70 presents the net methane volumes produced by the reactors on the 26th day, along with the calculated BMP values.

The co-digestion of OFMSW$_T$ and BC produced a net methane volume of 2295.36 NmL, resulting in a BMP for this mix equal to 555.78 NmL$_{CH4}$/gVS.

Table 70 – Summary of the results obtained from the co-digestion of OFMSW$_T$ and BC in trial T5

Test	**Reactor**	**Substrate**	**VS** **g**	**Net volume** **NmL$_{CH4}$**	**BMP** **NmL$_{CH4}$/gVS**
T5	R1	Inoculum	7.89	80.50	10.20
	R2	Inoculum	7.89	61.80	7.83
	R6	OFMSW$_T$ + BC	4.13	2295.36	555.78

The trend of specific methane production is shown below, relating the net daily volume produced by the $OFMSW_T$ + BC mix to the grams of volatile solids that generated it.

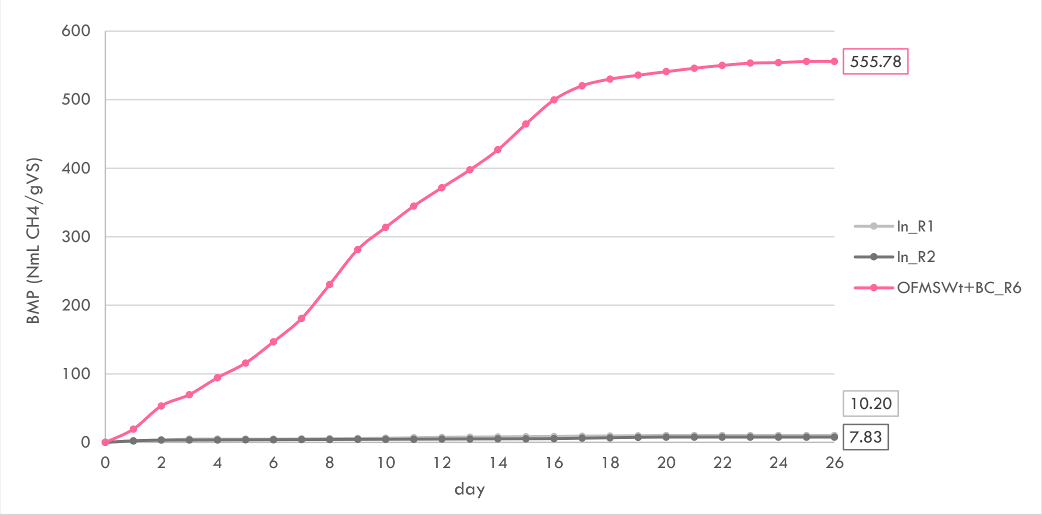

Figure 78 – Trend of BMP during the co-digestion of $OFMSW_T$ + BC

To assess if the yield of co-digestion of $OFMSW_T$ with biochar is actually improved, the results of this test need to be compared with the mono-digestions of the individual matrices, determined during tests T6 and T7. The comparison is presented in Table 71 and graphically illustrated in Figure 79, considering the average BMP values determined for each matrix during the tests.

Table 71 – Comparison between the BMP of the substrate mix $OFMSW_T$+BC and that of the individual substrates

Test	**Substrate**	**VS** **g**	**Net Volume** **NmL_{CH4}**	**BMP** **NmL_{CH4}/gVS**
T7	$OFMSW_T$	6.54	3323.58	508.19
T6	BC	5.47	128.63	23.51
T5	$OFMSW_T$+BC	4.13	2295.36	555.78

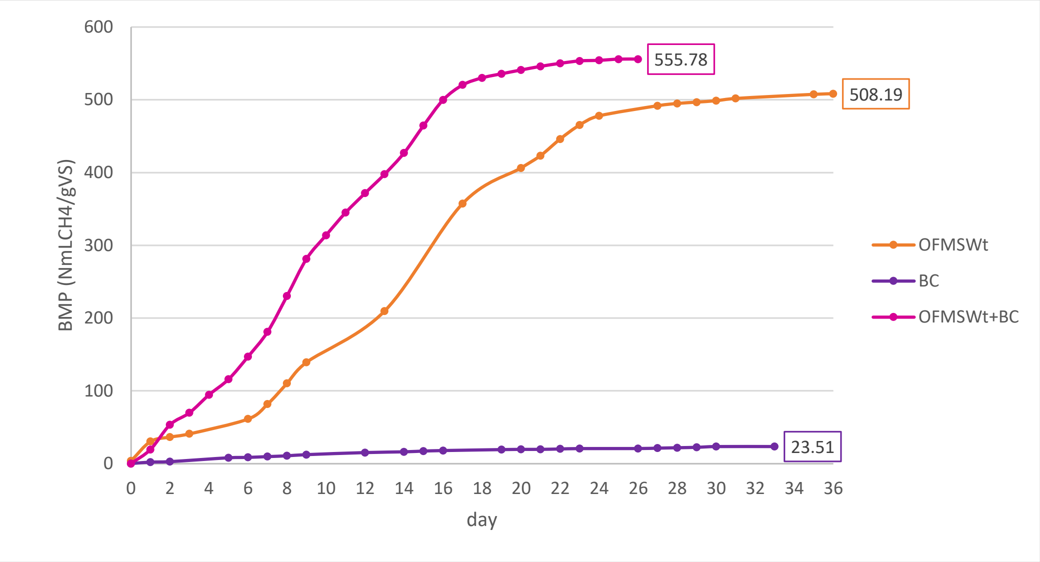

Figure 79 – Comparison between the trends of specific methane production in the co-digestion of $OFMSW_T$+BC and the individual mono-digestions

It can be observed that biochar, when analyzed individually, is characterized by a very low methane potential. However, even using a minimal amount of this material as an additive in the AD treatment of $OFMSW_T$ results in a BMP of approximately 550 NmL_{CH4}/gVS.

The outcome of the co-digestion test, however, must be evaluated by comparing the measured methane volume with the theoretical volume; the latter is the sum of the volumes derived by multiplying the known BMP values of the individual substrates by the grams of volatile solids used in co-digestion (as shown in Figure 80).

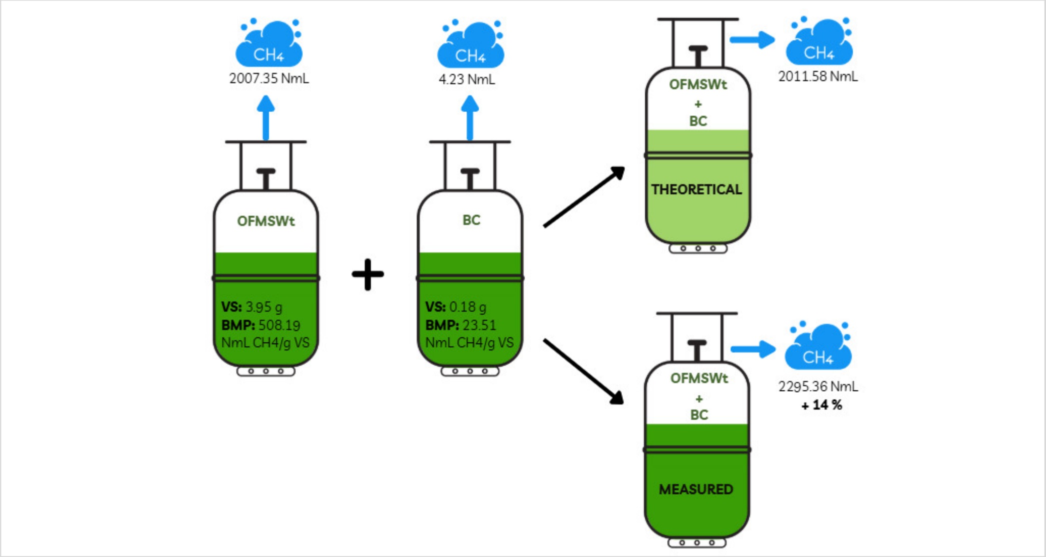

Figure 80 – Comparison between the theoretical methane volume and the measured volume produced from the co-digestion of $OFMSW_T$ and BC

From the analysis conducted, it is evident that the volume of methane that 3.95 gVS of $OFMSW_T$ and 0.18 gVS of BC should theoretically produce amounts to 2011.58 NmL, whereas the measured volume exceeds this by 283.78 NmL. This indicates that the co-digestion of these two matrices results in a 14% increase in methane production compared to the materials treated in mono-digestion.

