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A closed-loop valorization of the waste biomass through two-stage anaerobic digestion and digestate exploitation

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ABSTRACT

This review investigates the two-stage anaerobic digestion (TSAD) of organic waste to produce high-value products according to circular economy principles. The novelty of the study is the coupling of energy-carrying production including H_2 and CH_4, with the digestate treatments through closed-loop valorization.

The review's key findings highlight that in TSAD, the energy and digestate qualities can be improved through pre-treatments and co-digestion. Pre-treatments allow for the increase of soluble organic matter available for microorganisms. Co-digestion controls the optimal ranges of carbon-nitrogen ratios, nutrient balances, pH, and water contents, by increasing the TSAD efficiency without consuming resources like water or mineral nutrients. Digestate management is investigated for the whole, liquid, and solid fraction of the residue demonstrating a high yield in nutrient recovery and char production.

In this study, TSAD is not only considered a biochemical process but a sequential biorefinery that requires optimization to be scaled up at full scale.

The bottlenecks of TSAD emerged in the explorative energetic, environmental, and economic assessments, which point out the significant economic and environmental costs associated with transporting, storing, pre-treating biomasses, and dewatering and managing digestate.

1. Introduction

Society is facing the depletion of fossil fuels essential to producing chemicals and energy [1]. The exploitation of fossil resources contributes to the greenhouse effect. The Intergovernmental Panel on Climate Change (IPCC) of the United Nations (UN) elaborated statistical data on the CO_2 equivalent emitted per kilowatt hour of electricity. Results demonstrate that renewable energy production has lower CO_2 equivalent emissions than fossil fuels. However, renewable energy systems are not always the lowest-impactful solution in terms of emissions. As illustrated by Amponsah et al. [2], biomass-based technologies can emit a high quantity of CO_2 eq./kWh depending on biomass type, the treatment chosen, and the boundaries considered in the life cycle. Sustainable and renewable are not synonyms because there are lots of variables to consider in sustainability analysis which should be contextualized in the specific case of study.

Among renewable resources, waste biomasses represent a carbon-neutral alternative to fossil fuels according to circular economy pillars, which can produce both chemical products and bio-energy by developing waste management systems in agreement with the Waste Framework Directive 2008/98/EC of the European Parliament [3,4]. Waste biomasses, which are the organic fraction of industrial, agricultural, and urban waste, present environmental, economic, and social issues [5]. The exploitation of waste biomasses as secondary raw materials to produce bio-energy converts them from problem to resource, by enhancing their life cycle according to bioeconomy principles [6]. Second-generation biofuels could be produced as biodiesel, biogas, bioethanol, and biohydrogen from waste biomasses.

Hydrogen has gained interest as a chemical, for its key role in the production of ammonia, methanol, and oils and as fuel, due to its high heating value (~120 kJ/g) and low density. The conventional processes associated with hydrogen production are steam reforming of methane or

Abbreviations: C, carbon; N, nitrogen; P, phosphorous; K, potassium; LCA, life-cycle analysis; DF, dark fermentation; AD, anaerobic digestion; VFA, volatile fatty acids; TSAD, two-stage anaerobic digestion; HRT, hydraulic retention time; OLR, organic loading rate; TS, total solids; VS, volatile solids; TRL, technology readiness level; HTC, hydrothermal carbonization; PY, pyrolysis; SSA, specific surface area; GWP, global warming potential; ESA, energy sustainability analysis; ESI, energy sustainability index.

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hydrocarbons, noncatalytic partial oxidation of fossil fuels, autothermal reforming, and coal gasification. In these conventional processes, the raw materials employed are non-renewable and do not observe sustainability principles.

In 2021, the Italian government approved the "National Recovery and Resilience Plan" (PNRR), a program containing measures against the economic collapse caused by the COVID-19 pandemic. The word "recovery" refers to the intention to create occupation, invest in healthcare and school, and improve the quality of work, and "resilience" stands for the reinforcement of the ability to respond to economic, social, and environmental shocks and changes in a fair, sustainable, and inclusive way. The plan is part of the Next Generation EU (NGEU) program associated with a fund of 806.9 billion € to make Europe a healthier and greener continent. The PNRR consists of four missions. Mission 2 focuses on Italy's ecological transition, promoting waste recycling, renewable energy from waste resources, efficient building construction, and hydrogen research.

Among alternative hydrogen production, dark fermentation (DF) is a biological process cheaper compared to other solutions even though it does not fully exploit waste biomass potentiality. DF upgrading can be performed through a two-stage anaerobic digestion (TSAD), which is a process composed of two steps: the first is the DF to produce hydrogen; the second one is the anaerobic digestion (AD) of the residues of DF to produce methane and a solid-liquid residue called digestate.

This review examines the circularity of DF for hydrogen production in a TSAD system and the conversion of digestate into high-value products through closed-loop valorization.

Operative parameters in the fermentative processes, including DF, AD, and their sequential combination in TSAD, are analyzed. The upgrading techniques for digestate management highlight nutrient recovery for recirculation in the TSAD or in other processes, to foster integrated biorefinery development. In detail, this review attempts to answer the following research questions:

- R1: Identify technically feasible, environmentally sustainable two-stage configurations maximizing hydrogen and methane production from waste biomass.
- R2: Evaluate environmentally low-impact viable processes for digestate conversion, focusing on nutrient recovery or high-value conversion products.
- R3: Integrate findings from R1 and R2 to achieve circularity in TSAD, optimizing energy carrier production and digestate conversion.

The novelty of this study is the coupling of energy-carrying production like H_2 and CH_4, with the utilization of digestate within a circular economy perspective. The present review has been developed through relevant literature consultation regarding the TSAD of waste biomass, with a focus on municipal and agro-industrial waste followed by an insight into digestate conversion. These wastes were chosen as they are inevitable consequences of the industrial and domestic scenarios but if they are not correctly disposed of, represent an issue for the environment and human health [7]. Since these are organic waste their CO_2 equivalent emission can be considered mostly biogenic and part of the carbon cycle. The organic waste represents renewable material for the production of green energy essential in satisfying the global energy demand [8].

The answers to the three research questions will be of value to optimize TSAD and digestate conversion according to the Biogas Done Right.

Biogas Done Right represents a holistic approach to biogas production that balances energy generation with agricultural sustainability, environmental protection, and economic benefits for the farming community. Biogas Done Right involves the conversion of agricultural waste as substrate for digestion while employing digestate to enhance soil quality [9]. This innovative approach improves waste biomasses management and resource efficiency for energy and chemical production.

2. Review methodology

This review was based on the scientific literature with specific criteria as described. Information has been obtained through databases such as Science Direct, Scopus, and ResearchGate consulting articles and book chapters. Statistical data has been obtained from official website databases such as The Intergovernmental Panel on Climate Change (IPCC). The research focused on literature published within thirty years. The authors analyzed titles, abstracts, and conclusions, ensuring relevance to the topic before conducting a thorough review. At first, the research focused on biohydrogen and TSAD through the investigation of reviews and research papers. Then the possible substrates for digestion were scrutinized to optimize the operative parameters of DF, AD, and TSAD (including carbon: nitrogen ratios, pH, etc.). Lastly, digestate conversion and management were investigated focusing on biochar production and nutrient recovery. Keywords identified relevant articles, such as "dark fermentation", "biohydrogen production", "biogas production", "biofuels from biomass wastes" "two-stage anaerobic digestion", "wastes co-digestion", "nutrients balance", "digestate valorization". To deeper scrutinize the valorization and conversion of digestate in high-added materials as carbonaceous ones, further keywords have been added as "biochar from digestate", "nutrients recovery from digestate", and "biochar in anaerobic digestion". To explore the conversion of digestate into valuable materials, additional keywords were added like "biochar from digestate", "nutrients recovery from digestate", and "biochar in anaerobic digestion".

3. Two-stage anaerobic co-digestion

3.1. Bio-hydrogen and biomethane productions through biological processes

Anaerobic digestion (AD) is a biochemical process that degrades biomass into a CH_4-rich gas phase in an oxygen-free environment. AD occurs in four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The syntrophy between each species is essential to achieve the highest efficiency of the system [10]. Hydrolysis breaks down complex polymers in organic biomass into smaller components accessible to microorganisms. Hydrolytic bacteria secrete enzymes to convert carbohydrates, lipids, and proteins into sugars, long-chain fatty acids (LCFAs), and amino acids. Hydrolysis can be the rate-determining step and is optimized at 30–50 °C and pH 5–7. The presence of lignocellulosic biomasses slows down the process due to the recalcitrance of lignin [11].

