New insights in food waste, sewage sludge and green waste anaerobic fermentation for short-chain volatile fatty acids production: A review

Federico Battista [a,*], Giuseppe Strazzera [a], Francesco Valentino [b], Marco Gottardo [b], Marianna Villano [c], Mariana Matos [d,e], Fernando Silva [d,e], Maria.A. M. Reis [d,e], Joan Mata-Alvarez [f], Sergi Astals [f], Joan Dosta [f], Rhys Jon Jones [g], Jaime Massanet-Nicolau [g], Alan Guwy [g], Paolo Pavan [b], David Bolzonella [a], Mauro Majone [c]

[a] Department of Biotechnology, University of Verona, Via Strada Le Grazie 15, 37134, Verona, Italy
[b] Department of Environmental Sciences, Informatics and Statistics, Cà Foscari University of Venice, Via Torino 155, Mestre-Venice 30170, Italy
[c] Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy
[d] UCIBIO – Applied Molecular Biosciences Unit, Department of Chemistry, School of Science and Technology, NOVA University Lisbon, 2819-516 Caparica, Portugal
[e] Associate Laboratory i4HB - Institute for Health and Bioeconomy, School of Science and Technology, NOVA University Lisbon, 2819-516 Caparica, Portugal
[f] Department of Chemical Engineering and Analytical Chemistry, University of Barcelona, 08028, Barcelona, Spain
[g] Sustainable Environment Research Centre, University of South Wales, Llantwit Road, Treforest, Wales CF37 1DL, UK

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ABSTRACT

50.3 M tons of wastes are annually produced at urban level in the EU-27. Sewage sludge, Organic Fraction of Municipal Solid Wastes (OFMSW) and food industrial wastewaters, are the major typologies of wastes produced at urban level. OFMSW and sewage sludge account for the 28 % and 23 % of the EU-27 wastes streams, respectively. Their abundance and the high content of nutrients (nitrogen and phosphorous) make them very interesting as substrates in a biorefinery loop to produce biofuels and bio-based products. This review provides an overview on the conversion of urban wastes into Volatile Fatty Acids (VFAs) at different operational conditions, from small laboratory scales to full industrial plants. Mono-fermentation of no pretreated substrates OFMSW and Thickened Primary Sludge (TPS) led to low VFAs yields of 0.25–0.30 and 0.50 $g_{VFA\text{-}COD}/g_{COD}$, respectively. The co-fermentation of OFMSW and sewage sludge achieved higher VFAs yields (0.38 $g_{VFA\text{-}COD}/g_{COD}$). Co-fermentation yields was further improved (0.85 $g_{VFA\text{-}COD}/g_{COD}$) by the adoption of thermophilic temperature (55 °C). Regarding VFAs profile, it was observed that substrates with lower VFAs yields presented a higher concentration of acetic acid, while the improvement of the acidogenic fermentation's yield had as consequence the increasing of propionic and butyric acids' concentrations. Finally, innovative electro-driven approaches, electro-fermentation and electrodialysis, employing polarized electrodes have been investigated to favor the production of desired VFAs or to enhance acids separation from the fermentation broth.

1. Introduction

The European Commission approved the European Green Deal with the aim "to transform the EU into a fair and prosperous society, with a modern, resource-efficient and competitive economy where there are no net emissions of greenhouse gases in 2050 and where economic growth is decoupled from resource use" [1].

Sewage sludge (28.0 %), households and food industries waste (23.0 %), and manufacturing wastes (21.0 %) are the three major typologies of residues generated in the EU according to the European Environment Agency [2]. These wastes represent the 72 % of the total European waste generated in urban contexts, excluding major mineral wastes. In particular, their amount increased by 7.0 % (almost 50.3 million tons) in the EU-27 countries between 2010 and 2018, not as effect of the European population growth, which remained stable, so much as the economic growth. In the last decades these substrates started to be adopted for bioenergy production's purposes, essentially biogas, bioethanol and biodiesel. But the recent EU Directive 2018/851, which contains some amendments to the waste Directive 2008/98 EC, introduced relevant changes regarding the wastes management, and mainly their collection

and valorization. Compared to the previous Directive EU 2008/98, the most recent EU 2018/851 encourages the promotion of the "cascade pyramidal biorefinery hierarchy", where the production of valuable biomolecules or biological intermediates are considered priority than the bioenergy production [3]. Different Horizon2020 projects were successfully completed in the last years (Smartplant, AgroCycle, Circular Biocarbon, Fit for Food and Decisive 2020), with the scope to valorize the most abundant waste streams from industrial, agricultural and urban contexts [4–8].

The Food Use for Social Innovation by Optimizing Waste Prevention Strategies, defined food waste as "any food, and inedible parts of food, removed from the food supply chain to be recovered or disposed" [9]. Accordingly, food waste includes a very heterogenous types of products and by-products having different physical-chemical features and molecules.

This review focused the attention on Horizon2020 RES URBIS project which had the aim to valorize food wastes and sewage sludge, into valuable bio-based products, while minimizing any residual or consequent waste to be disposed of. The first task of the Work Package 2 (WP2) investigated on the acidogenic fermentation of urban wastes for the production of multiple bio-based innovative products and biofuels [10,11], and specifically for Volatile Fatty Acids (VFAs) production. VFAs production is an emerging research topic, as can be verified from the exponential trend of scientific articles published in the last decade on Scopus. The huge interest for VFAs is explainable for being biological precursors of different bioproducts, including polyhydroxyalkanoates (PHAs), various chemicals (e.g esters, ketones, alkanes), and biofuels (e.g. biogas and hydrogen) [11,12]. Moreover, the exploitation of urban organic wastes for VFAs production is supported by the existence of different full-scale plants for bioenergy purpose in the EU. They are essentially located in Germany and Italy where around 1600 and 600 full scale biogas plants are already in service [13]. They represent an extraordinary opportunity in a biorefinery context as they can be easily adapted in a two-stage anaerobic digestion (AD) for the simultaneous production of VFAs and methane.

The anaerobic acidogenic fermentation of food wastes and sewage sludge present different advantages: it is a flexible process as it can be performed under pure and mixed culture conditions. Moreover, it allows to obtain different VFAs concentrations and profile depending on both the initial chemical composition of the substrates and the operational parameters of the process, such as pH, temperature, Organic Loading Rate (OLR) and Hydraulic Retention Time (HRT) [14].