At the industrial level, it is possible to hypothesize a solution, illustrated in Figure 81, that enables the optimization of the anaerobic digestion process of OFMSW by increasing methane production through the addition of biochar as an additive.

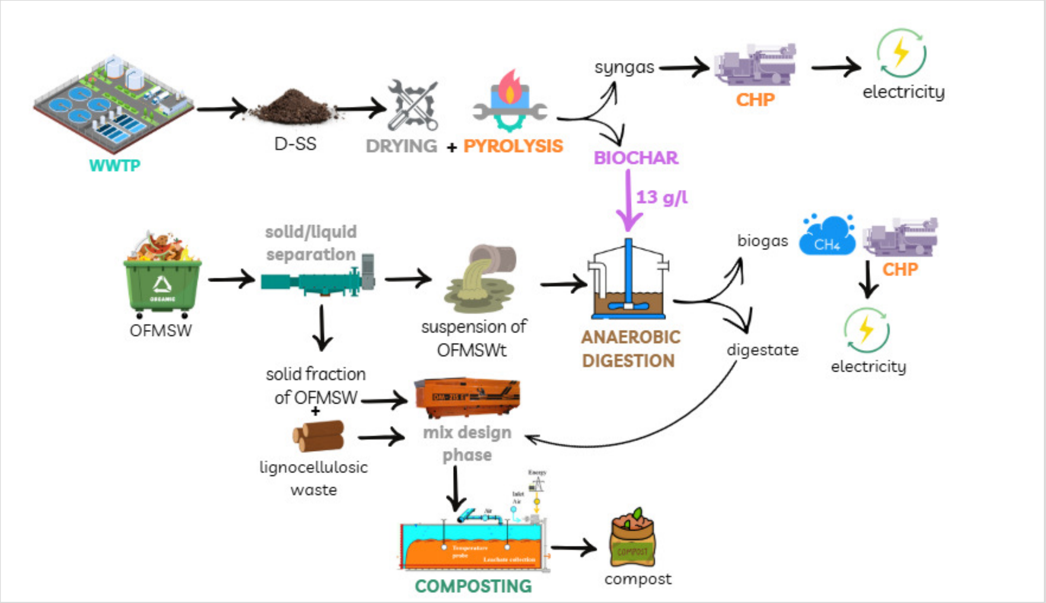

Figure 81 – Layout scenario of a biorefinery for the co-digestion of $OFMSW_T$ and biochar

It would therefore be possible to hypothesize an organic waste treatment hub where sewage sludge from treatment plants undergoes a pre-treatment process involving drying, followed by pyrolysis. The output of this technology generates both a high-calorific-value gas (syngas), which can be converted into electrical and thermal energy through CHP, and biochar, which could be utilized either in co-digestion with OFMSW or as a fertilizer in agriculture. This material could be integrated into the existing anaerobic digestion process of the organic fraction, enabling an improvement in process yields.

6.4.4. Scenario B-3: co-AD of $OFMSW_T$ and hydrochar

This scenario investigates the co-digestion of $OFMSW_T$ with hydrochar produced through the hydrothermal carbonization process described in Section 5.1.6. This alternative was examined in test T7, where $OFMSW_T$ was supplemented with hydrochar at the same concentration tested for biochar (13 g/L relative to the amount of $OFMSW_T$ added to the reactor). To assess the effectiveness of this combined treatment, its outcome was compared with the yields obtained from the respective mono-digestions.

The test lasted 36 days, and to determine the amount of $OFMSW_T$ to be treated, an ISR of 2 was adopted. The average characterization of the matrices used is reported in Table 72.

Table 72 – Average characterization of the matrices involved in the co-digestion of $OFMSW_T$ e HC

Parameter	Unit	Inoculum	$OFMSW_T$	Hydrochar
Total Solids	**%**	7.61	14.18	81.52
Water content	**%**	92.39	85.82	18.48
Ash	**%**	1.07	2.27	24.46
Volatile solids	**%**	6.54	11.91	57.06
Volatile solids	**%dm**	85.98	84.00	70.00

A quantity of 200 g of inoculum was added both to reactors R1 and R2, used to represent the "blank" and to reactors R8 and R9, which also contained the new mix under investigation. According to the material characterization, 200 g of inoculum contained 13.09 g of VS.

The amount of $OFMSW_T$ to be added was determined by selecting an ISR of 2 and knowing the volatile and total solids content of both the inoculum and the $OFMSW_T$. The hydrochar, on the other hand, was added at a concentration of 13 g/L_{OFMSW}. The quantities loaded into each reactor are reported in Table 73.

Table 73 – Amount of inoculum and substrate added to each reactor for the co-digestion of $OFMSW_T$ e HC

Reactor	Matrix	Inoculum		Substrate			
				$OFMSW_T$		Hydrochar	
		g	g VS	g	g VS	g	g VS
R1	Inoculum	200.00	13.09	-	-	-	-
R2		200.00	13.09	-	-	-	-
R8	Inoculum + Substrate	200.00	13.09	54.93	6.54	0.65	0.37
R9		200.00	13.09	54.93	6.54	0.65	0.37

The volume of CH4 produced by each reactor was recorded, and the data obtained from the milligas counters, after being normalized, were used to elaborate the cumulative methane production trends shown in Figure 82. In this figure, it is possible to compare the methane production of the inoculum alone with the reactors containing both inoculum and the mix.

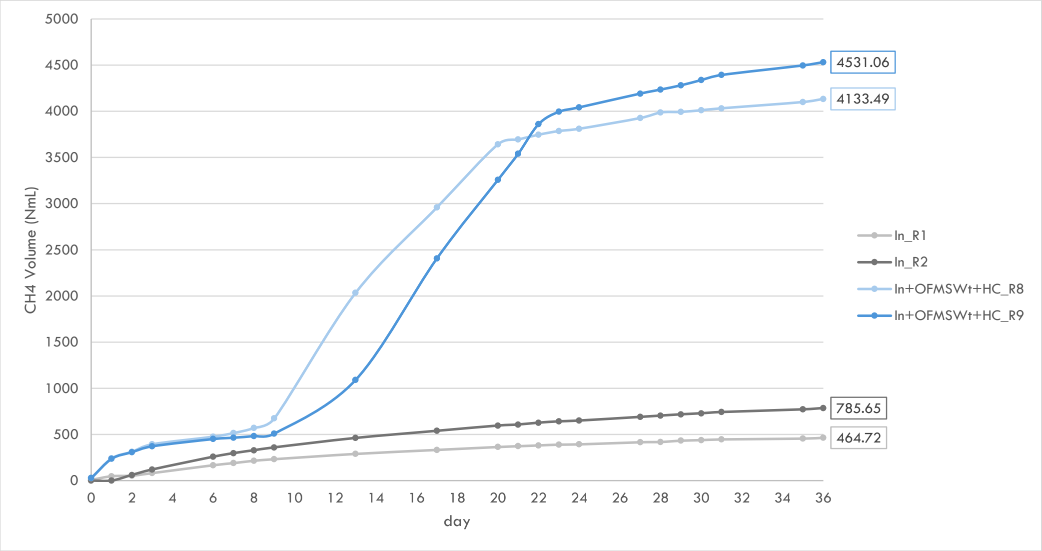

Figure 82 – Gross methane production during 36 days of AD of Inoculum and Inoculum with the $OFMSW_T$ and HC substrate mix

Reactors R1 and R2, containing inoculum, have a similar methane production trend, with an average volume of 625.19 NmL_{CH4}.