During acidogenesis, acidogenic microorganisms convert hydrolysis products into intermediate volatile fatty acids (VFAs), including acetic, propionic, and butyric acids, along with minor amounts of ethanol, and lactic acid. VFAs ratios vary depending on process conditions (pH, temperature, and feedstock). However excessive VFAs production can cause inhibition and consequently process failure. In protein-rich waste, the degradation of amino acids releases ammonia as a byproduct, which can inhibit AD. During acetogenesis, acetic acid, hydrogen, and CO_2 are produced from VFAs. Acetic acid can inhibit acetogenic microorganisms, but methanogens consume it, maintaining favorable conditions for acetogenesis. Lipids undergo acetogenesis via acidogenesis and β-oxidation, yielding acetate from glycerol and LCFAs [11].

The process is endothermic and hindered by H_2 partial pressure which should not exceed 10^{-4} atm [12]. This condition is avoided due to the presence of methanogens which, during the methanogenesis, employ H_2 as an electron donor to produce CH_4 through a hydrogenotrophic pathway. The energy carrier is also produced through acetoclastic methanogens which convert acetate through an energy-gaining process [13]. These microorganisms are highly sensitive to oxygen and thrive on a limited range of substrates. They require higher pH and lower redox potential. Methanogenesis typically takes 5–16 days, and in batch reactor digestion ends when biogas production ceases after about 40 days.

Dark fermentation (DF), encompassing the first three stages of AD (hydrolysis, acidogenesis, and acetogenesis), is the most widespread biological process to produce H_2. In this process, facultative or obligated anaerobes employ biomasses and waste biomass as substrates. The products of DF are H_2, CO_2, and VFAs such as acetic acid, butyric acid, and propionic acid. To achieve the highest hydrogen yield, the acetate path should be maximized as from 1 mol of glucose, 4 mol of H_2 can be obtained [14,15]. DF is an economic method compared to other techniques as photosynthetic technologies because it does not require a sterile environment and operations are simple and not energy-intensive [16]. However, DF is associated with low H_2 production, ranging from 10 to 180 mL/g_{VS} depending on the substrate, which limits its scale-up [17]. DF can process several waste biomasses due to its flexibility, but the technology readiness level (TRL) is 5. This indicates the process is not yet ready for industrial-scale application to replace traditional fossil fuel-based methods [18], hence its bottlenecks should be investigated to optimize the process.

A significant challenge in DF is managing VFAs. When acetogens and acidogens reach a steady production of VFAs, their accumulation decreases the pH inhibiting the activity of micro-organisms. VFAs are released into the medium to maintain cell stability, but their accumulation can lead to the lysis of cell walls by penetrating the cytosol of biocatalysts [19]. The liquid residue of DF has a high acid concentration and should not be dispersed into the environment due to pollution concerns. This VFAs-rich substrate is suitable for an AD step but when their concentration is above 8000 mg/L, methanogenesis cannot start [20,21].

A two-stage configuration consisting of DF to produce H_2 and subsequential AD of solid residue, containing VFAs, to produce CH_4 should be considered to exploit the waste biomass. This process is called two-stage anaerobic digestion (TSDA). TSAD separates acidogenesis-acetogenesis and methanogenesis as they require different optimal operational parameters, as shown in Fig. 1. The use of two reactors facilitates the control of process parameters and optimizes gas yield. This upgrading produces two energy carriers (H_2 and CH_4) by ensuring the exploitation of carbon-based biomass. Considering the energy recovery from CH_4, AD reaches 84 % efficiency using glucose, whereas TSAD achieves 86.3–89 %, depending on the glucose degradation route. TSAD demonstrates higher energy recovery than AD [22].

TSAD is an effective technique in biohydrogen production and presents advantages such as CH_4 production and the production of digestate, an interesting substrate to be converted into high-added-value products.

3.2. Two-stage anaerobic digestion parameters

3.2.1. Main process conditions

The main operational parameters of TSAD are presented as process conditions (pH, hydraulic retention time (HRT), organic loading rate (OLR), total solids and temperature as shown in Fig. 2), total solids fed in the reactor, the types and composition of biomasses and their pretreatments, and nutrient availability.

Controlling pH is fundamental because biological processes depend on the acidity or alkalinity of the process. DF thrives in acid conditions with a pH of 5.0–6.5, while AD performs better at higher pH of 6.5 and 8.0 [23].

H_2-producers grow faster than methanogens, hence DF and AD should be separated to manage different HRT: 2–5 days for H_2 production, and 10–20 days for CH_4 production [24–26].

OLR is the amount of organic material per unit of reactor volume that is biodegraded in the reactor in each unit of time. OLR is inversely proportional to HRT, and it usually ranges from 1.2 to 12 $kg_{VS}/m^3 \bullet$ day. Insufficient OLR results in inadequate substrate conversion, while excessive OLR can lead to inhibition [27].

Temperature influences the microorganisms' growth in TSAD which can be operated at psychrophilic (<20 °C), mesophilic (20–45 °C), or thermophilic conditions (55–70 °C) [21]. Higher temperatures accelerate metabolism, boosting biogas production and increasing VFAs, which potentially cause microbial inhibition [28]. Different temperatures can be applied in the first and second stages to optimize volatile

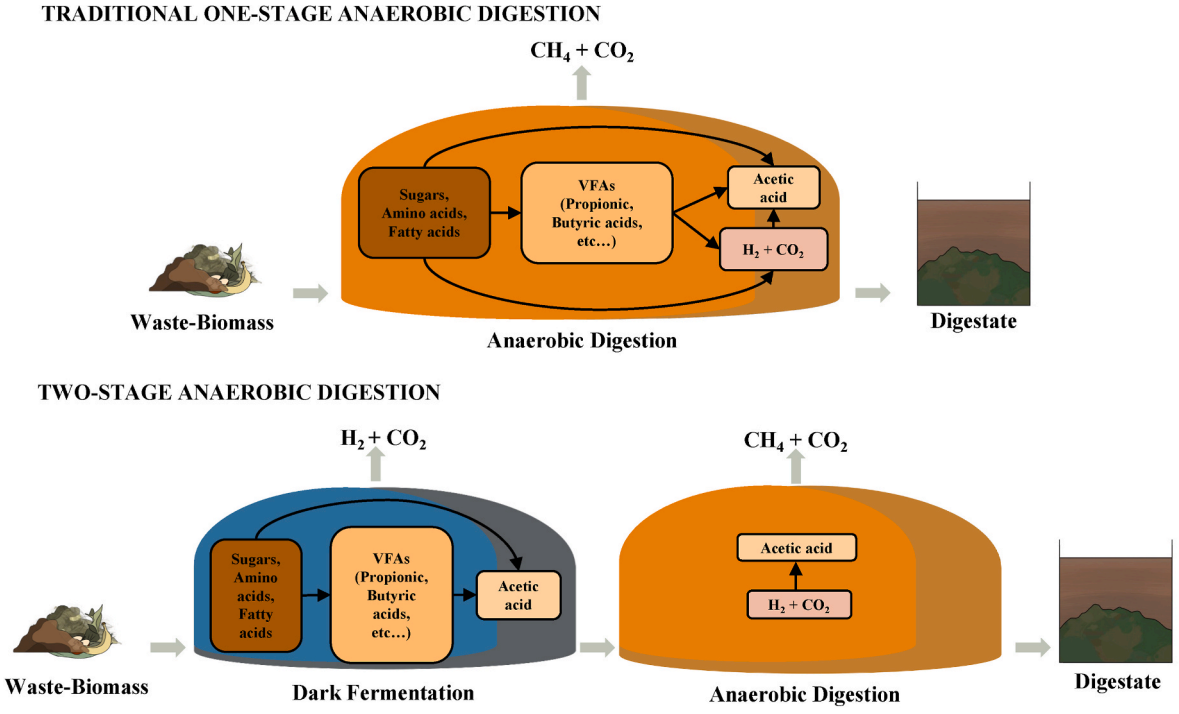

Fig. 1. Scheme of one-stage and two-stage anaerobic digestion: in the first case, waste biomass undergoes three degradation steps producing a mixture of CH_4 and CO_2; in the second case the process is carried out in two reactors: in the first, dark fermentation takes place producing a mixture of H_2 and CO_2 while its residue is fed to the second reactor where, through methanogenesis, biogas is produced. The acronym adopted is volatile fatty acids (VFAs).