This review aims to give an overview of the VFAs production from different waste's streams produced at urban level, focusing the attention essentially on the results obtained along Res Urbis project's implementation. At the best authors' knowledge, this is the only one review article on VFAs showing the evolution of the valorization of the urban wastes from small laboratory scales to full scale ones. Specifically, the discussion starts with the sewage sludge, whose VFAs yields were studied with and without hydrolysis. Then, the paper covered a very detailed discussion on VFAs productivity from one of the most abundant waste streams, the OFMSW derived from household, restaurant, canteen and industrial food's (fruit waste generated by a fruit juice producer) activities. Different aspects and operational conditions were investigated to increase the VFAs productivity from OFMSW: the effect of the different carbon sources in a synthetic OFMSW, the adoption of various temperatures, HRT, OLR both at laboratory and pilot scales. The effects of the addition of sewage sludge and garden/parks residues as co-substrates with OFMSW were discussed too. Finally, one of the most innovative techniques, the electro-fermentation, was investigated as a tool to control the distribution of VFAs produced during fermentation processes.

2. Characterization of the food wastes tested in the Res Urbis project

Res Urbis project addressed different technical challenges related to upstream, acidogenic fermentation of biomass feedstocks. The technologies explored throughout the project include biomass pre-treatments, co-fermentation of different substrates, and demonstration of fermentation processes at a range of scales up.

It was demonstrated that manipulation of VFAs production patterns is feasible by altering the parameters, such as fermentation temperature, pH, or the oxidation-reduction potential of the reaction medium. A number of pretreatment strategies were investigated including thermal treatment and enzymatic saccharification which has been successful in increasing substrate availability for more efficient conversion to VFAs.

The main urban wastes adopted for the main activities carried out along the experimental phase of the project were food wastes and sewage sludge. They were characterized by high levels chemical oxygen demand (COD), biological oxygen demand (BOD), high nutrients (nitrogen and phosphorus) which can be exploited in a biorefinery context for biofuels and bio-based compounds productions [15]. In particular, the features of the specific substrates and the activities performed along Res Urbis project were summarized in Table 1.

3. VFAs production from primary sludge

Thickness Primary Sludge (TPS), one of the major wastes produced at urban scale (Table 1), was processed with a previous hydrolysis operation to produce VFAs. In.

Two tests were carried out to evaluate COD solubilization of TPS under different temperature and pH values. In particular, TPS in tests A was hydrolyzed for 24 h at 60 °C, at two different pH (Table 2), while TPS in tests B was treated for shorter time (4.5 h) at different temperature and pH conditions. The results from tests A (1 A and 2 A) are summarized in Fig. 1a (authors unpublished recent work).

As emerged from authors' recent unpublished work, in the first 2 h of the experiments, pH 8.5 and 10 resulted in similar results and sCOD increased approximately 7-fold in both experiments (Fig. 1a). However, after 24 h of experiment, pH 10 resulted in a higher solubilization of COD (37.7 %).

In the second set of tests (Tests B), the aim was to understand if increasing pH from 10 to 11 and temperature from 60 ºC to 70 ºC could improve the solubilization of the COD. The results of these tests are summarized in Fig. 1b. Since most conversion of particulate COD into sCOD occurred at the beginning of the test in the previous experiment, tests using sludge B were shortened to 4.5 h (Fig. 1b) show that increasing the pH from 8.5 to pH 10 promoted organic matter solubilization (Fig. 1b), however, further increasing the pH to 11 had the opposite effect. The sCOD/tCOD was lower for pH 11 than for pH 10 at the end of the experiment (Fig. 1b), which means that pH 10 seems to be the optimal pH for the range of temperatures (60–70 °C) tested. The result obtained in Test 2B was similar to Test 1B, in which pH was not adjusted (pH 5–6). Regarding temperature, no significant improvement was achieved when the temperature increased from 60 to 70ºC. Therefore, 60ºC should be selected at a lower cost in energy expenditure.

After the individuation of the best operational parameters for the hydrolysis of TPS (4.5 h, at pH 10 and temperature of 60 ºC), a continuous stirred-tank reactor (CSTR) was inoculated with sludge from a full-scale anaerobic digester (Wastewater Treatment Plant (WWTP) Frielas, Portugal) and fed continuously with hydrolysed TPS to produce a VFAs-rich stream. pH of the fermenter was set to 5, temperature was kept constant at 30 ºC and sludge retention time was set at 5 d.

During the last 2 weeks of operation, an average VFAs concentration of 7.05 ± 0.39 gCOD/L was achieved, consisting mainly of acetate (34 %), butyrate (16 %), ethanol (16 %) and propionate (15 %). This result corresponds to a CODVFAs/sCOD ratio of 0.80 gVFA-COD/gCOD in the effluent and a degree of acidification of 0.52 ± 0.10 gCOD/gCOD,

Table 1
Substrates tested along the Res Urbis project.

Urban Waste tested along Res Urbis	Main characterization of the adopted substrates	Co-fermentation (Yes/No)	Reactor type (volume)	Main activities (pretreatments, variation of the parameters)
Thickened primary sludge (TPS)	TS= 50.5 g/L; VS= 42.9 g/L; COD= 91 g/L; N = 234 mg/L; P = 163 mg/L	No	Lab scale (1–1.5 L), batch	Influence of pH, T and reaction time on TPS Hydrolysis. Influence of the hydrolyzed TPS on VFAs production
Fruit waste	TS= 106 g/L; VS= 140 g/L; COD= 175 g/L; N = 1.26 mg/L; P = 2.39 mg/L	No	Pilot scale (60 L), continuous	Pre-Hydrolysis of TPS, influence of pretreatment on VFAs production
Synthetic OFMSW	TS = 257 g/L; VS= 250 g/L; COD 292 g/L; N = 9.90 g/L; P = 1.45 g/L	No	Lab scale (1 L), batch	Influence of different carbon sources (protein, carbohydrates, lipids) on VFAs production
Synthetic OFMSW	TS = 257 g/L; VS= 250 g/L; COD 292 g/L; N = 9.90 g/L; P = 1.45 g/L	No	Lab scale (4.5 L), batch	Influence of pH, T, OLR and HRT on VFAs production
Synthetic OFMSW	TS = 257 g/L; VS= 250 g/L; COD 292 g/L; N = 9.90 g/L; P = 1.45 g/L	Yes	Lab scale (4.5 L), continuous	Influence of Sewage Sludge on the VFAs production from OFMSW
Grass Waste (at 5 % TS)	TS= 4.9 g/L; VS= 34.9 g/L; COD= 31.9 g/L	No	Pilot Scale (82 L), continuous	Influence of in situ electrodialytic VFAs recovery on VFAs yields
Grass Waste (at 5 % TS)	TS= 4.9 g/L; VS= 34.9 g/L; COD= 31.9 g/L	No	Pilot Scale (82 L), continuous	Influence of in situ combined pervaporative and electrodialytic VFAs recovery on VFAs yields
OFMSW	TS= 130–280 g/L; VS= 120–250 g/L; COD= 74–88 g/L; N = 39–45 g; P = 14–16 g/kgTS	No	Pilot Scale (230 L), continuous	Influence of digestate recirculation (two-phases process)
OFMSW	TS= 45–100 g/L VS= 40–80 g/L; COD= 20–40 g/L; N = 22–35 g/kgTS; P = 2–10 g/kgTS	Yes	Pilot Scale (380 L), continuous	Influence of Sewage Sludge addition on VFAs production from food waste
OFMSW	TS= 45–100 g/L; VS= 40–80 g/L; COD= 20–40 g/L; N = 22–35 g/kgTS; P = 2–10 g/kgTS	Yes	Pilot Scale (380 L), & Lab scale (1.0 L), continuous and batch	Influence of Sewage Sludge addition on VFAs production from food waste; influence of temperature and thermal pre-treatment
OFMSW from MBT plant	TS= 56–70 g/L; VS= 41–53 g/L; soluble COD= 38–73 g/L; TAN= 2200–3100 mg/L	No	Lab scale (4.5–30 L), continuous and batch	Influence of pH, T and reaction time
Food Wastes (FW) from University canteen	TS= 44–76 g/L; VS= 38 – 65 g/L; soluble COD= 15–52 g/L; TAN= 13–153 mg/L^{-1}	No	Lab scale (4.5 L), continuous and batch	Influence of pH, T, reaction time and biological pretreatment (mature compost addition)
Waste activated sludge (WAS)	TS= 30–58 g/L; VS= 23 – 43 g/L; soluble COD= 0.3–1.3 g/L; TAN= 53–152 mg/L	Yes, FW & Oleic acid	Lab scale (0.25 L), batch	Influence of cofermentation and co-substrate proportion