Regarding the methane production curves from reactors R8 and R9, which contain inoculum and substrate, it can be noted that in the first week, the production rate is low, resulting in a pseudo-horizontal production trend. From the ninth day onward, production increases significantly, and from the ninth to the 23rd day, more than 75% of the final volume is produced, reaching a plateau at an average value of 4332.28 NmL_{CH4}.

Next, the net methane volume produced by R8 and R9 is calculated by subtracting the daily production increase of each reactor by the average daily production of the inoculum alone (R1 and R2). Table 74 shows the net methane volumes produced by the reactors on the 36th day and the BMP subsequently calculated. The co-digestion of $OFMSW_T$ and HC produced an average net methane volume of 3859.72 NmL_{CH4}, resulting in an average BMP for this mix of 558.57 NmL_{CH4}/gVS.

Table 74 – Summary of the results obtained from the co-digestion of $OFMSW_T$ and HC in test T7

Test	Reactor	Substrate	VS g	Net volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T7	R1	Inoculum	13.09	464.72	35.50
	R2	Inoculum	13.09	785.65	60.02
	R8	$OFMSW_T$ + HC	6.91	3638.23	526.52
	R9	$OFMSW_T$ + HC	6.91	4081.22	590.63

The trend of specific methane production is shown below, relating the daily net volume produced by $OFMSW_T$ + HC to the grams of volatile solids that generated it.

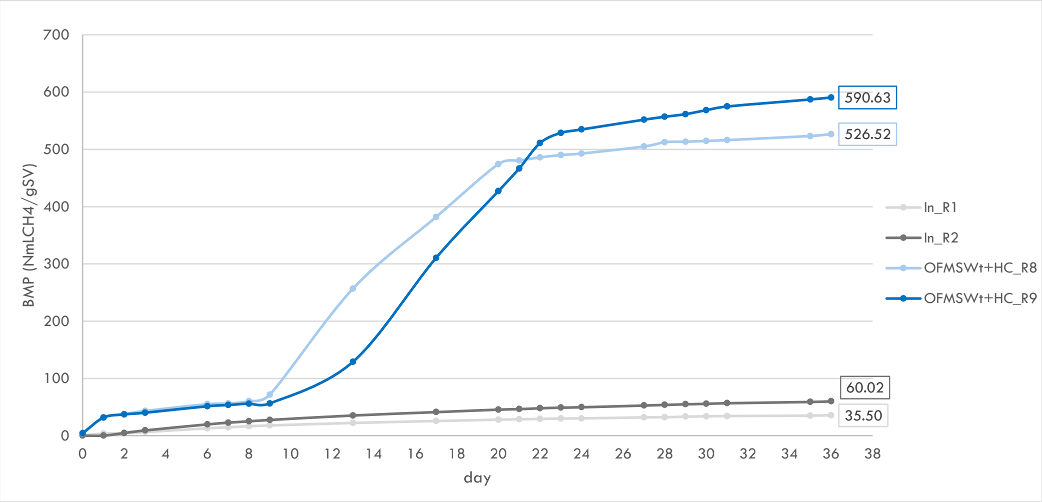

Figure 83 – Trend of BMP during the co-digestion of $OFMSW_T$ + HC

After the calculation of the BMP, to evaluate if the co-digestion yield is indeed improved, the results of this test need to be compared with the mono-digestions of the individual matrices, determined during tests T6 and T7. The comparison is shown in Table 75 and graphically in Figure 84 considering for each matrix the average BMP values determined during the tests.

Table 75 – Comparison between the BMP of the substrate mix $OFMSW_T$+HC and that of the individual substrates

Test	Substrate	VS g	Net Volume NmL_{CH4}	BMP NmL_{CH4}/gVS

T7	$OFMSW_T$	6.54	3323.58	508.19
T6	HC	5.47	862.86	157.74
T7	$OFMSW_T$+HC	6.91	3859.72	558.57

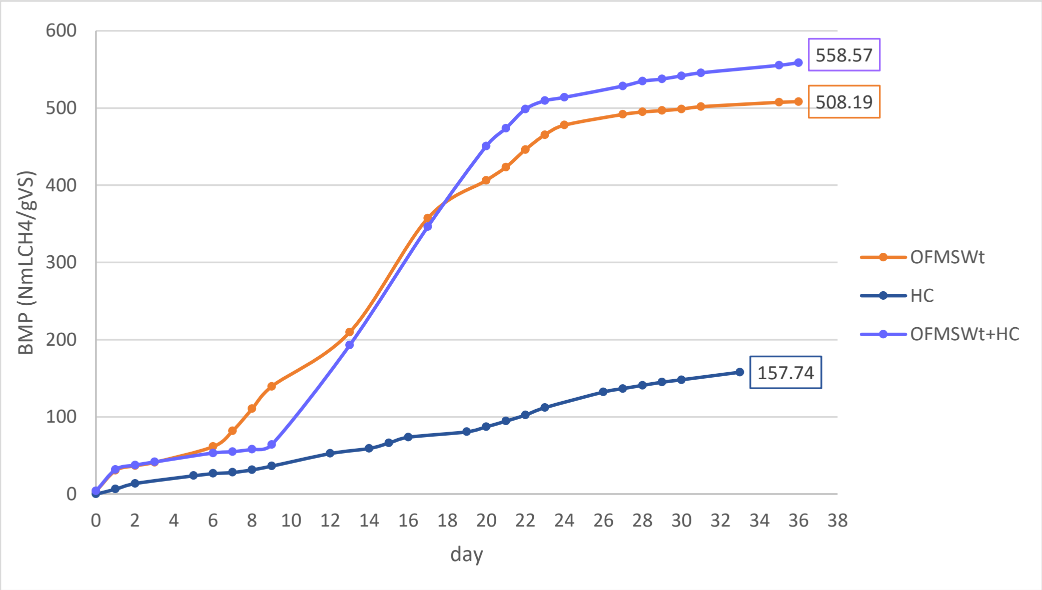

Figure 84 – Comparison between the trends of specific methane production in the co-digestion of $OFMSW_T$+HC and the individual mono-digestions

From the graph in Figure 84, it can be observed that hydrochar is characterized by a relatively low methanogenic potential. However, from this experiment, it can be seen that even a minimal amount of this material (0.65 g) added to the AD treatment of $OFMSW_T$ results in a new substrate with a BMP greater than that of $OFMSW_T$ alone. The methane production from this mix is initially slow but significantly increases after the first ten days. The first phase has limited methane production because it corresponds to the period during which the microbial consortium is acclimatized and begins to degrade the easy biodegradable substances; afterward, there is an exponential growth phase in which the microorganisms are able to metabolize a greater amount of acids, eventually reaching a stationary biogas production phase.

However, the outcome of the co-digestion test must be evaluated by comparing the measured methane volume with the theoretical volume; the latter is obtained summing the volumes calculated by multiplying the known BMPs of the individual substrates by the grams of volatile solids added in co-digestion (as shown in Figure 85).