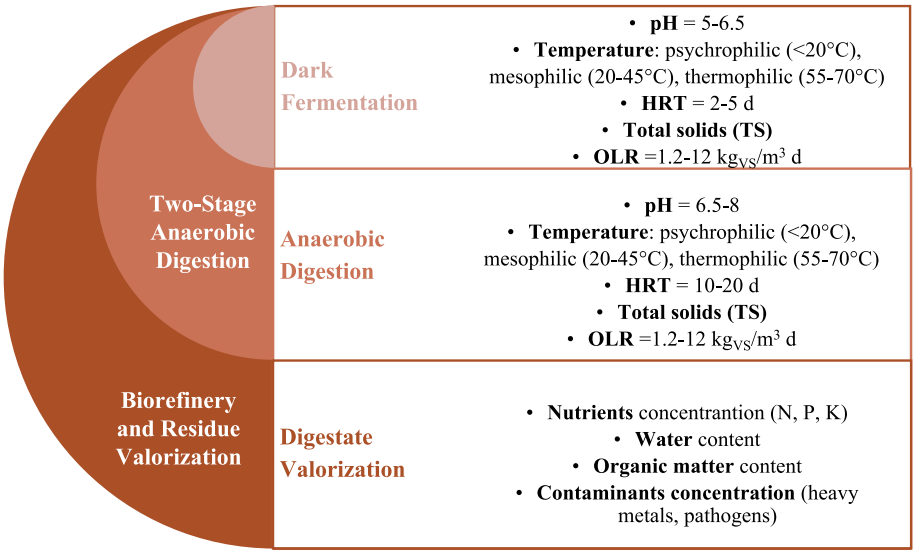

Fig. 2. Main parameters of dark fermentation and anaerobic digestion to perform two-stage anaerobic digestion followed by digestate valorization and its main parameters The acronyms adopted are hydraulic retention time (HRT) and organic loading rate (OLR).

solid (VS) removal and methane yield.

Nabaterega et al. [29] highlighted the impact of thermophilic conditions in the first stage and mesophilic conditions in the second one, noting the importance of evaluating energy costs associated with higher temperatures.

Depending on total solids (TS) content, digestion can be defined as dry or wet. Dry anaerobic digestion involves TS of 20–40%w/w, while wet digestion accounts for less than 15%w/w TS [30]. Dry digestion presents advantages as low reactor volume, more flexibility in terms of feedstocks, and reduced water and energy requirements [31]. However, dry digestion limits diffusion leading to VFAs accumulation that can lower pH and inhibit microorganisms' growth [32]. The dry process is also associated with lower biogas yield, long digestion time, and the release of bad odors [33]. Wet digestion, which requires a significant amount of water and energy to move biomass, ensures better nutrient diffusion, resulting in higher biogas production and potential economic benefits compared to dry digestion [31,34].

3.2.2. *Waste biomasses type and characteristics*

TSAD is applied to several waste biomasses that differ in composition, geographical availability, time, and rate of degradation. The main compounds present in biomass are carbohydrates, lipids, and proteins, which microorganisms consume at different rates. Simple sugars (mainly mono- and disaccharides) are quickly digested compared to lipids and proteins. The latter ones present a faster degradation than complex organic polymers such as hemicellulose and lignin. Waxes and greases, despite being highly biodegradable, are associated with the formation of inhibitors during lipid digestion, which stops the process [21,35]. Waste biomass is affected by seasonality, which does not assure the total availability of raw materials (i.e. brewery residues are season-dependent) [36]. In contrast, agro-industrial and municipal residues are constantly produced during the year, and they can be considered to produce bioenergy.

Table 1 reports waste biomass employed in biological processes like DF, AD, and TSAD classified into four categories: urban biomass, animal-based agro-biomass, cereal agro-biomass, and industrial biomass. This classification agrees with the EU 2009/28/CE and Eurostat database. EU 2009/28/CE biomass classification includes wastewater and sludge, organic fraction municipal solid waste (OFMSW), agro-biomasses, and industrial-biomasses. In Table 1, urban biomasses include OFMSW and sewage sludge, animal-based agro-biomasses concern manure and animal wastewater, cereal agro-biomasses include rice residues and wheat straw, and industrial biomasses comprise bakery waste, dairy residues, olive pomace, oil mill wastewater, and wine sector residues. Table 1 reports each waste biomass, the details about the availability at the European level, the physical structure, and the elemental and biochemical compositions. Then, the biomethane theoretical specific potential was calculated through the Buswell and Neave equation.

Lignocellulosic, the most abundant waste biomass in Europe [37], presents a complex crystalline structure mostly composed of three polymers: cellulose, hemicellulose, and lignin [38] showing a low biodegradability for the structure which is not easily attached by enzymes or pre-treatments [39]. There are almost no examples in the literature of TSAD of only lignocellulosic biomasses as it is typically coupled with an easily degradable substrate such as food waste or cheese whey [40–42].

Before digestion, waste biomasses usually undergo pre-treatments to increase the digestibility of organic waste biomass for microorganisms.

3.2.3. *Substrate pre-treatments*

The pre-treatments are classified as physical, chemical, enzymatic, and hybrid (a combination of types of pre-treatments) and selected based on waste biomass composition and structure. The pre-treatments enhance the biomass availability and consequently, its capability to be converted.

Easily degradable biomasses like food waste and OFMSW often undergo mild physical pre-treatments such as shredding or water dilution. In contrast, lignocellulosic biomasses, with their complex, cross-linked polymers, require stronger pre-treatments to break down barriers inhibiting bacterial action and increasing organic matter availability. Lignin pre-treatments include chemical, physical, and enzymatic ones [72].

Chemical methods include, acidic, alkaline, oxidative, and ionic-liquid pre-treatments are employed to disrupt hydrogen and covalent bonds between the main components of biomass [73]. Physical pre-treatments break the lignin barrier causing surface area increase, crystallinity modifications, and size reduction which make biomass available for hydrolysis [74]. Thermal pre-treatments often involve the utilization of environmentally friendly additives such as water, air, or CO_2 to modify biomass structure at high temperatures and overcome structure recalcitrance [75]. Enzymatic pre-treatments enhance sugar degradation through bacteria and enzymes in mild process conditions [76].

Table 1
Waste biomasses are classified into four categories and for each waste biomass physical, chemical, and biochemical compositions are reported. The acronyms adopted are organic fraction of municipal solid waste (OFMSW), total solids (TS), and volatile solids (VS).

Category	Name	EU Availability (Mt/y)	TS %	VS/TS %	Elemental Composition on TS basis %						Biochemical Composition %			CH_4 (Nm^3/kg_{VS})	References
					C	N	S	H	O	C/N	Lipid	Protein	Carbohydrate		
Urban biomass	OFMSW	177	19.32	96.76	48.42	6.76	2.97	0.2	41.65	7.16	11.90	5.40	55.00	0.28	[43–45]
	Sewage sludge	550	2.00	65	50.00	3.00	1.9	8.6	36.5	16.67	12.00	9.90	27.30	0.57	[46–48]
Animal-based agro-biomass	Manure	1400	92.25	59.13	33.07	2.90	0.63	4.87	58.53	11.40	0.40	9.55	41.15	0.22	[49–51]
	Animal wastewater	N.A.	18.53	89.4	54.90	5.90	1.00	8.50	29.70	9.31	N.A.	N.A.	N.A.	0.62	[52]
Cereal agro-biomass	Rice residues	3.35	94.00	98	36.02	1.12	0.38	6.63	55.85	32.16	1.61	4.12	71.47	0.32	[53–55]
	Wheat straw	144	27.2	84.6	46.60	2.90	0.30	6.60	43.60	16.07	1.38	7.92	36.22	0.45	[56–58]
Industrial biomass	Bakery waste	N.A.	74.1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	NA	3.00	10.50	46.00	N.A.	[59,60]
	Dairy residues	192.5	12.5	97	46.50	4.90	5.62	8.43	34.55	9.49	13.50	29.5	45.50	0.55	[61–63]
	Oil pomace	36.69	90.00	86.1	51.28	0.95	0.11	5.86	41.8	53.98	2.33	2.48	29.48	0.50	[64–66]
	Oil mill wastewater	23.35	76.60	91.6	N.A.	N.A.	N.A.	N.A.	N.A.	NA	2.14	5.345	6.86	N.A.	[66–68]
	Wine residues	24750	0.40	87.2	49.80	2.00	0.00	5.80	42.40	24.9	N.A.	N.A.	N.A.	0.47	[69–71]

3.2.4. Importance of nutrients balance

Nutrient balance is important to guarantee process control and maximize process energy production by realizing a suitable environment for microorganisms. Finding a unique value of carbon, nitrogen, and phosphorous (C: N:P) is hard as different ratios are reported in the literature. The main adopted condition to design digestion is a C: N:P equal to 200:7:1 [77].

Nutrient balance can be achieved by adding artificial nutrients or anaerobic co-digestion, which means simultaneous digestion of different biomasses. Co-digestion in DF and AD is essential since most waste biomass lacks adequate nutrients. Co-digestion, allowing the mixing of various waste biomass, can reach a proper C: N:P balance, ensuring the growth of microorganisms and consequently the effectiveness of the overall fermentative process.

Nitrogen has a buffering capacity, essential during VFA production, to guarantee microbial propagation [78]. A carbon and nitrogen ratio of around 20–30 can enhance digestion performance [79,80]. P is essential for optimal microbial growth and a good control of pH. P should account for 15 % of N content in the digestion [81]. Even if N and P presence enhances biogas yield, their concentration should not exceed the abovementioned C: N:P ratio because it is associated with inhibition phenomena like precipitation of N and P salts (causing nutrient unavailability), higher costs, and water pollution due to the release of N and P [77].