Table 2
Summary of the conditions used for the tests of hydrolysis of TPS.

	1A	2A	1B	2B	3B	4B
pH	8.5	10	Not adjusted	11	10	10
T (°C)	60	60	60	60	60	70
t (h)	24	24	4.5	4.5	4.5	4.5

suggesting that the soluble COD that was generated in the hydrolysis step, was converted into VFAs in the fermentation step.

4. Optimization of the VFAs production from OFMSW and industrial food wastes (FW)

OFMSW represents one of the major waste streams produced annually at urban context. It is a very heterogenous substrate, containing the organic matter (residues of fruits, vegetables, meat, fish, bread, pasta and other carbohydrates wastes) which can be valorized after the separation of the improper materials (plastic, wood and glass fractions). OFMSW was usually damped in landfill or sent to the incineration for the energy recovery. In the last decades, AD has gained popularity due to its capacity to obtain a methane-rich biogas. The main byproduct, the digestate, still rich in nitrogen and phosphorous compounds was further exploited for compost, soil improvers and fertilizer production [16].

The high organic content and the great abundance makes OFMSW an ideal substrate for VFAs production. The exploitation of OFMSW was investigated by almost all the RES URBIS partners which covered different parameters from laboratory and pilot scales, both in mono- and co-fermentation conditions. The VFAs production of OFMSW is variable
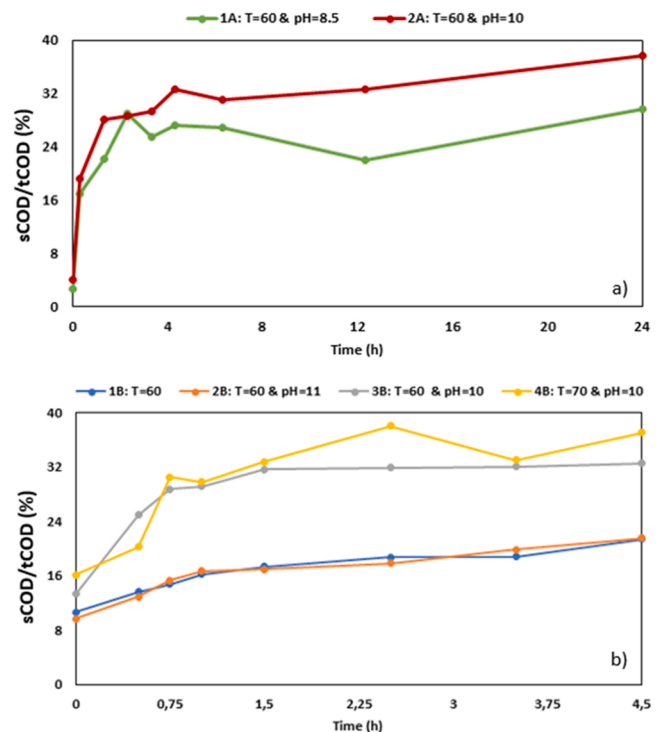

Fig. 1. Effect of the different hydrolysis conditions tested on the variation of the sCOD/tCOD ratio over time using sludge A – a) - and sludge B – b).

as it depends on the heterogenous composition of it. The differences of OFMSW are influenced by several factors such as the seasonality, the area of recollection and the regions of provenience. For example, the fruits and vegetables content increases in summer months, while fish and meat are preferentially consumed in winter. Moreover, Mediterranean countries present higher concentrations of carbohydrates (from pasta, bread, rice) than Middle and Northern European countries [17]. Despite these differences, OFMSW has some common features: (i) high levels of organic matter (around 15–20 % TVS), and (ii) high nitrogen and phosphorous concentrations (2–15 g/kg and 0.5–1.0 g/kg, respectively), indispensable nutrients for the metabolic pathway of the microorganisms.

4.1. Effect of the different carbon sources on VFAs production from a synthetic OFMSW

The discussion on the potentiality of VFAs production from OFMSW started with the adoption of a synthetic substrate. As reported, OFMSW is characterized by a high heterogeneity. The use of the synthetic OFMSW in the first phases of the project was justified by the need to assure constant feeding conditions to the tests in order to: (i) evaluate the VFA performances from the different carbon fractions derived from the same OFMSW from batch tests and (ii) reach in shorter time steady conditions along semi- continuous tests and to individuate the best conditions to increase the VFA yields.

A recent work by Strazzera et al. [10] studied the effect of the chemical nature of the main carbon fractions (carbohydrates, proteins, lipids, cellulosic compounds, etc.) contained in food waste both on the quantity and profile of VFAs production. This study started with the formulation of a synthetic Household Food Waste which simulated a real OFMSW from the Mediterranean Countries, composed by different ingredients commonly present in the real OFMSW [10]. The ingredients were classified into five organic fractions according to the main carbon chemical nature: lipids, proteins, cellulose, starch, fibers and sugars which were separately batch fermented at mesophilic (37 °C) at different pH (uncontrolled, 5.5, and 7).

The higher VFAs production was obtained from the OFMSW protein fractions at pH 7 with a final concentration of almost 14 gCOD/L. The VFAs productivity was lower at 5.5 and uncontrolled pH with a VFAs concentrations of 12 and 10 g/L, respectively. Regarding the VFAs composition, butyric acid was predominant acid (50 % w/w of the total), followed by valeric, acetic and propionic acids accounting for 14 %, 7 % and 6.5 %, respectively. The good results can be explained considering that proteins-rich fraction was the only carbon source which can avoid a rapid acidification of the reaction medium being rich in ammonia derived from the nitrogen compounds' degradation. The VFAs yield for the protein-rich fraction of OFMSW, expressed in term of $g_{VFA-COD}/g_{COD}$, were of about 80 %, 70 % and 60 % at 7, 5.5 and uncontrolled pH.