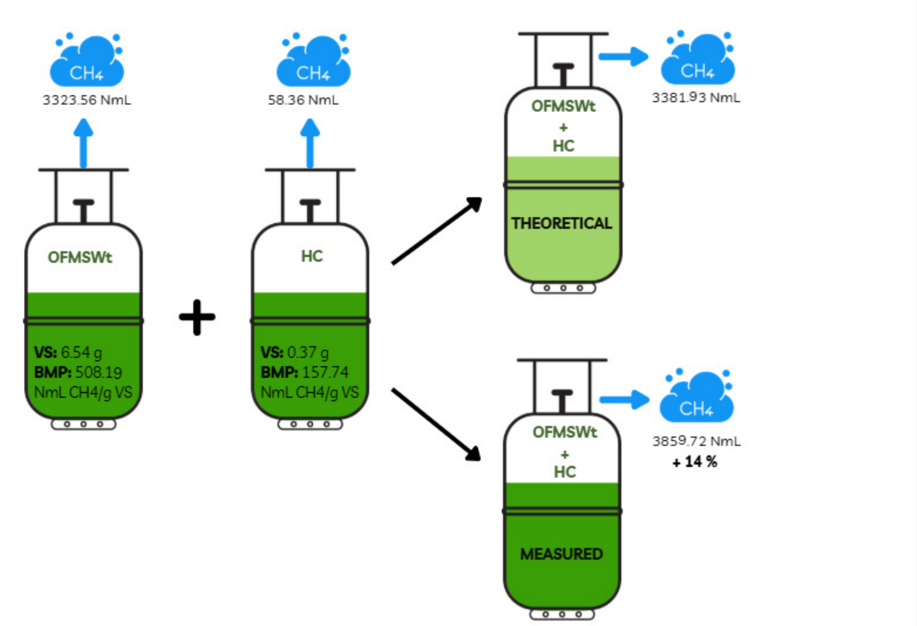

Figure 85 – Comparison between the theoretical methane volume and the measured volume produced from the co-digestion of $OFMSW_T$ e HC

From the analysis, it can be observed that the methane volume that 6.54 gVS of $OFMSW_T$ and 0.37 gVS of HC should produce by simply overlapping the effects is 3381.95 NmL_{CH4}, while the volume measured during the test is 3859.72 NmL_{CH4}. Therefore, it can be concluded that the co-digestion of these two matrices at the chosen concentration of 13 g/L_{OFMSW} results in an improvement of the process, with a 14% increase in methane production compared to the materials treated in mono-digestion. The BMP of this new substrate is 558.57 NmL_{CH4}/gVS, which is higher than that of the individual matrices.

A possible implementation, at the industrial level, of this solution which results in an improvement in the anaerobic digestion yield of OFMSW in terms of methane production, is shown in Figure 86.

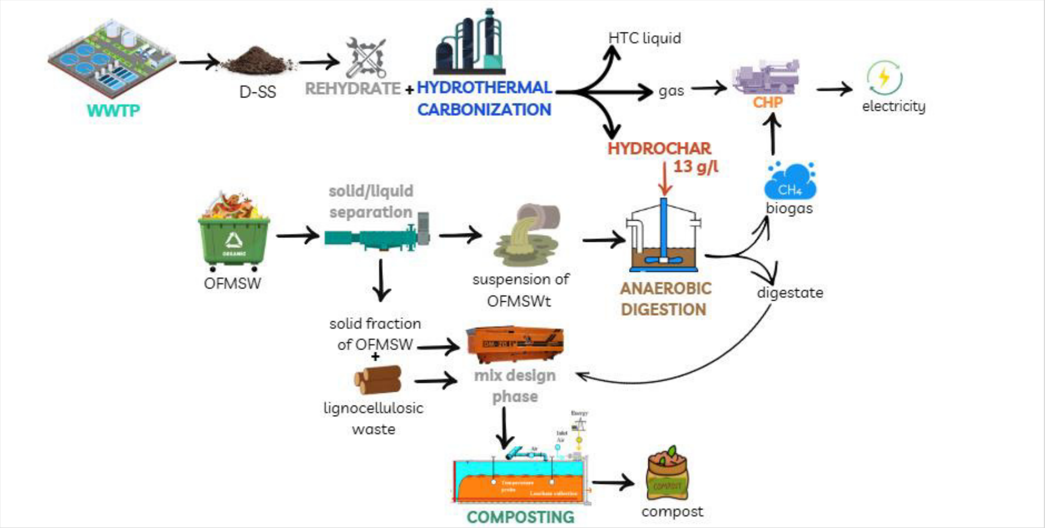

Figure 86 – Layout scenario of a biorefinery for the co-digestion of $OFMSW_T$ and hydrochar

It would therefore be possible to hypothesize a hub for the treatment of organic matrices, where the sludge from WWTP is pre-treated and then subjected to hydrothermal carbonization. The output of this technology results in the production of both a liquid fraction, which could be further valorized through biological processes, and a solid fraction, such as hydrochar, which could be partially used in co-digestion with OFMSW, resulting in an increase in methane production, as tested in this experiment.

6.4.5. Scenario B-4: co-AD of $OFMSW_T$ and HTC liquid

Scenario B-4 represents the co-digestion of $OFMSW_T$ with the HTC liquid produced by the hydrothermal carbonization process of wastewater sludge. These two matrices were co-digested in test T8 to determine the BMP of this new substrate, which consists of 70% $OFMSW_T$ by weight and 30% HTC-L, and to compare it with the yields obtained from the mono-digestions. The test lasted 37 days, the ISR of 2 in terms of volatile solids was applied, and the average characterization of the matrices used is shown in Table 76.

Table 76 – Average characterization of the matrices involved in the co-digestion of $OFMSW_T$ and HTC-L

Parameter	Unit	Inoculum	$OFMSW_T$	HTC liquid
Total Solids	%	7.63	8.50	1.41
Water content	%	92.37	91.50	98.59
Ash	%	0.72	1.67	0.07
Volatile Solids	%	6.91	6.83	1.34
Volatile Solids	%dm	90.55	80.39	94.94

It was decided to insert 150 g of inoculum into each of the two reactors (R1 and R2) used to represent "the blank" as well as into reactors R5 and R6, which also contain the new mix to be investigated. According to the material characterization, 150 g of inoculum contains 10.36 g of VS.

The quantity of substrate to be added was determined using the Formula 22 where, having an ISR of 2 and knowing the volatile and total solids of both the inoculum and the two matrices constituting the substrate, and knowing the desired weight percentage to be used, the total mass of substrate to be added to each reactor was calculated. Consequently, given the desired weight percentages (70% $OFMSW_T$ and 30% HTC-L), the quantities to be added for each matrix were calculated, and these are shown in Table 77.

Table 77 – Amount of inoculum and substrate added to each reactor for the co-digestion of $OFMSW_T$ e HTC-L

Reactor	Matrix	Inoculum		Substrate			
				$OFMSW_T$		HTC Liquid	
		g	g VS	g	g VS	g	g VS
R1	Inoculum	150.00	10.36	-	-	-	-
R2		150.00	10.36	-	-	-	-
R5	Inoculum + Substrate	150.00	10.36	69.90	4.78	29.96	0.40
R6		150.00	10.36	69.90	4.78	29.96	0.40

The methane volume produced by each reactor was recorded, and the data collected by the milligas counters were then normalized. These normalized data were used to plot the cumulative production trends shown in Figure 87, where the methane production of the inoculum alone is compared with that of the reactors containing both inoculum and the mix. It is specified that reactors R2 and R5 malfunctioned from the early stages of the test, so only the results obtained from reactors R1 and R6 are considered reliable.