3.3. Co-digestion

Anaerobic co-digestion represents an opportunity to overcome the drawbacks of DF, AD, and TSAD by simultaneously digesting two or more feedstocks. Co-digestion can balance nutrients, and manage pH value by coupling acid biomasses rich in C with alkaline ones rich in N. In addition, moisture content can be adjusted using a mix of different wet biomasses, minimizing clean water usage [80].

Food waste, rich in carbon but low in nitrogen, may cause acidification and inhibit cell growth. To avoid this problem, it's often coupled with nitrogen-rich biomass like manure or sludge, which helps buffer the system and prevent acidification from fatty acids [82].

Similarly, dairy products like whey can lead to excessive acidification and are usually combined with nitrogen-rich manure or sludge [26,41].

Table 2 illustrates the conditions and yields of TSAD processes for different substrates, highlighting that coupling carbon-rich substances with nitrogen or phosphorus-rich feedstock is crucial. Co-digestion often results in higher H_2 and CH_4 yields compared to DF and AD, particularly for household solid waste and OFMSW. However, not all biomasses, such as spent mushroom substrate, are suitable for co-digestion. Higher temperatures don't always enhance H_2 production significantly. Lignocellulosic biomasses alone are not ideal for TSAD but are promising when co-digested with manure and degradable substrates like food waste or whey [40–42].

4. Digestate management according to circular economy

At the end of TSAD, digestate is not completely degraded by microorganisms but still contains carbon and other elements. The digestate is a solid-liquid substrate whose water content depends on the process conditions. If digestion is performed under wet conditions, a high amount of water is available in the digestate, and water can be recirculated in the digestion process or used as an irrigation fertilizer [100].

Innovative techniques enable nutrients and water recovery. The solid fraction of digestate can be converted into char through thermal treatment, as shown in Fig. 3 [101]. Additionally, bio-stimulants as humic and fulvic acids can be obtained from digestate [102].

Table 2
Examples of two-stage anaerobic digestion applied on the different types of feedstocks under different operative conditions. The first part of the table contains modo-digestion process conditions and yield. In the second part, co-digestion processes are presented. The acronym adopted is hydraulic retention time (HRT).

Substrate	Pre-treatments	COD content	Operative conditions	H_2 and CH_4 yields	References
Mono-digestion					
Food waste	Ground and diluted with water	57 g/L	1st stage: 37 °C, pH = 6, HRT = 35 h 2nd stage: 37 °C, pH = 7, HRT = 72 h	H_2: 55 mL/g_{VS} CH_4: 94.8 mL/g_{VS}	[83]
Cheese whey	Diluted with phosphate buffer	60–80 g/L	1st stage: HRT = 1 d 2nd stage: HRT = 7.5 d	H_2: 120 mL/g_{VS} CH_4: 340 mL/g_{VS}	[25]
Sewage sludge	None	42.3 g/L	1st stage: 35 °C, pH = 5.5, HRT = 2 d 2nd stage: 35 °C, pH = 7, HRT = 12 d	CH_4: 200 mL/g_{VS}	[84]
Raw tomato plant waste	Dried, milled and sieved	N.A.	1st stage: 37 °C, pH = 6, HRT = 14 d 2nd stage: 37 °C, pH = 6, HRT = 28 d	H_2: 11.6 mL/g_{VS} CH_4: 252.3 mL/g_{VS}	[85]
Cattle manure	Thawed, blended, and diluted with tap water	N.A.	1st stage: 68 °C, HRT = 3 d 2nd stage: 55 °C, HRT = 12 d	CH_4: 260 mL/g_{VS}	[86]
OFMSW	Milled and diluted with water	52 g/L	1st stage: 55 °C, pH = 5.5, HRT = 2 d 2nd stage: 55 °C, pH = 7.3, HRT = 10 d	H_2: 20–85 mL/g_{VS} CH_4: 329–364 mL/g_{VS}	[87]
Household solid waste	Shredded and diluted with water	N.A.	1st stage: 37 °C, pH = 5.5, HRT = 2 d 2nd stage: stage: 37 °C, pH = 7.5, HRT = 15 d	H_2: 43 mL/g_{VS} CH_4: 500 mL/g_{VS}	[88]
Organic market waste	Grounded and diluted with water	N.A.	1st stage: 35 °C, pH = 5.5, HRT = 12 d 2nd stage: 35 °C, pH = 7–7.5, HRT = 12 d	H_2: 50 mL/g_{VS} CH_4: 179 mL/g_{VS}	[89]
Peach waste	Diluted with tap water	21.2 g/L	1st stage: 30 °C, pH = 5.5, HRT = 1 d 2nd stage: 30 °C, pH = 7–7.5, HRT = 5 d	CH_4: 320 mL/g_{COD}	[90]
Vinasse	Diluted with tap water	20 g/L	1st stage: 55 °C, pH = 5.5, HRT = 4 h 2nd stage: 30 °C, pH = 7–7.5, HRT = 18 h	H_2: 150 mL/g_{COD} CH_4: 240 mL/g_{VS}	[91]
Palm oil mill effluent	None	85.85 g/L	1st stage: 55 °C, pH = 6.5, HRT = 2 d 2nd stage: 35 °C, pH = 7.5, HRT = 15 d	H_2: 135 mL/g_{VS} CH_4: 414 mL/g_{VS}	[24]
Bagasse bioethanol fermentation residue	Centrifuged and supernatants discarded	30.6 g/L	1st stage: 37 °C, pH = 6, HRT = 9 h 2nd stage: 37 °C, HRT = 8 h	H_2: 8.24 mL/g_{COD} CH_4: 345.2 mL/g_{COD}	[92]
Co-digestion					
Food waste, corn straw, chicken manure	Food waste crushed and sieved, corn straw crushed, sieved, and treated with urea	5.75 g/L (soluble)	1st stage: 55 °C, pH = 5.5 2nd stage: 55 °C, pH = 7	H_2: 106 mL/g_{VS} CH_4: 515.9 mL/g_{VS}	[40]
Food waste and brown water	Food waste is sorted out and blended with tap water	127 g/L	1st stage: 37 °C, pH = 5–5.5, HRT = 8 h 2nd stage: 37 °C, pH = 7–7.5, HRT = 20 d	H_2: 99.8 mL/g_{VS} CH_4: 728 mL/g_{VS}	[93]
Sludge and food waste	None	23.6 g/L	1st stage: 37 °C, pH = 5.5 2nd stage: 37 °C, pH = 7	H_2: 106.4 mL/g_{VS} CH_4: 353.5 mL/g_{VS}	[94]
Sludge and wine vinasse	None	63.8 g/L	1st stage: 35 °C, pH = 5.5, HRT = 4 d 2nd stage: 35 °C, pH = 7, HRT = 4 d	H_2: 16.4 mL/g_{VS} CH_4: 159.5 mL/$g_{CODremoved}$	[95]
Corn silage, cattle manure, olive pomace, orange peels	None	N.A.	1st stage: 37.5 °C, HRT = 15 d 2nd stage: 37.5 °C, HRT = 15 d	CH_4: 570 mL/g_{VS}	[42]
Corn silage, cattle manure, malt	None	N.A.	1st stage: 37.5 °C, HRT = 20 d 2nd stage: 37.5 °C, HRT = 20 d	CH_4: 370 mL/g_{VS}	[42]
Cheese whey and cattle manure	Diluted with water and sieved	35.3 g/L	1st stage: 35 °C, pH = 5, HRT = 5 d 2nd stage: 35 °C, pH = 7.5, HRT = 20 d	H_2: 84 mL/g_{VS} CH_4: 258 mL/g_{VS}	[26]
Sorghum and cow manure	Sorghum shredded/sieved, diluted with water, alkaline on ensiled sorghum	N.A.	1st stage: 37 °C, pH = 5, HRT = 5 d	H_2: 209 mL/$g_{Carbohydrates}$ CH_4: 295.3 mL/g_{VS}	[96]

(*continued on next page*)

Table 2 (*continued*)

Substrate	Pre-treatments	COD content	Operative conditions	H_2 and CH_4 yields	References
			2nd stage: 37 °C, pH = 7.5–8, HRT = 25 d		
Leachate and starch waste	Crushed, blended, and homogenated	5.84 g/L	1st stage: 35 °C, HRT = 5 d 2nd stage: 35 °C, pH = 7.5, HRT = 25 d	CH_4: 125.1 mL/g_{VS}	[97]
Seaweed and solid cow manure	Seaweed grinded and both diluted with water	11.8 g/L	1st stage: 37 °C, pH = 7 2nd stage: 37 °C, pH = 7.5	CH_4: 110 mL/g_{VS}	[98]
Spent mushroom substrate and chicken manure	Spent mushroom substrate crushed, ground, treated with acid	N.A.	1st stage: 35 °C, pH = 7 2nd stage: 55 °C, pH = 7	CH_4: 84.3 mL/g_{VS}	[99]
Cheese whey, cow manure, and ensiled sorghum	Sorghum ensiled, grounded and alkaline pretreated	80 g/L	1st stage: 37 °C, pH = 5.5, HRT = 0.5 d 2nd stage: 37 °C, pH = 8, HRT = 24 d	H_2: 0.7 mol/$mol_{CarbohydratesConsumed}$ CH_4: 326 mL/g_{VS}	[41]