Even in the case of starch-rich fraction, the best performance was achieved when the pH was set at neutrality, with a maximum VFAs production of 12.50 g/L, corresponding to a VFA yield of 76 % $g_{VFA-COD}/g_{COD}$. The VFAs productivity decreased for pH 5.5 (10.50 g/L), dropping at around 1 g/L under uncontrolled pH condition, as consequence of the rapid acidification of the system.

Sugars and fibers demonstrated to be poor substrates for VFAs production regardless of the pH. Without pH control, the pH quickly dropped to values of about 3.5 negatively affecting the VFAs production, which final concentration was 1.7 g/L. The adjustment of the starting pH at 5.5 and 7 improved the performance with final concentrations of 6.5 and 9 g/L, respectively. These values corresponded to a VFAs yields of 40 % and 55 % $g_{VFA-COD}/g_{COD}$, respectively. Finally, cellulose-rich and lipids-rich fractions showed very low yields in every condition for the slow cellulose degradation and the formation of inhibiting long chain fatty acids, respectively [18].

4.2. VFAs continuous production from synthetic OFMSW at different operational conditions

The VFAs production from acidogenic fermentation does not depend only on the chemical composition of the OFMSW, but also on the fermenter's operational conditions. Strazzera et al. [14] tested different OLR, pH and temperature to optimize the VFAs production. The experimental campaign had a duration of almost 450 days, adopting as substrates the same synthetic OFMSW adopted for batch tests to evaluate the carbon fraction able to optimize the VFAs yield. For the continuous tests, the entire OFMSW was tested at two OLR (22 and 11 gTS/Ld), different pH values (uncontrolled, 5.5 and 7) and at mesophilic and thermophilic temperatures. The conditions that provided the highest VFAs yield were: OLR of 11 gVS/Ld, pH of 7 and thermophilic temperature. Under these conditions, the VFAs yield was of 0.38 $g_{VFA-COD}/g_{COD}$, corresponding to a solubilization rate of 0.63 g sCOD/g tCOD. The VFAs productivity of almost 0.40 $g_{VFA-COD}/g_{COD}$ is one of the highest present in the scientific literature. Jones et al. [19] achieved a similar result of 0.35 $g_{VFA-COD}/g_{COD}$, but after a combination of filtration and electrodialysis on food wastes. The operational conditions also comported a variation of the profile of the VFAs produced. Acetic acid was the main product when the process was not optimized and the VFAs productivity was low. Instead, under the optimal conditions, butyric acid was the predominant VFAs (more than the 60 % of the total acids) followed by caproic acid (almost the 20 %).

4.3. VFA production from a real OFMSW stream

Fernández-Domínguez et al. [20] evaluated over the course of 4 months the composition of four different internal streams of a full-scale mechanical-biological treatment (MBT) plant in Barcelona (Spain). Although the treatment process did not include a fermentation unit, the anaerobic digester influent had a remarkably high content of VFA (0.23–0.32 $g_{VFA-COD}/g_{COD}$) and a slightly acidic pH (6.2–6.8). In the MBT plant, OFMSW is mixed with the anaerobic supernatant in the pulper which could have accelerated OFMSW fermentation by providing hydrolytic-fermentative bacteria, adjusting the moisture content and increasing the pH while providing buffer capacity. Moreover, the residence time of the OFMSW in its subsequent hydrocyclones treatment increased the VFAs concentration (9.3–17.1 g COD/L), where acetic, propionic and butyric acids represented the 27–30 %, 30–36 % and 25–33 % (COD-basis), respectively. Previous studies have also reported that in a 2-stage OFMSW AD system (acidogenic fermentation + AD configuration), the recirculation of supernatant from the AD to the fermentation unit could lead to an enhancement of VFAs production since it increases the alkalinity of the process and avoids the pH drop to highly acidic values [21].

The influence of temperature was analyzed by Fernández-Domínguez et al. [20] in fermentation batch assays. In these tests, no external inoculum was added and pH relied on the recirculation alkalinity which led to pH values above 5.8 in all the assays. At 35 °C, the maximum VFAs yield ranged between 0.49 and 0.59 g COD_{VFAs}/gVS and it was dominated by acetic (28–35 %), propionic (22–28 %) and butyric acid (23–27 %), accounting for 75 % and 86 % of the total COD_{VFAs} (see summary in Table 3).

Fermentation batch tests carried out to assess the impact of temperature on fermentation performance (20–70ºC) showed that the $COD_{VFAs}/sCOD$ ratio decreased from 53 % to 41 % as the temperature increased from 20° to 70°C, due to the favorable impact of temperature on VS solubilization and hydrolysis. Despite the enhancement of hydrolysis at higher temperature, the differences in the maximum VFAs yield were only statistically significant for the test carried out at 70 °C, in which the lowest maximum VFAs yield was reached (0.45 $\pm$ 0.01 $g_{VFA-COD}/g_{COD}$). Regarding the VFAs profile, the combined contribution of acetic, propionic and butyric acids in the fermentation liquor decreased over time from nearly 90 % to 75–80 % on COD basis,

Table 3

Summary of the main characteristics of the OFMSW effluents obtained at mesophilic conditions under acidic conditions in batch assays and semi-continuous reactors at 35 ºC.

Reference	Fernández-Domínguez et al., 2020	Cheah et al., 2019a		
Fermenter configuration	Batch assays	Semi-continuous (period 1)	Semi-continuous (period 2)	Semi-continuous (period 3)
HRT (days)	–	3.5	3.5	3.5
T (ºC)	35	35	35	35
TS (% w/w) of feed stream	5.58–7.02	6.60 ± 1.46	5.63 ± 0.76	6.41 ± 0.59
VS (% w/w) of feed stream	4.07–5.30	5.15 ± 1.25	4.18 ± 0.63	4.87 ± 0.53
Effluent pH	5.80–6.50	5.98 ± 0.26	6.34 ± 0.21	5.63 ± 0.05
Influent sCOD (g COD/L)	38.20–54.50	72.39 ± 11.50	72.75 ± 18.47	57.50 ± 12.51
Influent TAN (g NH$_4^+$-N/L)	2.20–3.10	–	2.84 ± 0.85	2.31 ± 0.54
Effluent TAN (g NH$_4^+$-N/L)	3.80–4.80	–	3.07 ± 0.10	3.21 ± 0.07
VFA yield (g COD$_{VFAs}$/gCOD)*	0.49–0.56	0.34 ± 0.02	0.36 ± 0.03	0.36 ± 0.02
COD$_{VFAs}$/sCOD (g COD$_{VFA}$/g COD)	0.44–0.50	0.230 ± 0.04	0.232 ± 0.036	–
Effluent VFAs (g COD/L)	22.40–29.10	17.52 ± 0.85	14.88 ± 1.38	17.40 ± 1.10
% Acetic acid (COD)	28–35	26.0 ± 0.80	28.50 ± 1.50	27.20 ± 2.50
% Propionic acid (COD)	22–24	19.70 ± 0.50	20.60 ± 1.30	17.80 ± 0.40
% Butyric acid (COD)	23–27	22.00 ± 1.00	19.80 ± 2.70	23.40 ± 4.20
% Valeric acid (COD)	9–14	14.20 ± 0.90	12.90 ± 1.10	15.20 ± 1.50
% Caproic acid (COD)	4–9	8.30 ± 0.90	8.30 ± 1.10	9.70 ± 2.00
% Heptanoic acid(COD)	1–3	9.90 ± 1.30	10.00 ± 1.60	6.90 ± 2.70