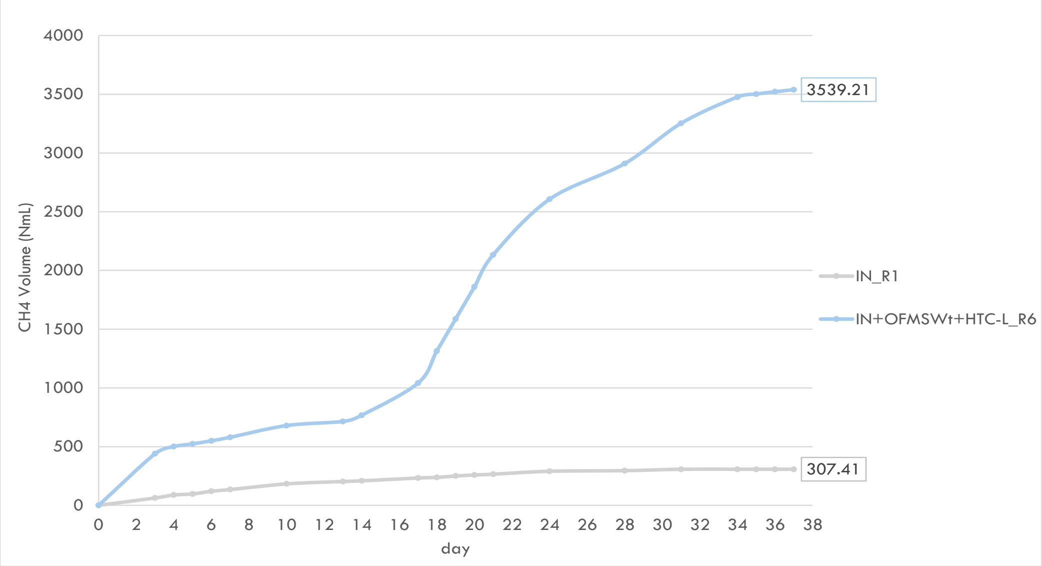

Figure 87 – Gross methane production during 37 days of AD of Inoculum and Inoculum with the $OFMSW_T$ and HTC-L substrate mix

The trend of CH4 volume produced by reactor R1 indicates a rather slow and gradual methane production by the inoculum alone, while the trend of reactor R6, although starting at higher methane production values, shows a lag phase of about 2 weeks, after which an exponential growth is recorded. The pattern of this curve indicates an initial need for adaption by the microorganisms to the system, followed by a sudden increase in methane production, indicative of high availability and rapid degradation of the organic substances present in the substrate. The production plateau is reached at 3539.21 NmL_{CH4}.

Below, the net methane volume produced by R6 is calculated by subtracting the daily production of the inoculum alone (R1) from its daily increment. Table 78 shows the net methane volumes produced by the reactors on the 37th day and the subsequently calculated BMP. The co-digestion of $OFMSW_T$ and HTC-L produced an average net methane volume of 3231.80 NmL, resulting in an average BMP of 623.90 NmL_{CH4}/gVS for this mix.

Table 78 – Summary of the results obtained from the co-digestion of $OFMSW_T$ and HTC-L in test T8

Test	Reactor	Substrate	VS g	Net volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T8	R1	Inoculum	10.36	307.41	29.67
	R6	$OFMSW_T$ + HTC-L	5.18	3231.80	623.90

Below is shown the trend of specific methane production by relating the daily net volume of methane produced by $OFMSW_T$ + HTC-L to the grams of volatile solids that generated it.

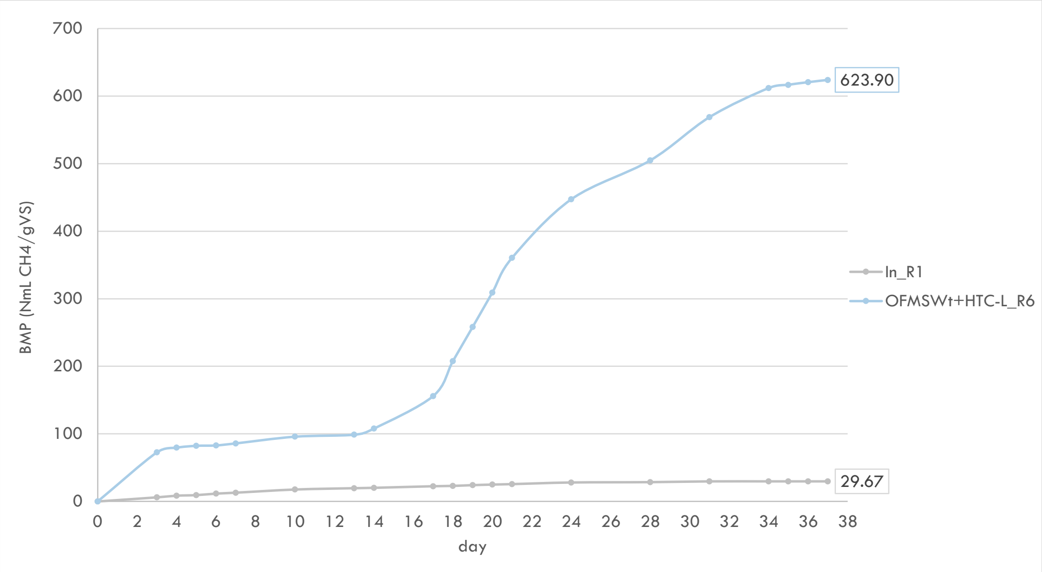

Figure 88 – Trend of BMP during the co-digestion of $OFMSW_T$ + HTC-L

As already highlighted in the previous graph, from the methane production trend of the R6 reactor, it can be observed that the new substrate tested has an initial stationary phase corresponding to the time needed for microorganism adaptation, followed by an exponential growth in methane production due to the rapid degradation of the considerable amount of organic matter present in the mix. The BMP reached by this substrate is high, indicating that the co-digestion treatment of $OFMSW_T$ and HTC liquid is effective in increasing methane production. However, to define if the co-digestion yield is improved, the result of this test must be compared with the mono-digestions of the individual matrices, determined during tests T7 and T8. The average values shown in Table 79 were considered for each matrix.

Table 79 – Comparison between the BMP of the substrate mix $OFMSW_T$+HTC-L and that of the individual substrates

Test	Substrate	VS g	Net Volume NmL_{CH4}	BMP NmL_{CH4}/gVS
T7	$OFMSW_T$	6.54	3323.58	508.19
T8	HTC-L	5.18	1112.31	214.73
T8	$OFMSW_T$ +HTC-L	5.18	3231.80	623.90

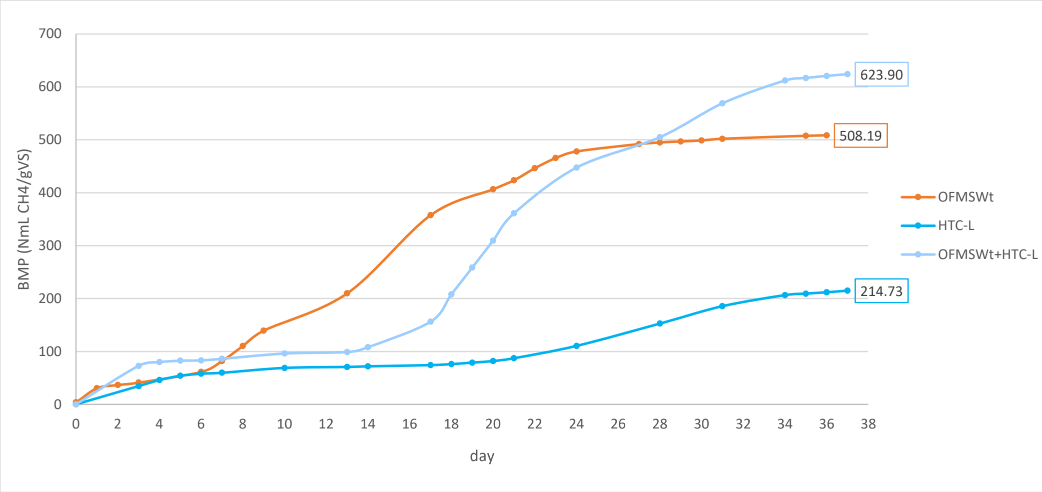

Figure 89 – Comparison between the trends of specific methane production in the co-digestion of $OFMSW_T$+HTC-L and the individual mono-digestions

It can be observed that by co-digesting $OFMSW_T$ and HTC-L in a 2.3:1.0 ratio, a mixture is obtained that will be characterized by a biomethanation potential of 623.90 NmL_{CH4}/gVS, which is 23% higher than the BMP of $OFMSW_T$ alone.