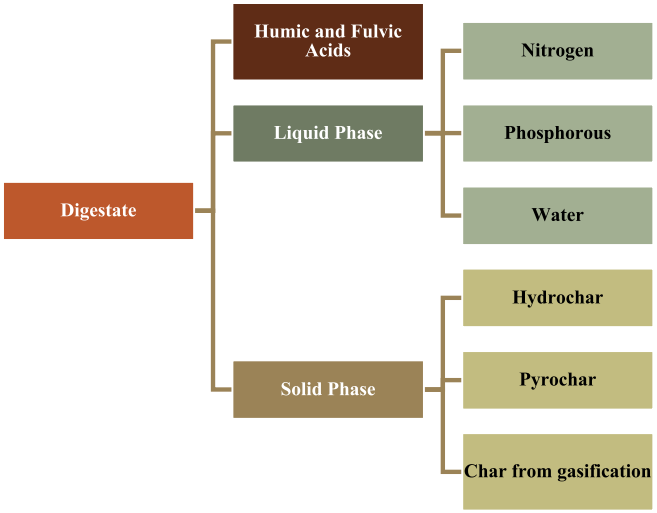

Fig. 3. Scheme of different high-added products recoverable from digestate.

4.1. Digestate composition and traditional utilization

Digestate composition depends on the feedstock and process conditions. Digestate typically contains 15–55 % carbon (C) deriving from substrate and inoculum carbon. DF and AD reduce COD and BOD_5, by stabilizing organic matter and accumulating the recalcitrant compounds in the digestate. Comparing the substrate before and after digestion, an increase in carboxyl-C, aromatic-C, and aliphatic-C is evident while a drop in alkyl compounds can be observed suggesting a degradation of alkanes [103].

Digestate contains inorganic species as nitrogen (N), phosphorus (P), and potassium (K) which are non-renewable materials, and their availability depends on their recycling [104].

Digestate can be exploited in three forms: whole, liquid (rich in N and K), and solid (rich in C and P) [105]. The two phases are produced during separation processes through mechanical separators, centrifuges, stripping, drying, or evaporation. Common techniques like precipitation and flocculation, which facilitate the formation of larger particles, aid in the separation phase [106]. Chemical methods can improve particle coagulation through the neutralization of particles' surface charges [107]. A common method for utilizing digestate is land application, as it serves as a nutrient source (N, P, K) for crops, making it an effective fertilizer [108]. However, nutrient concentration in digestate is highly variable, and excessive quantity of a certain element leads to soil pollution. For instance, an excess of N can cause eutrophication or over-saturation of nutrients, which excludes digestate land application. Additionally, logistical challenges such as transportation costs and competition from cheaper inorganic fertilizers hinder its widespread use [109]. Legislative restrictions also limit digestate utilization, with the European Union only approving biofertilizers legislation in 2019 through the Fertilizing Product Regulation 1009/2019. This regulation promotes the safe circular management of digestate but prohibits its use as a soil amendment if derived from mixed municipal waste, sewage sludge, or certain animal by-products [110].

Digestate is rich in macro-elements, but contaminants are also present. Heavy metals are not commonly found in biomasses, but they can be tracked down in digestate due to anthropogenic activity [111]. Ni, Zn, Cu, Pb, Cd, Cr, and Hg are common elements in digestate even if their concentration is highly variable depending on substrates [112]. Manure-derived digestate often contains high levels of Zn, Cu, and As due to animal feed and antibiotics, which concentrate during the biological processes [113]. Arsenic (As) is a concerning element due to its toxicity and lack of necessity in microbial activity. When digestate is applied to soils, metals can reach a more stable phase and become more bioavailable necessitating careful monitoring of their concentrations [114].

Digestate may contain organic pollutants such as pathogens, pesticides, and steroid hormones [115].

Proper treatment of these contaminants is essential to prevent the spread of diseases to plants or humans when digestate is applied to soils. Its direct soil application is not always suitable, leading to a shift towards nutrient recovery to control the element quantities provided to crops and ensure fertilizer quality [116].

The liquid fraction of digestate contains less than 3 % of total suspended solids [117]. Improper use of liquid digestate in land disposal can cause soil pollution. Alternative applications concern the extraction of nutrients which can balance nutrients in digestion or be applied as fertilizer.

4.2. Liquid phase conversion

4.2.1. Nitrogen recovery

Nitrogen is the most abundant element in liquid digestate with 70–80 % of its dissolvable fraction present in the liquid phase [117]. N is mineralized to ammonia, affecting the digestate's alkalinity [118]. Various nitrogen recovery techniques are employed, including chemical approaches such as ozonation and stripping, physical methods like microwave irradiation, vacuum evaporation, and membrane technologies, and biological processes often yield higher recovery rates.

Traditional methods of N recovery are being complemented by innovative technologies, as reported in Table 3. These methods differ in TRL, with newer processes typically operating at the laboratory scale due to their development stage.

Among these, ammonia-nitrogen stripping is the most developed with a TRL of around 8–9 [126]. This process involves capturing ammonia from the liquid phase through contact with a gas, which is then treated in a scrubber to separate ammonia from the stripping gas. This method is convenient when the direct utilization of digestate in land can be harmful to crops due to excessive nitrification of soil [128]. Nitrogen released is controlled while the low ammonia digestate can be

Table 3
Pros and cons of nitrogen recovery techniques from digestate.

Technique	Benefits	Disadvantages	Removal efficiency (on total N-compound content)	TRL	References
Microwave radiations	• High removal efficiencies • Fast and easy to control	• High energy cost	82.6 %	4–5	[119]
Ozonation	• Removal of pathogens, organic matter, and inorganic contaminants	• Ozone requirements	85 %	4–5	[120]
Biological processes	• Degradation of unstable biomass	• Not complete consumption • Leachate and odors	83.7 %	4–5	[121,122]
Vacuum evaporation	• Concentration of ammonia	• Elevated operational costs • Great variability	97.5 %	4–5	[123]
Stripping	• High degree of development • High efficiency	• Scrubbing step is necessary • Production of wastes	70–80 %	8–9	[110, 124–126]
Membranes	• High removal efficiencies	• Not selective • Fouling	70–75 %	4–5	[110,127]

recirculated to the digester to adjust the alkalinity of the system. Although air is the most common stripping gas, it can inhibit microbial activity. However, alternative gases are often more expensive or hazardous than air [125]. Inorganic acid solutions, such as sulfates or nitrates, are typically used in the scrubbing step to capture ammonia, but they are expensive and generate waste [124].

Biological processes, including autotrophic nitrification and heterotrophic denitrification, represent another well-established method for nitrogen extraction from liquid digestate. Enhancing bacterial activity through the addition of carbon sources can improve these processes [122,129].

Innovative methods include microwave irradiation, ozonation, vacuum evaporation, and membranes. These techniques, with TRLs not exceeding 4–5, are still in the experimental phase due to various technical limitations hindering their scalability [110].

Microwave radiations heat the digestate causing the evaporation of volatile ammonia molecules in solution [119]. Ozonation is commonly used in wastewater treatment to remove pathogens, organic matter, and inorganic contaminants [120]. However, high costs and reagent requirements limit the large-scale application of these techniques. Vacuum evaporation concentrates digestate, by evaporating water under negative-pressure conditions. Then, it is collected in tanks after condensation [123]. Despite its efficiency, this method has elevated operational costs and great variability in ammonia content in the two phases which depends on digestate characteristics [130].

Membrane technology captures ammonia-nitrogen through hydrophobic polymers. Ammonia-nitrogen permeates the membrane and is transferred to an acid solution, forming commercial fertilizer salts. Sulfuric acid is typically used as receiving liquid even if phosphoric or nitric acid can also be used [127]. While this method yields high nutrient recovery, issues like membrane fouling due to high dry matter content in digestate can occur. Enzymatic pre-treatment may mitigate this problem by reducing molecule size [131].

4.2.2. Phosphorous recovery

Phosphorous (P) compounds are concentrated mainly in solid digestate (55–65 %), but the liquid phase contains a significant percentage (35–45 %) [132]. Traditional phosphate rock extraction for P production is unsustainable since, according to the European Commission, P is a critical raw material [133]. Precipitation is widely employed in P recovery, and it can be applied in different forms as illustrated in Table 4.