* In batch experiments the VFAs yield is the maximum obtained during the assay.

indicating that when the VFAs yield increased, the proportion of VFAs with more than 4 carbons also did.

To test the long-term VFAs production from this OFMSW real stream two semi-continuous jacketed lab-scale reactors (4.5 L working volume) were operated at mesophilic conditions under (i) acidic pH around 6 (no external chemicals needed) and (ii) alkaline pH near 10 (adding NaOH solution). In both fermenters an HRT of 3.5 d was applied, corresponding to an OLR in the range of 11.9–14.7 kg VS/(m³ d). An enhanced COD solubilization was obtained under alkaline conditions, but it did not lead to an increase of VFAs yield and consequently a lower COD$_{VFAs}$/sCOD ratio was recorded. Regarding the VFAs profile, the high initial VFAs content of the feeding substrate affected the individual VFAs distribution and lead to fermentation broths not highly differentiated under acidic and alkaline conditions. However, a higher acetic concentration and a lower butyric and valeric acids concentrations were detected under alkaline conditions.

Under acidic conditions, the VFAs distribution reported in Cheah et al. [22] (Table 3) was very similar to that obtained by Fernández-Domínguez et al. [20]. Interestingly, the VFAs yield remained nearly the same during the whole operation of the fermenter at acidic conditions (0.34–0.36 g$_{VFA-COD}$/g$_{COD}$) and the acetic and propionic acids were monitored in the range of 4.2–4.6 and 3.0–3.9 g COD/L, respectively. However, when a higher OLR was applied (due to higher VS concentration in the influent), the butyric and valeric acid concentration increased accordingly. In the fermentation liquor the COD$_{VFAs}$/sCOD

ratio was approximately 0.23, a value that was affected by the non-biodegradable or slowly biodegradable soluble COD present in the supernatant of AD recirculated to adjust the TS content of this stream. Other studies related to OFMSW fermentation have recorded higher COD$_{VFAs}$/sCOD ratios up to 0.90 ± 0.03 COD$_{VFAs}$/sCOD [23] when working with screw pressed OFMSW.

The VFA yields and distribution obtained (0.34–0.36 g$_{VFA-COD}$/g$_{COD}$) were in good agreement with other results reported in the literature. Lim et al. [24] recorded a VFAs yield of 0.26–0.32 g$_{VFA-COD}$/g$_{COD}$ when working with a semi-continuous fermenter treating food waste at an HRT of 4 days at 35ºC and acetic, propionic, butyric and valeric acids represented the 35.7–37.5 %, 30.0–31.5 %, 16.1–17.0 % and 15.1–17.1 % of the total VFAs, respectively. Micolucci et al. [25] operated a two-stage process (fermentative + methanogenic step with recirculation of part of the digestate) at 55 °C treating food waste of urban origin previously pretreated (199–216 g VS/kg; 211–230 g COD/kg) and recorded in the first fermentation stage a VFAs yield of 0.31–0.32 kg COD$_{VFAs}$/kg COD fed (acetic, propionic and butyric acids represented the 25 %, 19 % and 33 % on COD basis, respectively) when working at an HRT of 3.3 days, OLR of 19 kg VS/(m³.day) and pH around 5.5. These results were in line with those reported by Valentino et al. [26], who obtained a VFAs-rich fermentation effluent dominated by acetic (23.4 %), propionic (13.2 %) and butyric (37.2 %) acids when treating squeezed liquid fraction of OFMSW in a thermophilic (55ºC) fermenter working at an HRT of 3.3 days, OLR of 20.0 kg VS/(m³ day) and maintaining an acidic pH of 5.0–5.6 thanks to digestate recirculation. In another study, Valentino et al. [23] treated screw pressed OFMSW (120 g TS/kg; 107 g VS/kg) in a two stage AD process (mesophilic fermentation at 37 °C + AD at 55 °C) with digestate recirculation. When the fermentation unit was operated at an HRT of 5 days and an OLR of 14–15 kg VS/m³d, the fermented OFMSW presented a VFAs yield of 0.33 g$_{VFA-COD}$/g$_{COD}$. Under these working conditions, Valentino et al. [23] found that a 56 % (on COD basis) of the total VFAs was represented by propionic and valeric acids. These results suggest that the working pH (around 6.6) could have had a considerable impact, since recent literature studies have reported that neutral and/or alkaline environment could lead to higher fraction of VFAs with even carbons. In any case, the reported VFAs yields under semi-continuous operation were lower than those obtained by Fernández-Domínguez [20] in batch assays using the same substrate (0.49–0.59 g$_{VFA-COD}$/g$_{COD}$), which could be attributed to the longer retention times of batch assays.

4.4. Co-fermentation of OFMSW with sewage sludge

The co-fermentation of OFMSW with sewage sludge represents a common practice as sewage sludge, rich in N and P compounds, can supply fundamental macronutrients to OFMSW [27]. In particular, the role of different parameters such as pH, hydraulic retention time (HRT), organic loading rate (OLR), temperature in fermentation's process applied to urban organic waste, more specifically OFMSW and waste activated sludge (WAS) in a different mixture, to produce VFAs and to obtain reproducible VFAs' distribution. The WAS has been obtained from the static thickener of the Treviso WWTP sludge line and the OFMSW was originated from the source sorted collection in 50 districts of the Treviso province (Northeast Italy). After collection, the OFMSW was transferred into a dedicated plant where it was squeezed and homogenized; the recovered liquid fraction was transferred in Treviso's WWTP (Table 1).