However, the outcome of the co-digestion test must be evaluated by comparing the measured methane volume with the theoretical volume, which would be obtained by summing the volumes derived from multiplying the known BMPs of the individual substrates by the grams of volatile solids inserted in co-digestion (as shown in Figure 90).

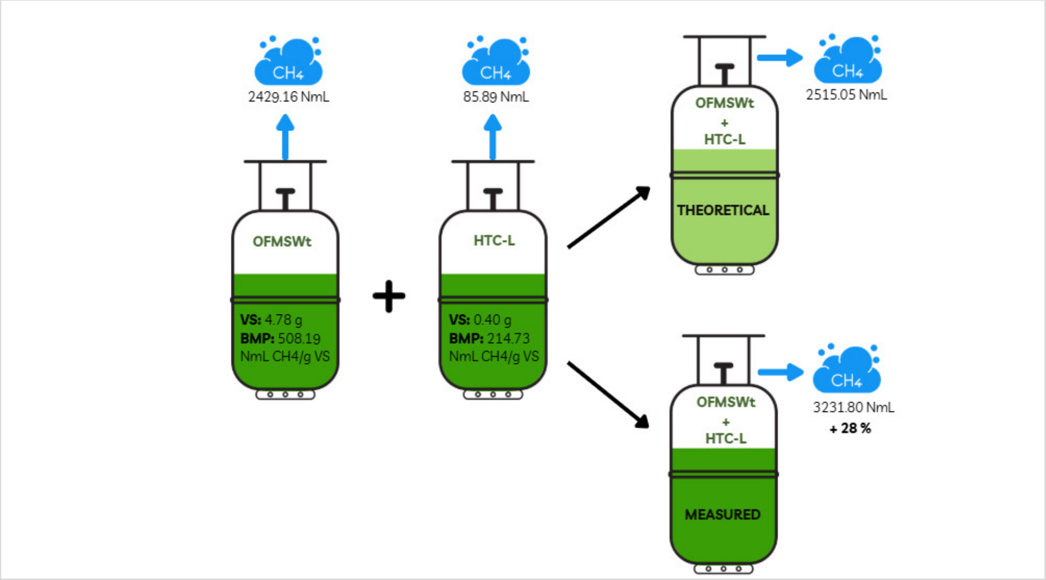

Figure 90 – Comparison between the theoretical methane volume and the measured volume produced from the co-digestion of $OFMSW_T$ and e HTC-L

From the analysis, it can be observed that the volume of methane that 4.78 gVS of $OFMSW_T$ and 0.40 gVS of HTC-L should produce is 2515.05 NmL_{CH4}, while the measured volume is 3231.80 NmL_{CH4}. Therefore, the co-digestion of these two matrices results in a substantial improvement in methane production, with a 28% increase compared to what would be obtained with the same materials treated in mono-digestion. The BMP of this new substrate is 623.90 NmL_{CH4}/gVS, a value higher than that of the individual matrices.

Thus, the above test highlights the significant effectiveness of this joint treatment with the use of HTC liquid, which initially is a waste product of hydrothermal carbonization but, thanks to the nutrients it contains, proves to be a valuable substrate for enhancing the methanization process, resulting in a relevant increase in methane production during AD processes. A possible implementation of this solution at the industrial level, which improves the yields of AD of OFMSW in terms of methane production, is shown in Figure 91.

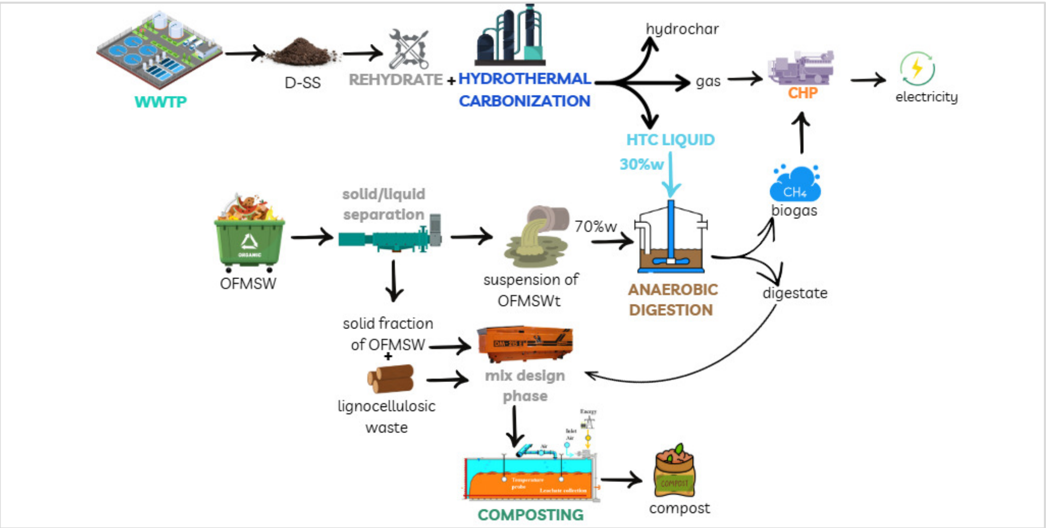

Figure 91 – Layout scenario of a biorefinery for the co-digestion of $OFMSW_T$ and HTC-liquid

It would therefore be possible to hypothesize an organic waste treatment hub that involves pre-treating the sewage sludge from WWTP and then subjecting it to hydrothermal carbonization. The output of this technology produces a solid and a liquid contribution, both of which can still be valorized through biological processes in co-digestion with OFMSW, resulting in an increase in methane production in any case.

6.4.6. Comparison of B-scenarios

The scenarios presented in the previous paragraphs define the biomethanation potential of substrates composed of $OFMSW_T$ analyzed in co-digestion with different organic matrices. The BMPs of the investigated co-digestions, calculated from the volume of biomethane produced from each substrate related to the mass unit of volatile solids that generated it, were compared to each other to determine which solutions are the most effective. Figure 92 shows the trend of specific methane production over the test days for each of the new substrate mixes investigated.

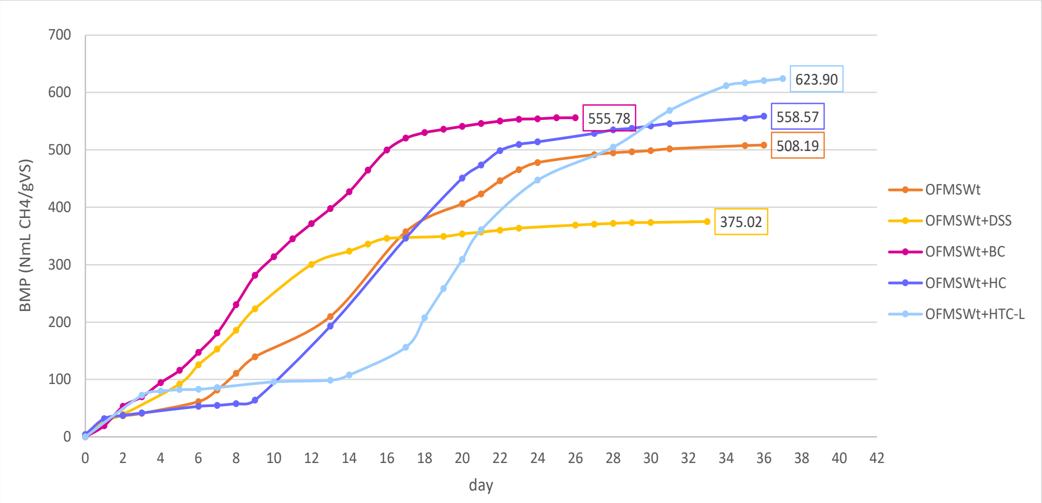

Figure 92 – Comparison of co-digestions tested with the $OFMSW_T$ matrix

A summary of the results obtained from the different $OFMSW_T$ co-digestions of B-scenarios is shown in Table 80.