Struvite is a mineral combination of nitrogen, phosphorous, and magnesium, beneficial for slow-release fertilization [136]. The precipitation of struvite requires equimolar concentrations of NH_4^+, Mg^{+2}, and PO_4^{-3} under alkaline pH conditions [135]. This method needs a relatively high concentration of magnesium which usually is insufficient in the digestate, necessitating additives or alternative sources. Siciliano & De Rosa [141] proposed the use of magnesium-rich waste materials like seawater bittern, a by-product of the marine salt industry. They have also dealt with phosphorous lack in liquid digestate through the employment of bone meal, a residue from the thermal treatment of meat wastes. Both proposals are meaningful from a circular economy perspective as each choice reuses waste.

An alternative approach is the replacement of struvite with vivianite. Vivianite($[Fe(PO_4)_2{\cdot}8H_2O]$) offers simpler production conditions compared to struvite and can be used as a P fertilizer. This method can be coupled with membrane separation to reach almost 100 % of P removal efficiency, but further studies are required to scale up the process [137].

Lastly, the precipitation of calcium phosphate should be considered. Calcium phosphate is a complex process requiring a supersaturated environment and basic pH. In wastewater treatment, NaOH addition is needed for calcium phosphate precipitation because the presence of organic acids and carbonates lowers pH and hinders precipitation. However, hydroxide is a costly reagent hence some studies have been conducted on electrochemical precipitation, a technique that avoids the utilization of additives [138]. Deeper studies should be carried out on this method to state which path is more technically feasible and profitable.

Membrane technology aids ammonia capture and, combined with precipitation, facilitates simultaneous nitrogen and phosphorous

Table 4
Pros and cons of phosphorous recovery techniques from digestate.

Technique	Benefits	Disadvantages	Removal efficiency (on total P content)	TRL	References
Struvite precipitation	• Simultaneous recovery of N, Mg, and P	• Need for high Mg concentration • Alkaline chemicals required	88 %	7–9	[134–136]
Vivianite precipitation	• Simpler conditions of production	• New technology to be further deepened	~100 %	6	[137,138]
Calcium phosphate precipitation	• Efficient and economic	• Complex process conditions	57 %	6–7	[139,140]

recoveries. After the recovery of ammonia through membrane separation, the alkalinity of the system is reduced, and the P precipitation is enhanced [142]. Magnesium chloride is used as an additive to form magnesium phosphates which precipitate and allow P recovery [143]. Vacuum membrane distillation is an innovative alternative to traditional membrane technology to recover N and it can be coupled with P precipitation. The P recovery can be done by adding lime or through struvite precipitation. After P recovery, ammonia can be recovered under mild temperatures (50–60 °C) and vacuum conditions (50–100 mbar). The process allows the recovery of almost 90 % of ammonia but more studies are needed to investigate the process [144].

4.3. Humic and fulvic acids

Bio-stimulants enhance plant growth, improving productivity and resilience to damaging events. Among them, humic and fulvic acids are interesting as they can be obtained from digestate. Humic acids, heavier and soluble in alkaline solutions compared to fulvic acids, play a crucial role in returning carbon to the soil, thereby enhancing soil quality [100,145]. Humic acids promote root growth by incorporating essential metals necessary for plant development, since they enhance nutrient absorption and increase tolerance to saline conditions such as NaCl [146]. Whereas fulvic acids facilitate the uptake of micronutrients, by mobilizing and transporting nutrients like iron [147]. Their action on soils includes an improvement in their water retention and structure. The extraction of humic and fulvic acids from digestate typically involves an acid-alkali method [102,148]. These substances can be released by degrading flocs and cells which constitute digestate. NaOH is recommended as it is the most efficient [149]. NaOH solution coupled with centrifugation allows a separation between insoluble and soluble humin particles. This method involves centrifugation to separate insoluble humin particles, with soluble fulvates recovered in the supernatant and concentrated using ultrafiltration membranes. Acidification with HCl then yields humic and fulvic acid [150].

4.4. Solid phase conversion

Carbon content in the solid phase accounts for 15–55 % w/w and it could be a carbon source employed in subsequent processes [109,151]. Pre-treatments, including mechanical, thermal, chemical, and biological, improve digestate biodegradability [152]. Mechanical pre-treatments avoid inhibitory substances like furans and polyphenols (that are released under thermal and chemical pre-treatments), reduce particle size, and decrease polymer crystallinity, by improving biodegradation [153].

Chemical pre-treatments use acid or alkaline additives such as sulfuric acid or sodium hydroxide. The latter compound is more effective for saccharification, mostly in lignocellulosic residues, as lignin is decomposed while acidic compounds cause the disruption of fibers and hinder their release [154]. Wang et al. [155] proved the importance of combining pre-treatment, by optimizing ethanol production by coupling ozonation and aqueous ammonia treatments to degrade the fiber of the digestate from rice straw. If the carbon-rich residue is not further biologically degraded, a thermochemical process, promising for char production, should be considered.

4.4.1. Char from the solid fraction of digestate

Thermochemical processes, such as pyrolysis, gasification, and hydrothermal carbonization, allow the exploitation of solid digestate.

Pyrolysis is a promising method to efficiently degrade biomass in the absence of oxygen. This process produces three products: bio-oil (a liquid), biochar (a solid), and pyrogas (a gaseous mixture of CO, H_2, CH_4, ethylene, and C3-compounds) [156]. The process operates within a range of temperatures between 300 °C and 1000 °C. Depending on the heating rate, pyrolysis can be defined as slow or fast. Slow pyrolysis involves longer residence time (from minutes to hours) and moderate heating rates (0.1–10 °C/min), resulting in higher biochar yields (25–35 % of the biomass). Fast pyrolysis operates with shorter residence times (0.5–5 s) and higher heating rates (10–10000 °C/min) [157,158].

Gasification is another thermochemical process that degrades the biomass at sub-stochiometric oxygen concentration. Typical process temperatures are between 600 and 1300 °C which led to the formation of syngas (a gas), a tar (a liquid) composed of aromatics compounds, and char (a solid) [159]. Both pyrolysis and gasification require low moisture content in biomass to avoid energy losses due to water evaporation. Consequently, a drying step is often necessary to remove water [160].

Humid digestate can be treated through hydrothermal carbonization (HTC) or liquefaction (HTL) which occur in the aqueous phase. HTC is performed at mild temperatures up to 180–250 °C, and the reactor pressure is influenced by steam and gas pressure [161]. The main products are a gas mixture (mainly CO_2), a liquid fraction containing water and soluble compounds, and a solid called hydrochar, which is often rich in phosphorus and can be recovered through precipitation or extraction [162].

When temperatures between 200 and 380 °C are applied, the process shifts to liquefaction sterilizing the residue and forming a higher quantity of liquid product compared to HTC [169]. The liquid phase can be divided into bio-oil, which has a high heating value (30–40 MJ/kg) like petroleum, and an aqueous phase rich in nutrients, which can be recycled in the digestion process or for nutrient recovery. A solid residue is still produced which is typically employed as soil amendment [163,164].

Char is a porous substance that can contribute to mitigating climate change by sequestering CO_2 making it a valuable material for carbon capture. When added to the soil, char enhances nutrient retention, water-holding capacity, and microbial activity. Both in DF and AD char can boost microbial activity and nutrient release [165].

Char's structure contains various chemical functional groups, making it a versatile material that can be modified through physical or chemical activation to enhance its properties [166]. Physical activation enhances surface area and porosity by exposing the char to gases like steam or CO_2, forming micropores and oxygen functional groups that efficiently remove contaminants from water and soil [167]. Chemical activation involves doping char with chemical agents, such as zinc chloride, phosphoric acid, and potassium hydroxide, which modify functional groups on the surface. These processes need a lower temperature and shorter time than physical activation [168]. Subsequently, a thermal treatment is typically performed to dehydrate the sample, enhance porosity, reduce tar production, and generate volatile compounds [169]. The properties of biochar and hydrochar vary based on the production method, as reported in Table 5. Biochar from pyrolysis and gasification has a higher ash content than hydrochar, due to the retention of inorganic fractions during HTC. This results in different pH values of the two solids: biochar is alkaline (pH up to 9–10) while hydrochar is acid (pH 4–7) [170]. The morphology of biochar and hydrochar also differ due to the higher temperatures and gas flow involved in pyrolysis and gasification, leading to a higher surface area in biochar [171]. Compared to hydrochar, biochar has a higher aromatic content and a greater H/C and O/C ratios [172]. and is a conductive material, which can assume the role of electron shuttle between species as syntrophic bacteria and methanogens [173].

5. Explorative assessment of energetic, environmental, and economic sustainability

The literature lacks comprehensive studies on the energetic, environmental, and economic aspects of TSAD and digestate conversion. The energy balance and efficiency of the biorefinery are essential in determining its overall sustainability.