In Valentino et al. [28], the fermentation process was carried out in a 230 L reactor with the OFMSW as the only substrate, under the following conditions: HRT 3.3 d, OLR 20.5 kgVS/m³d, 55 °C. In this case the pH was maintained to 5.0 by operating a pH control with digestate recirculation in a two-phases system. In Valentino et al. [26,29] both mesophilic (37–42 °C) and thermophilic (55 °C) conditions were investigated with WAS-OFMSW mixture (at different volumetric ratio), in a 380 L CSTR reactor, HRT 6 d, OLR 6.5–12.2 kg VS/m³d. The pH was

maintained at 5.0–5.5 without any control strategy since the mixture was rich in buffering capacity due to the high volumetric content of the sludge (60–70 % v/v). In Moretto et al. [30], the role of a thermal pretreatment (72 °C, 48 h) was investigated; the acidogenic fermentation process of a 70 % WAS and 30 % OFMSW (v/v) mixture was carried out in batch mode, using a 380 L reactor without pH control.

In Moretto et al. [31] the role of pH and temperature was investigated in different batch tests conducted at laboratory scale, with OFMSW-WAS (30 % and 70 % v/v, respectively). Initial pH was adjusted with NaOH addition in two tests (out of three) to achieve the following values: 5.0, 7.0 and 9.0. For each pH value, thermophilic (55 °C) and mesophilic (37 °C) conditions after thermal pretreatment (72 °C-48 h) were investigated. The best performing condition in terms of acidification performances was replicated in a lab scale CSTR reactor under different HRT (6.0, 5.0, 4.1) and OLR (7.7, 9.3, 11.3).

The performance of the acidogenic fermentation depended on several factors. The presence of the OFMSW affected the VFAs distribution compared to literature studies where only WAS has been utilized. Acetic acid was usually the most abundant in fermentation process performed with sludge only [32,33]. The predominance of butyric acid in fermentation test reported in Valentino et al. [29] was related to the presence of OFMSW in the feedstock, as reported elsewhere [34]. This was also evident in Valentino et al. [26], where different volume percentage of WAS-OFMSW mixture (Fermentation Liquid, FL) were investigated: in terms of VFAs composition, in the first fermentation run (FL-I) with a mixture of 40 % v/v of OFMSW and 60 % v/v of WAS at 55 °C, the butyric acid was the most abundant, with a content of 46 % (COD-basis) of the total VFAs. The butyric acid decreased to 28 % COD/COD_{VFAs} in the following FL-II run, where the OFMSW content decreased to 30 % v/v. In the following FL-III run, performed in mesophilic mode (42 °C) and using the same OFMSW-WAS mixture of FL-II, the VFAs composition was similar, and this suggested that temperature did not have relevant effect on the final VFAs distribution. Decreasing the OFMSW amount from FL-I to FL-II, caused a decrease of the applied OLR; on the contrary, the buffering capacity of the system increased, due to the higher amount of sewage sludge, and VFAs production was steadily maintained for the whole operation period in run FL-III. In the first FL-I run, the higher OFMSW volumetric percentage (40 %) led to frequent spot of high VFA concentration, not properly balanced by the buffering capacity of the mixture. This caused an unstable VFAs production for both concentration and composition, which made the process not attractive and suitable for application at industrial scale.

4.4.1. Role of temperature and thermal pretreatment

The two temperature regimes investigated were mesophilic (37–42 °C) and thermophilic (55 °C). The mesophilic fermentation appeared more technically attractive since the VFAs-rich stream features were more stable over time. In Valentino et al. [26,29], after the achievement of the steady state, the VFAs content in mesophilic fermentation liquid was constantly maintained close to 20 g COD_{VFAs}/L. In both cases, the pH values were not strongly affected by the VFAs increasing since the buffer capacity of the mixed liquor, which came from the sludge [35], was high enough to sustain the acidification process. In both studies, thermophilic fermentation produced a stream with higher VFAs concentration, fluctuating over time. Accordingly, the pH decrease was not properly balanced by the buffering capacity of the feedstock. Hence, OFMSW-WAS mixture fermentation at 55 °C appeared more difficult in terms of process control and stability. As expected, thermophilic temperature solubilized more solids and increased COD_{SOL} and nutrients in the mixed liquor compared to mesophilic one. In Valentino et al. [29] the solubilization in mesophilic and thermophilic fermentation was 0.06 gsCOD/gVS$_0$ and 0.34 gsCOD/gVS$_0$ respectively. However, a not negligible fraction of solubilized COD remained unconverted into VFAs: by comparing COD_{VFAs}/sCOD ratio in the two runs, the higher value was obtained under mesophilic temperature (0.72

gCOD$_{VFA}$/gsCOD), as well as the VFAs yield (0.28 g$_{VFA-COD}$/g$_{COD}$).

Also in a batch configuration, the tests in Moretto et al. [36] showed that the mesophilic condition was better performing in terms of VFAs production rates and yields. Also in that case, thermophilic temperature favored the organic matter solubilization without sustaining a consistent acidification process (the COD_{VFAs}/sCOD ratio was 0.22–0.36 g$_{VFA-COD}$/g$_{COD}$). In this study, thermophilic test, carried out with three different initial pH (5.0, 7.0 and 9.0), were characterized by lower final VFA content (independently from the initial pH). In these batch tests, the role of a thermal pretreatment of the substrates was also investigated. Thermal pretreatment increased the solubilization yield in the mesophilic fermentation process compared to tests performed without such pretreatment. Moreover, a pretreated hydrolyzed substrate was particularly suitable for a following acidification process, since the concentration of achieved VFA in mesophilic condition was in the range 22.5–41.0 gCOD/L (in all the pH investigated), higher than values obtained at the same temperature (37 °C) without pretreatment (19.2–30.0 gCOD/L). These results were also confirmed in Moretto et al. [30] where the presence of a thermal pretreatment was the only difference between the two mesophilic fermentation runs conducted at pilot scale in batch mode. The maximum VFA concentration and the COD_{VFA}/sCOD ratio obtained in the mesophilic run with no pretreated substrate were lower than the values obtained with pretreated substrate (19 gCOD/L and 0.73 gCOD/gsCOD vs 30 gCOD/L and 0.86 gCOD/gsCOD respectively). In addition, VFA yield was also higher in the fermentation run conducted with the pretreated feedstock (0.62 g$_{VFA-COD}$/g$_{COD}$) as further demonstration of the crucial role played by the thermal hydrolysis as pretreatment of the feedstock.

4.4.2. The role of the pH

The role of pH on fermentation's performances was investigated in batch tests performed by Moretto et al. [36]. In this study, each different thermal regime was applied in lab-scale experiments carried out at an initial pH of 5.0, 7.0 and 9.0. The pH strongly affected hydrolyzation and fermentation rate; in particular, when the pH value decreased below 5.0, the bacterial activity was negatively affected and totally inhibited when pH reached values close to 4.0. Alkaline conditions appeared the most suitable since sustained acidification process for longer time, achieving the highest VFAs concentration. The lowest concentration obtained in acidified environment (initial pH of 5.0) was due to a sudden decrease of pH to 4.2 which caused a total inhibition of fermentative bacteria. In addition, comparing with the other pH, the initial alkaline condition favored the substrate solubilization. Higher sCOD was achieved in the alkaline fermentation tests (37–46 gsCOD/L); such values were associated with higher VFAs production (27–41 gCOD/L). The highest COD/sCOD of 0.91 was achieved with combined alkaline pH and thermal pretreatment of the substrate. Both alkaline fermentation condition and thermal pretreatment raised the substrate solubilization with the benefit of mesophilic temperature in the fermentation process, in terms of robustness and stability. Good results were also observed with neutral pH, even though not comparable with the alkaline conditions.