Table 80 – Comparison of substrate mix BMP derived in scenarios B

Scenario	**Test**	**Substrate**	**VS g**	**Net Volume NmL_{CH4}**	**BMP NmL_{CH4}/gVS**	**BMP variation**
B-0	T7	$OFMSW_T$	6.54	3323.58	508.19	0%
B-1	T6	$OFMSW_T$+DSS	5.47	2051.35	375.02	-26%
B-2	T5	$OFMSW_T$+BC	4.13	2295.36	555.78	9%
B-3	T7	$OFMSW_T$+HC	6.91	3859.72	558.57	10%
B-4	T8	$OFMSW_T$+HTC-L	5.18	3231.8	623.90	23%

The BMPs obtained from the various co-digestion scenarios indicate that, for the same amount of volatile solids, the substrate mix composed of $OFMSW_T$ and HTC-L in a 2.3:1.0 ratio is the one capable of producing the highest methane volume from the anaerobic digestion process, resulting in a BMP 23% higher than that of $OFMSW_T$ alone.

It is also considered that both biochar and hydrochar, used as additives at a concentration of 13 g/L_{OFMSW}, produced substrate mixes with a higher methane potential than that of $OFMSW_T$ alone, with an increase of 9% and 10%, respectively.

However, it must be noted that, to obtain a more meaningful comparison of the advantages or disadvantages of thee co-digestion, each mix tested in the scenarios must be compared in terms of methane volume produced with the amount that would be produced from the single digestions of the starting matrices, as presented in the previous sections and summarized in Figure 93.

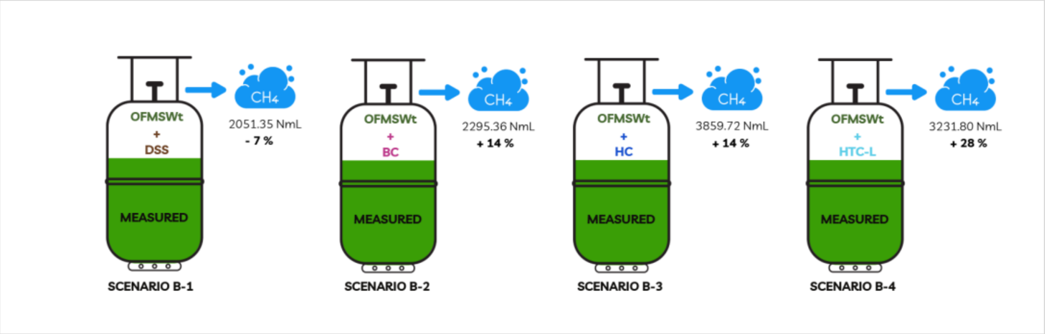

Figure 93 – Comparison of four type b scenarios based on theoretical and measured methane volume
Confronto tra gli scenari di tipo B in base al volume di metano teorico e misurato

Figure 93 shows the outcomes in terms of the methane volume actually produced by co-digestion and how much that value differs from the calculated one obtained from the simple overlapping effects. These comparisons have been presented from time to time in the individual scenario paragraphs and are also briefly reported in Table 81.

Table 81 – Summary of the comparison of A-scenarios

scenario	**Co-digestions with OFMSW_T**	**BMP sub 1 NmL/gVS**	**BMP sub 2 NmL/gVS**	**gVS sub 1**	**gVS sub 2**	**V sub 1 NmL_{CH4}**	**V sub 2 NmL_{CH4}**	**V co-dig calculated NmL**	**V co-dig measured NmL**	**ΔV NmL**	**ΔV %**
B-1	sub 1: OFMSW_T sub 2: **D-SS**	508.19	194.21	3.67	1.80	1865.07	349.57	2214.64	2051.35	-163.29	-7%
B-2	sub 1: OFMSW_T sub 2: **BC**	508.19	23.51	3.95	0.18	2007.36	4.23	2011.59	2295.36	283.77	14%
B-3	sub 1: OFMSW_T sub 2: **HC**	508.19	157.74	6.54	0.37	3323.58	58.37	3381.95	3859.72	477.77	14%
B-4	sub 1: OFMSW_T sub 2: **HTC-L**	508.19	214.73	4.78	0.40	2429.16	85.89	2515.05	3231.80	716.75	28%

From this comparison, in line with the previous analysis, it emerges that the HTC liquid is the most advantageous substrate when used in co-digestion with OFMSW_T in a 2.3:1.0 ratio (OFMSW_T:HTC-L), followed by hydrochar and biochar, which, as carbonaceous solids added at a concentration of 13 $\text{g/L}_{\text{OFMSW}}$, achieve the same results, resulting in a 14% increase in methane volume produced in co-digestion compared to the individual mono-digestions.

On the other hand, the co-digestion of OFMSW_T with dehydrated sewage sludge (DSS) produces a slightly lower volume of methane compared to that generated from the AD of the individual matrices. However, since this variation is less than 10%, it is considered that the addition of DSS does not interact synergistically with OFMSW_T, leaving the methane volume produced by the matrices unchanged as if they were processed separately.

7. CONCLUSIONS

This study explored the potential of integrated biorefineries for the treatment of organic waste, with a particular focus on optimizing the anaerobic digestion (AD) of the organic fraction of municipal solid waste (OFMSW) and maximizing the recovery of wastewater sewage sludge (WW-SS). The aim was to develop anaerobic digestion plants, based on biorefinery concepts, where different technologies are combined to enhance resource recovery and methane production. The BMP tests carried out during this experimental activity demonstrated how the co-digestion of OFMSW with additives produced from innovative sewage sludge treatments, as pyrolysis and hydrothermal carbonization, can significantly improve process efficiency, contributing to circular economy goals.

The experimental activities of this research were entirely carried out at the Environmental Technologies laboratory of the Politecnico di Bari. The experimental plan included an initial phase in which the pre-treated suspensions of organic fraction of municipal solid waste coming from two combined AD and composting plants were characterized; these matrices became the central material of the study. Specifically, the $OFMSW_A$ is originated from a wet-type anaerobic digestion plant and the $OFMSW_T$ from a semi-dry anaerobic digestion plant.

BMP of the individual substrates was determined as an intrinsic characteristic of each material, which defines its capacity, per unit of volatile solids, to produce methane. The results obtained show that the OFMSW matrices have the highest biomethanation capacities ($OFMSW_A$: 731.14 NmL_{CH4}/gVS; $OFMSW_T$: 508.19 NmL_{CH4}/gVS), as they are characterized by easily biodegradable substances. On the other hand, biochar has the lowest BMP value (23.51 NmL_{CH4}/gVS), followed by hydrochar (157.74 NmL_{CH4}/gVS). This low methane production capacity from these additives is due to their structure, as they are carbonaceous solids with a high ash content (BC: 60%, HC: 24.3%), and consequently, limited biodegradability. Dewatered sewage sludge has a BMP of 194.21 NmL_{CH4}/gVS, which is consistent with the range reported in the literature for this matrix. Among the additives, the HTC liquid presents the highest BMP at 214.73 NmL_{CH4}/gVS and in fact, when co-digested with OFMSW, it reaches the highest methane production.