Energy sustainable analysis (ESA) is performed at two levels: the first is in the short term, utilizing the Energy Sustainability Index (ESI) to quantify if the energy generated is sufficient to cover the direct energy

Table 5
Characteristics of char obtained through hydrothermal carbonization (HTC) and pyrolysis (PY) in terms of process temperature, char yield, char pH, % of fixed carbon, specific surface area (SSA), porosity, and application. N.A = not available.

Type	Substrate	T (°C)<	Yield (wt %)<	pH	Fixed carbon (%)	SSA (m^2/g)<	Pore volume (cm^3/g)	Application	References
HTC	Digestate from AD of sewage sludge	220	73.4	7.14	9.05	N.A.	N.A.	In addition to the anaerobic digestion of process water from HTC	[174]
HTC	Digestate from AD of corn silage, grass silage, and cattle manure	190	70.0	N.A.	19.40	14	0.35	Upgrading to activated carbons to adsorb CO_2 in biogas purification	[175]
HTC	Digestate from AD of maize silage	190	72.0	5	N.A.	12.3	0.096	N.A.	[176]
HTC	Digestate from AD of sewage sludge	150	90.0	6.5	6.60	N.A.	N.A.	Soil amendment	[177]
PY	Digestate from AD of food waste	400	44.3	N.A.	29.49	73.99	0.1	N.A.	[178]
PY	Digestate from AD of food waste	600	33.6	N.A.	13.09	89.23	0.07205	Adsorbent for pollutants, soil amendment catalyst to enhance the biorefinery	[179]
PY	Digestate from AD of food waste	400	73.0	9.81	4.65	53.13	0.1	N.A.	[180]
PY	Digestate from AD of sewage sludge	550	63.0	10.3	N.A.	58.6	0.065	Soil amendment	[181]

costs of operating the technology, and the second one is in the long term, encompassing all indirect energy requirements, like the additional energy needs by the technology and the energy required for replacing the technology at the end of its life [181].

ESI is an indicator calculated through eq. (1):

$$ESI = \frac{E_{produced} - E_{already\ spent} + E_{avoided}}{E_{direct}} \quad (1)$$

where $E_{produced}$ represents the total energy produced in the process, $E_{already\ spent}$ is the energy used in producing the source of the process, $E_{avoided}$ is the energy saved when the source is a waste as disposal costs are not present and E_{direct} is the fuels and electricity employed in operating the process [182]. ESI should be higher than 1 to be associated with a sustainable process. This consideration should be applied to the case presented in this review where a TSAD is coupled with digestate conversion. At this point, key questions arise: is this approach energetically sustainable? Should TSAD be avoided or stopped after the first stage of DF and convert its digestate? Should waste biomasses be directly degraded through a thermochemical process avoiding digestate production?

In a sequential process involving TSAD and digestate conversion, the produced energy includes hydrogen, methane, and any energy carriers from digestate management.

If ESI is equal to 1, the energy produced and energy directly spent in the process have the same value. Knowing the energy required to run TSAD and digestate plants helps calculate the minimum energy needed for balance.

This is a simplified approach as, even knowing how much energy carriers should be theoretically produced, biomass-based processes are extremely variable. Biomass composition strongly depends on nutrient content and humidity while its biodegradability is a fundamental parameter as it causes the need for pre-treatments.

Di Addario et al. [182] highlighted the importance of thermal balance in AD, considering the thermal energy required for pre-treatments and biomass heating during AD, and the energy produced through the CH_4 formed. The study focused on 15 studies and only 6 of them presented an ESI>1, indicating energy sustainability. The authors suggested that the energy produced should be 4–5 times higher than the energy spent to assess a real energetic profit from the process. Comparing traditional AD and TSAD, the latter proved to be more energetically sustainable. Gomez-Camacho et al. [183] evaluated the ESI of AD applied to 5 different biomasses: two livestock residues (cattle and pig manure), OFMSW, and two energy crops (maize and sorghum silage). Even if each process presented an ESI >1, energy crops reached the lowest values, and the long-term analysis demonstrated their inefficiency as AD substrate due to the anthropogenic contributions associated with their production (which contribute to the already spent energy burden). Life Cycle Assessment (LCA), a standardized methodology (ISO 14040-44), quantifies the environmental impacts associated with the process flows and identifies process bottlenecks.

LCA assesses the impact of a single process or compares multiple processes by utilizing the same functional unit and boundary conditions. Based on the literature data, no technical data and LCA of sequential TSDA and digestate are available. Table 6 summarizes available LCA studies about single-process DF, AD, TSAD, and digestate conversion. These studies cover numerous impact categories but primarily focus on climate change due to the European climate law, aiming to reduce EU emissions by at least 55 % by 2030 and achieve climate neutrality by 2050, according to the Regulation “Fit for 55 %” [184].

TSDA and digestate conversion should be designed as restorative and auto-regenerative systems and evaluated using a cradle-to-cradle approach. This approach encompasses biomass collection, transport, storage, and pre-treatment, followed by fermentation (DF, AD, and TSAD), and digestate conversion for nutrient recovery or biomaterial production.

The study of Sinsuw et al. [185] compared the environmental impacts of the pilot and commercial TSAD plants. The pilot plant faced challenges with slurry storage, releasing ammonia emissions that caused acidification and eutrophication. In contrast, the primary impact on the commercial scale was photochemical ozone creation potential due to the release of volatile organic matter from the digester [185].

DF studies are mostly available at the laboratory scale, with few environmental analyses scaled up to the pilot plant level. An LCA study on DF [186] demonstrated that bio-H_2 production from various feedstocks (sugar beet molasses, wine wastewater sludge, and cheese whey) was competitive with hydrogen production from steam reforming, emitting 12.08 kg CO_2eq/Nm^3 H_2.

Regarding digestate conversion, five key LCA studies on struvite recovery, thermochemical, and composting processes are identified. LCA studies have shown the environmental benefits of nutrient recovery from the liquid phase of digestate, with the combination of ultrafiltration, struvite crystallization (SC), and liquid-liquid membrane contactor (LLMC) achieving the lowest environmental impact and highest struvite recovery [187].

Cucina et al. [188], quantified that for a mix of manure and crop, AD and composting have a lower environmental impact compared to incineration and landfills. Angouria-Tsorochidou et al. [189] reported that the traditional use of liquid digestate as fertilizer led to significant emissions during storage and spreading. They recommended nutrient extraction from digestate to mitigate environmental impacts. Additionally, Inalegwu et al. [190] demonstrated the technical feasibility and environmental sustainability of sequential AD of food waste and pyrolysis (ADCo-Py). The pretreatment in ADCo-Py, including solids separation and drying, enhanced environmental sustainability compared to Py

Table 6
The environmental evaluation of dark fermentation (DF), anaerobic digestion (AD), two-stage anaerobic digestion (TSAD), and digestate conversion. The adopted acronyms are Global warming (GW), Bio compressed natural gas BCNG, Gasoline gallon equivalent (GGE), Pyrolysis (PY), and Hydrothermal carbonization (HTC).