VFAs distribution was affected by initial pH more than temperature. At acidic condition, a net dominance of acetic acid (72 %) was obtained as well as for neutral condition. Alkaline condition raised the propionic acid production (25 %), as well as butyric (25 %) and valeric (15 %) acid; acetic acid remain the most abundant (26 %) but the molar ratio between the VFAs with odd number of carbon's atoms and the total VFAs was more than doubled (0.36 mol/mol) if compared to the molar ratio quantified at acidic (0.17 mol/mol) and neutral (0.16 mol/mol) condition. These results were related to the progressive increased of propionic and valeric acid. To better control the VFAs production in acidic fermentation (and so obtained a high COD_{VFA}/COD ratio and stable VFA distribution), a pH controlled-fermentation strategy was conducted in Valentino et al. [28], where the co-fermentation was not investigated and the OFMSW was utilized as the only carbon source. To maintain pH level between 5.2 and 5.6, a recirculation rate (RR) of

digestate was applied in a two-phases fermentation and AD process. The pH-controlled fermentation of the OFMSW gave high value of $COD_{V\text{-}FAs}/sCOD$, over the long stability period, which was equal to 0.91, with a VFAs yield of 0.31 $g_{VFA\text{-}COD}/g_{COD}$ and VFAs concentration of 16.0 $gCOD/L$. In terms of VFAs distribution, butyric acid was predominant (38 %), followed by acetic (21.5 %), propionic (12.7 %), valeric (11.6 %) and caproic (10 %) acids, on a COD basis.

4.5. VFAs production from real FW from a canteen

A specific typology of OFMSW, composed by food residues from a university canteen, was tested two semi-continuous mesophilic lab-scale acidogenic fermenters under an HRT of 3.5 days [22] at acidic and alkaline pH (near 6 and 10, respectively). The applied OLR varied between 11.3 and 18.3 kg VS/m^3d depending on the VS concentration of the feeding stream (in the range of 4–6 % VS) and the VFAs yields varied within the range of 0.11–0.25 $g_{VFA\text{-}COD}/g_{COD}$, depending on the FW collection period and the applied OLR, as summarized in Table 4. Operation at alkaline conditions (pH ~10) enhanced VS solubilization and the production of acetic acid, which was the predominant product (up to 84.8 % on COD basis of the total VFAs produced).

Moreover, a higher VFAs production at neutral pH values was recorded at long term conditions in the study of Cheah et al. [37], where mesophilic lab-scale fermenters were operated treating FW (3.8–6.4 % VS) at an HRT of 3.5–5.0 d under several controlled pH (6−7) conditions. In this study, a VFAs yield enhancement was observed at pH 7.0 when compared to that obtained at pH 6.0, as well as a higher presence of propionic and valeric acids in the fermentation broth (see Table 4). In

fact, an enhanced VFAs yield at pH near neutrality have been also highlighted by other studies [10], as well as higher propionic and valeric acids production [23,36] when compared to results at slightly acidic conditions around 5.0–6.0 under mesophilic conditions.

Considering that the use of mature compost produced in MBT plants could improve the solubilization of organic matter [38] and, hence, VFAs production in the fermentation unit evaluated the effect of dosing mature compost in the range of 1.5–3.5 % w/w on VFAs production in semi-continuous fermenters treating FW [37]. When working at an HRT of 3.5 d, the addition of an optimum compost dosage of 2.5 % w/w improved the VFAs yield at pH 6.0, especially for the periods of lower applied OLR due to a lower VS content of FW. This higher VFAs yield led to an increase of butyric acid concentration (see Table 4). Under pH near neutrality, mature compost addition also led to a higher VFAs production, although its impact was not as high as when working at slightly acidic conditions.

4.6. Acidogenic fermentation of fruit pulp

Another specific typology of FW was represented by fruits wastes. They were fed in an upflow anaerobic sludge blank (UASB) reactor, inoculated with granular sludge from a Portuguese brewery wastewater treatment plant (Leça do Balio) and operated for 166 days. The reactor was fed continuously with fruit waste, starting with an OLR of 7.5 gCOD/Ld at start up, in order to acclimatize the biomass to the feedstock and slowly increased as methanogenic archaea became inactive and methane production was neglegible. The HRT was set to 1 day. Nitrogen and phosphorus were supplemented to the reactor in the form of NH_4Cl

Table 4
Summary of the main characteristics of the FW effluents obtained at mesophilic conditions under several pH conditions in semi-continuous reactors at 35ºC.