The next phase involved the execution of BMP tests to investigate the co-digestion with various additives of the two matrices: OFMSW$_A$ and OFMSW$_T$, in scenarios A and B, respectively. It should be noted that biochar and hydrochar were tested by adding a quantity of 13 g/L$_{OFMSW,}$ while dewatered sludge and HTC liquid were both tested in a ratio of 1.0:2.3 (by weight) to OFMSW.
The anaerobic digestion of OFMSW$_A$ represents scenario A-0, which serves as the starting point for comparing the results of the co-digestions with the individual additives. From the analysis of the A scenarios, it emerges that in scenario A-4, the new substrate mix composed of OFMSW$_A$+HTC-L (with the additive at a concentration of 13 g/L$_{OFMSW}$) achieved the highest BMP, with a 45% increase compared to the BMP of the OFMSW$_A$ alone. Co-digestions in scenarios A-2 and A-3, respectively with BC and HC, also result in a higher biomethanation potential compared to the original matrix, while the co-digestion with DSS in scenario A-1 results in a substrate mix with a BMP significantly lower than that of the sole OFMSW.
However, the analysis to understand the actual effectiveness of the co-digestion involved comparing the methane produced volume with the theoretical volume that the two matrices would produce — without any synergistic action — based on the volatile solids added and their respective BMP. From this comparison, it emerges that, similarly to what was previously reported, the volume produced by OFMSW$_A$+HTC-L shows an increase of 96% compared to the volume that would be produced by the individual matrices, indicating a clear synergistic effect between the matrices involved. Similar benefits are observed for the substrate mixes OFMSW$_A$+BC and OFMSW$_A$+HC. On the other hand, the co-digestion with DSS shows a volume variation of only 6% compared to the volume that the matrices would produce without interacting; being lower than 10%, is considered not significant.
Therefore, this co-digestion allows a methane production similar to that obtained with the mono-digestions of the individual matrices, meaning that this valorization path can still be pursued. Although it does not result in an increase in methane production, this combined process enables the recovery of an organic waste that would otherwise be sent to landfill. Furthermore, sewage sludge is characterized by a high nutrient content,

and therefore, could enrich the compost produced by a combined AD and composting plant, such as the ones under consideration.

A similar analysis was conducted for the $OFMSW_T$ matrix and the B scenarios, in which the results of the co-digestions of this matrix with the various organic additives are presented.

Scenario B-0 represents the mono-digestion of the $OFMSW_T$ matrix, which shows a biometanation potential lower than that of $OFMSW_A$, but still high. The difference is due to the intrinsic heterogeneity of the materials, as well as in the way organic fraction is collected and the mechanical pre-treatments it underwent. From the comparison of the co-digestions reported in the B scenarios, it emerges that, similarly to the results obtained in the A scenarios, the additive that results in the highest biometanation potential when co-digested with $OFMSW_T$ is HTC-L, leading to a 23% increase in BMP for the new substrate mix compared to the BMP of the sole $OFMSW_T$. The substrate mixes with BC and HC result in a BMP variation within 10%, which is not significant, while similarly to the results obtained for $OFMSW_A$, the $OFMSW_T$+DSS mix also results in a BMP 26% lower than that of the sole $OFMSW_T$. However, this outcome does not indicate an actual disadvantage of co-digesting these matrices, as it is necessary to compare the methane volume produced by the co-digestion with the theoretical volume that the matrices would produce, in the absence of interactions, based on the volatile solids added to the reactor and their respective BMPs. From this comparison, a decrease of 7% in the measured volume compared to the theoretical volume emerges, which, being less than 10%, is considered not significant and represents a condition of no synergy between the matrices. Therefore, the sole advantage of this co-digestion is the recovery of an organic waste that would otherwise contribute to increasing the landfill disposal rate. From the comparison of the measured and theoretical volumes in the B scenarios it emerges that for co-digestion with HTC-L, there is a 28% increase in the measured volume compared to the theoretical one, and 14% increases for co-digestion with both BC and HC.

It can therefore be concluded that the experimentation demonstrated — through BMP tests that replicated batch-type anaerobic digestion — that the co-digestion of OFMSW with organic additives from innovative sewage sludge treatments, such as pyrolysis and HTC, proves to be advantageous. This is because it allows an increase in methane production and, in any case, the valorization of a material that, despite having been subjected to valorization treatments, is still considered a waste.

The HTC liquid proves to be the additive that, in a 1.0:2.3 ratio with OFMSW, provides the highest methane production yield. This is due to the fact that with hydrothermal carbonization, the liquid phase becomes rich in soluble organic compounds and nutrients, making this matrix capable of providing soluble nutrients such as nitrogen, phosphorus, organic acids, and readily degradable substrates to stimulate microbial activity. Also solid additives such as biochar and hydrochar, added at a concentration of 13 g/L_{OFMSW}, are able to work synergistically with the OFMSW, offering high carbon content and adsorptive properties. Furthermore, they also help to improve the structural quality of the digestate.

The experimental configurations highlighted the potential to effectively combine anaerobic digestion with pyrolysis and HTC technologies, creating centralized plants capable of processing heterogeneous organic waste streams in the concept of biorefinery. This synergic integration offers significant advantages in terms of material and energy recovery. Specifically, the analysis of both solid and liquid additives revealed their potential to improve process stability, stimulate microbial activity, and provide essential nutrients which can enhance anaerobic digestion.

However, some limitations emerged, particularly with dewatered sewage sludge, which showed low advantages. This suggests that further optimizations are needed in testing different co-digestion ratios.

Future research will focus on further developing and optimizing these processes, exploring other complementary technologies, and studying the scalability of the proposed solutions by testing such co-digestions at pilot scale and with continuous processes for a future industrial implementation.

In conclusion, transforming traditional waste treatment facilities into integrated biorefineries represents a crucial opportunity in the framework of a circular economy. Biorefineries are designed to process heterogeneous organic waste streams and this study highlights the potential of using combined technologies to optimize AD process and underlines how useful the joint processes of multiple organic matrices can be to increase material and energy valorization.

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NOTES

[1] FOS in German stands for «Flüchtige Organische Säuren» and it means Volatile Fat Acids (VFAs); while TAC stands for «Totales Anorganisches Carbonat» which means Alkaline Capacity.

[2] It’s referred to total solids (TS) content of the feedstock greater than 15%w/w.

[3] Task Group for the Anaerobic Biodegradation, Activity and Inhibition (ABAI Group) of the Anaerobic Digestion Specialist Group of the International Water Association (IWA).

[4] UNI 11853:2022 “Specifics of biochar obtained from hydrothermal carbonization (HTC) treatment of residues from municipal wastewater treatment plants or industrial sludge with organic matrix”.

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Annamaria Giuliano was born in Monopoli, Bari (Italy) in 1995, she graduated at Polytechnic University of Bari in 2021, with a Master Degree in Environmental Engineering, discussing the thesis in Waste Management: “Study of a performance model for the mechanical-biological treatment of municipal solid waste: optimization of the selection phase”, with supervisor Prof. Michele Notarnicola, with final grade 110/110 cum laude. She spent 3 months at TUHH in Amburg (Germany) as visiting student.

From November 2021 to December 2024, she was a PhD student in Risk and Environmental, Territorial, Building Development PhD program at the Polytechnic University of Bari. From October 2023, she started to work as environmental engineer in the Control Room of Acquedotto Pugliese SpA.

Her research aimed to highlight the great potential of using combined technologies to optimize the anaerobic digestion process with joint processes and multiple organic matrices to enhance material and energy valorization. In particular, the results show the crucial role of biorefineries in transforming organic waste management, aligning environmental and economic objectives.

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