	Process	Biomass	Functional unit	Approach	Impact methods	Impact category	Impactful phase	Main findings	References
DF	H_2-production from different biomasses	1. Wine molasses + wastewater (WWS), 2. Cheese whey (CW) 3 Sugar beet molasses (SBM).	1 Nm^3 H_2/h	Cradle to gate	ReCiPe 2016 Midpoint (H)	GW	$kgCO_2$ eq/FU SBM: 3.56 CW 39.74 WVS 9.13	SBM and WVS are competitive with steam reforming which emits 12.08 kg CO_2 eq/FU CW bottleneck is the fermentation.	[186]
AD	BioCNG in liquid (L) and solid (S) AD	L-AD: Dairy manure + food waste S-AD: crops	1 GGE of BioCNG	Cradle-to-grave	IPPC 2021	GW	17 kg CO_2 eq/FU	AD and upgrading.	[195]
	OLR effect	Animal manure	1 t of COD of substrate in the digester	Cradle-to-grave	IMPACT 2002+v2.12 methodology	GW	At OLR = 5.45 kgvs/m^3d: 1.6 t CO_2 eq/FU	Increasing the OLR over 5.45 kg vs/m^3 • d, the impacts increased	[200]
	AD + wastewater treatment	Olive mill wastewater (OMWW)	1 t OMW.	Cradle-to-grave	ReCiPe 2016 Midpoint (H)	GW Human non-carcinogenic toxicity	GWP = 89.3 kg CO_2 eq/FU HT = 57.5 kg 1,4-DCB	High-energy requirement, which can be solved through co-digestion.	[199]
TSAD	High pressure AD	Cattle manure and sugar beets	1 m^3 CH_4	Gate to grave	IPPC 2021	GW	109 gCO_2 eq/FU	The highest impact item is the biogas upgrade through hydrogen methanation	[201]
	TRL effect: pilot (P) vs commercial (C) scale	Pig slurry and cow dung	10950 t/y slurry	Gate-to-grave	CML-baseline 2001	GW	$kgCO_2$ eq/FU P $1.27 \bullet 10^{-2}$ C: $1.24 \bullet 10^{-4}$	Increasing the scale reduced the environmental impact potential	[185]
	Effect of COD load in portable TSAD	65 % Food waste +35 % cardboard	1 MJ of heat produced	Cradle-to-grave	ReCiPe mid-point 1.08	GW	37.4 ± 0.7 g CO_2 eq/FU	The highest impacts are due to insufficient or excessive COD loading). The best operative condition COD 16 g/Ld	[202]
	Biohythane production	Microalgae and food waste (FW)	1 MJ of upgraded biohythane	Cradle-to-grave	CML method	GW	124 g CO_2 eq/FU	The highest impacts are energy generation and pretreatments. The emissions from FW treatment are lower compared to AD	[203]
	AD *vs* TSAD	Second cheese whey (SCW)	3285 t SCW/y	Gate to gate	IPPC 2021	GW	$kgCO_2$ eq/FU AD: 76.3 TSAD:123.6	Low energy recovery in AD	[25]
Digestate conversion	Recovery of struvite from supernatant of AD	Wastewater	100,000 m^3/d of wastewater	Cradle-to-grave	ReCiPe 2016 Midpoint (H)	GW	200 kg CO_2 eq/FU	The highest impacts are ultrafiltration and membrane	[187]
	Comparison AD + PY AD PY	Food waste (FW)	1 kg FW	Cradle-to-gate	TRACI	GW	$kgCO_2$ eq/FU ADCo-PY -1.726 AD - 0.855 PY - 0.181	Pretreatment has the highest environmental impact	[190]
	AD + composting	21900 t of manure +9125 t of crops	1 Mwhe	Cradle-to-gate	IPPC 2021	GW	−167.77 $kgCO_2$ eq/FU)	The highest impact is the item of transport	[188]
	Biofertilizer (S1) raw digestate on the soil.< (S2) Separate liquid and solid phases of soil	Digestate from manure	1 kg of dry digestate	Cradle-to-gate	ReCiPe 2016 Midpoint (H)	GW	$kgCO_2$ eq/FU S1: −0.36 S2: −0.47	Membrane technology has the highest environmental costs	[189]
	AD + HTC	OFMSW and wood waste	1 kWh of exergy	Cradle-to-grave	ReCiPe 2016 Midpoint (H)	GW	0.25 $kgCO_2$ eq/FU	Low substrate feeding increases the impacts	[191]

alone. The highest impact in ADCo-Py was the energy-intensive drying of digestate, but product recovery balanced this impact.

HTC is another thermochemical process for digestate conversion. Mayer et al. [191] indicated that AD followed by HTC could have low environmental impacts if HTC was performed at high substrate utilization, reducing impacts associated with additional exergy generation.

Comparing thermochemical (Py and HTC), biological (composting), and chemical (struvite and biofertilizer) recoveries, thermochemical methods showed the lowest environmental impacts due to the potential for material (char) and energy recovery (pyrogas and refined oil), offsetting process energy costs. Compost recovery from digestate is an environmentally viable process but the main bottleneck is the biomass transport due to water contents and storage [188].

Economic evaluation is necessary to state the feasibility of a process at an industrial scale and both capital and operating costs must be considered [192].

AD is capital-intensive, but in TSAD the capital effort increases due to the double reactor being controlled (one for DF and the other for AD) [192].

Lenzuni et al. [193] showed that capital costs account for almost 50 % of the minimum selling price of the product while operating stands for 15 %, confirming the magnitude of equipment costs as usually the highest.

The collection and transport of biomass can be expensive. Many studies estimate biomass transportation costs independently of location, assuming a uniform spatial distribution of biomass and road infrastructure, without considering the size of biorefinery plants. Recent studies show that biomass yield density (t/ha • y) varies with biomass supply distance (km) from the plant. Golecha et al. [194] highlighted the interdependence between biomass yield density, supply distance, and the tortuosity road factor, developing a first-order Taylor polynomial series to approximate these factors as linear functions of supply distance. Using this model, they defined a biomass transport cost model depicting transport costs for different biomasses.

Another important item cost is the biogas purification and upgrading, which involves energetic and economic expenditures impacting both capital and operating costs but assuring a high-quality biomethane [195]. A tradeoff between high costs and process yield should be guaranteed [196].

The scale effect is a significant factor and usually, the increase of scale decreases the operative costs enhancing the revenues [197]. This result is also important for TRL evaluation which does not exceed 5 in DF and 5–7 in several valorization techniques meaning that the technologies are not ready to be fully exploited at large scale.

Digestate handling is essential to avoid pollution and social issues. The study by Czekała et al. performed on agricultural biogas plants in Poland stated that the selling price of the digestate is lower than the one of commercial mineral fertilizers, due to the high moisture of the digestate. Czekała et al. calculated that the daily income for a biogas plant of 1 MW is €1414 for energy, and the digestate produced value of €334.4, proving that the management of digestate could enhance the economic balance of the plant [198].

6. Challenges and future perspective

The challenges faced by DF and TSAD concern the low H_2 yields, the limit of scale-up, and digestate management.

In DF, the low H_2 yield is due to the inefficient conversion of substrates and the formation of inhibitors. Process conditions should be optimized both as type of feedstocks (origin and composition) and process parameters (OLR, inhibitors, and pH) [16]. These issues can be overcome by selecting easier degradable biomasses (i.e. carbohydrates and simple sugars), reducing the OLR to allow complete degradation of the substrate [204], and adopting co-digestion to manage the fluctuation of pH and avoiding the addition of chemicals [205]. Changing the perspective, according to circular economy principles, the accumulation of VFAs (acetic, propionic, and butyric acids) could be considered not as an inhibitor of DF but as a further product to be recovered from digestate and sold after upgrade [204]. In the world, the market price of acetic acid, and butyric acid range between US $1200 and $1600 per ton and US $4780 per ton respectively [204]. VFAs can be removed by the digestate of DF through the adsorption with biochar. Depending on the specific surface area, pore volume, functional groups, and pH, biochar can physically and chemically adsorb VFAs (through van der Waals forces, or hydroxyl, carboxyl, and phenolic functional groups) [204]. The strength of this solution is the management of the stability of DF through valorized waste (biochar from waste biomass) and recovering valuable products (VFAs), converting a problem (inhibition) into opportunity (selling VFAs and increasing H_2 yields).

The scaling up of DF is limited due to the process instability and inefficiency. Integrating DF with other processes, like TSAD, can optimize energy recovery, minimizing waste, costs, and environmental impacts. TSAD produces two energy carriers and complete exploitation of biomass, but it presents some bottlenecks, like the management of DF and AD under different process conditions and double reactors (investment and operative costs). The first challenges can be overcome by a deeper study of the OLR to prevent inhibition from passing from the DF to the AD stage [204]. Whereas economic profitability depends on a plant scale, consequently a trade-off between expenditure and revenues must be detected. Hence, future works must analyze the economy of scale to understand at what size of plant the TSAD process is economically viable as done in Ref. [197] for a sequential biorefinery (lactic acid fermentation followed by AD).

Digestate management is challenging because its valorization depends on national regulations. The wrong information about the quality reduces the exploitation of its potential, resulting in inefficient management [206]. Addressing these challenges requires a holistic approach and development in microbiology chemical engineering, and process optimization. Collaboration between universities, research centers, industry stakeholders, and policymakers is crucial for advancing the commercial development of DF and TSAD.

7. Conclusion

This study critically reviewed the TSAD for the sequential production of bio-hydrogen, bio-methane, and the conversion of their residues into high-added value products. In TSAD, the key process parameters are pH, HRT, OLR, temperature, and nutrient balances, which could be managed through co-digestion to achieve a C:N:P ratio equal to 200:7:1. Digestate liquid fractions can be exploited to recover nutrients (N and P) and water reaching more than 95 % efficiency. The solid fractions can be thermally treated to produce char, which can act as a catalyst in digestion, soil amendment, and carbon capture material. Sequential TSAD and digestate conversion are facing challenges like inhibitor formation and low H_2 production (10–180 mL/g_{VS}). The inhibitors could be adsorbed through carbonaceous material, recovered, and sold, while H_2 yield can increase. Energetic analysis points out how biomass type can influence energy expenditures due to the necessary anthropogenic actions on substrates which concur to lower ESI beneath 1. Environmental evaluations highlight that sequential TSAD and digestate conversion can reduce climate change impacts compared to the stand-alone DF, AD, and conventional digestate treatment. From an economic perspective, capital costs account for 50 % of the total representing the heaviest cost item. The scaling up of the sequential biorefinery could be overcome by the analysis of economic-scale profit to detect at which scale the plant could be economically profitable.

This review underlines the necessity of a multidisciplinary approach to face these issues and realize a feasible sequential TSAD to produce bio-energy and digestate exploitation fulfilling a closed-loop valorization of waste biomass.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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