Reference	Cheah et al., 2019a (Operation period B4)		Cheah et al., 2019b (Collection period FW3)		Cheah et al., 2019b (Collection period FW8)			Cheah et al., 2019b (Collection period FW11)		
Fermenter configuration	Semi-continuous	Semi-continuous	Semi-continuous	Semi-continuous	Semi-continuous	Semi-continuous	Semi-continuous	Semi-continuous	Semi-continuous	Semi-continuous
HRT (days)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	5.0	5.0
T (ºC)	35	35	35	35	35	35	35	35	35	35
Effluent pH (controlled)	5.9 ± 0.6	9.2 ± 0.3	5.9 ± 0.2	6.1 ± 0.2	6.0 ± 0.3	6.1 ± 0.1	7.1 ± 0.1	6.1 ± 0.2	7.0 ± 0.2	7.0 ± 0.2
TS (% w/w) of feed stream	5.0	5.0	7.27 ± 0.35	7.27 ± 0.35	7.03 ± 0.44	7.03 ± 0.44	7.03 ± 0.44	6.10 ± 1.23	6.10 ± 1.23	6.10 ± 1.23
VS (% w/w) of feed stream	4.1	4.1	5.71 ± 0.24	5.71 ± 0.24	6.40 ± 0.84	6.40 ± 0.84	6.40 ± 0.84	5.64 ± 1.18	5.64 ± 1.18	5.64 ± 1.18
% mature compost (% w/w to feed)	0	0	0	2.5	0	2.5	2.5	0	0	2.5
Influent sCOD (g COD/L)	23.6 ± 6.7	23.6 ± 6.7	38.7 ± 4.3	38.7 ± 4.3	51.8 ± 4.7	51.8 ± 4.7	51.8 ± 4.7	31.9 ± 5.4	31.9 ± 5.4	31.9 ± 5.4
Influent TAN (g NH_4^+-N/L)	0.05	0.05	0.05 ± 0.00	0.05 ± 0.00	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	0.11 ± 0.01	0.11 ± 0.01	0.11 ± 0.01
Effluent TAN (g NH_4^+-N/L)	0.44	0.39	0.67 ± 0.04	0.83 ± 0.18	0.46 ± 0.07	0.56 ± 0.22	0.74 ± 0.29	0.95 ± 0.15	1.31 ± 0.01	1.56 ± 0.09
VFAs yield (g COD_{VFAs}/g VS)	0.17 ± 0.04	0.18 ± 0.04	0.25 ± 0.01	0.29 ± 0.02	0.12 ± 0.03	0.15 ± 0.03	0.25 ± 0.02	0.11 ± 0.02	0.26 ± 0.03	0.29 ± 0.04
COD_{VFAs}/sCOD (g COD_{VFAs}/g COD)	14.6 ± 1.9	19.3 ± 2.0	26.8 ± 2.4	34.6 ± 6.2	16.1 ± 3.7	21.5 ± 32.6	19.2 ± 2.1	19.6 ± 2.0	34.4 ± 1.1	23.1 ± 2.2
Effluent VFAs (g COD/L)	6.8 ± 1.8	7.2 ± 1.7	14.1 ± 0.8	16.7 ± 1.1	7.8 ± 1.6	9.4 ± 1.6	16.1 ± 1.4	6.0 ± 1.1	11.3 ± 6.4	12.9 ± 7.3
% Acetic acid (COD basis)	42.2 ± 4.9	84.8 ± 1.5	44.3 ± 2.6	30.7 ± 2.7	40.8 ± 5.5	24.3 ± 10.6	38.3 ± 1.5	34.1 ± 2.7	27.4 ± 2.9	34.6 ± 1.1
% Propionic acid (COD basis)	1.2 ± 1.2	2.6 ± 0.4	1.3 ± 0.1	1.9 ± 0.5	0.8 ± 0.3	0.7 ± 0.2	7.7 ± 1.7	0.9 ± 0.2	4.7 ± 2.0	4.8 ± 0.8
% Butyric acid (COD basis)	13.4 ± 2.6	6.1 ± 0.7	16.5 ± 2.0	15.9 ± 2.4	14.5 ± 2.1	24.0 ± 4.9	23.1 ± 1.5	22.0 ± 1.9	22.7 ± 3.3	23.6 ± 3.2
% Valeric acid (COD basis)	3.7 ± 1.0	4.8 ± 0.8	3.5 ± 0.4	4.6 ± 1.0	3.6 ± 1.3	3.9 ± 1.0	8.1 ± 3.3	8.1 ± 1.5	10.0 ± 1.9	11.1 ± 1.1
% Caproic acid (COD basis)	37.5 ± 3.6	0.9 ± 0.3	33.2 ± 2.8	35.5 ± 2.6	38.9 ± 3.3	46.2 ± 6.0	20.5 ± 3.2	33.8 ± 2.0	31.9 ± 4.1	21.9 ± 4.2
% Heptanoic acid (COD basis)	2.1 ± 0.3	0.8 ± 0.0	1.3 ± 0.1	1.4 ± 0.2	1.4 ± 0.6	0.9 ± 0.1	2.3 ± 0.9	1.0 ± 0.5	3.3 ± 1.7	4.0 ± 0.6

and KH$_2$PO$_4$, respectively, at a COD/N/P ratio of 100:0.5:0.1 (% wt.). Other minerals were supplemented as follows: MgSO$_4$.7 H$_2$O: 120 mg/L, CaCl$_2$: 480 mg/L, FeCl$_3$.6 H$_2$O: 0.8 mg/d. The effluent was recirculated at 2.88 m/h with internal recirculation and temperature of the reactor set to 30.0 $\pm$ 0.5 °C. The pH of the reactor was set to 4.7 $\pm$ 0.2, adjusted with NaHCO$_3$ [39].

A summary of VFAs produced during operation of the reactor is shown in Fig. 2. For the pseudo-steady period where the highest OLR was imposed (30 $\pm$ 2 gCOD/Ld, from day 59 onwards) a degree of acidification of 0.72 $\pm$ 0.07 gCOD/gCOD was obtained. This resulted in a VFAs productivity of 0.88 gCOD/Lh and VFAs concentration of 21 $\pm$ 2 gCOD/L, consisting mainly of butyrate (41 %), acetate (13 %) and valerate (5 %). This VFAs concentration was higher than in other reported acidogenic reactors using a complex feedstock, where a VFAs concentration of 10.6 gCOD/L was reported by Duque et al. [40] using cheese whey and 18.1 gCOD/L was reported by Mateus et al. [41] using fruit pulp waste. It worth of noting that the concentration of VFAs as well as their composition kept very stable (fluctuations following the feed changes) during the operation time (from day 60 onwards). These results showed that fruit waste was successfully fermented into VFAs and the reactor reached stable conditions during long time operation.

4.7. Producing volatile fatty acids from sewage biosolids and OFMSW: the effect of ammonia stripping

As discussed, OFMSW co-fermentation with N rich effluents is a common practice to provide macronutrients but not only. This practice is possible if ammonia content is not high enough to inhibit the acidogenic microorganisms, with a consequent lowering of the VFAs amount in the reaction medium. Ammonia stripping was investigated to prevent an eventual inhibition.

Ye et al. [42] found ammonia stripping with pH correction enhanced propionic, n-butyric, i-butyric, and i-valeric acid production over acetic acid. During control, waste activated sludge (WAS) was screened and gravity settled, then fermented in 600 mL bioreactors at pH 10 with nitrogen sparging for 108 h. The resultant fermentation broth had total VFAs concentrations of 390 mg/L, consisting of 248, 37, 11, 6, 0, and 88 mg L^{-1} of acetic, propionic, n-butyric, i-butyric, n-valeric, and i-valeric acids, respectively. During ammonia stripping, total VFAs concentrations increased to 436 mg L^{-1}, while acetic acid concentration decreased from 248 to 183 mg/L, propionic, n-butyric, i-butyric, n-valeric, and i-valeric acid concentrations all increased to 70, 17, 22, 6, and 140 mg/L, respectively.

The effect of OLRs on VFAs production from food-waste and sewage sludge fermentations has been studied [43]. In mesophilic 3 L leach-bed fermenters OLRs of 50, 100, 150 and 200 g/d food-waste were studied. At 50 g/d, the dominant VFAs was acetic acid, peaking at 2395 mg/L. Propionic and butyric acid concentrations were 825 and 1564 mg/L, respectively. At OLRs of 100 and 150 mg/L, butyric acid was dominant, peaking at 4819 and 6431 mg/L respectively. Total VFAs concentrations

peaked at 150 g/d at 11,723 mg/L. At 200 mg/d, lactic acid production began, and the total VFAs concentration was just 4650 mg/L. This is consistent with Iglesias-Iglesias et al. and Khan et al. [44,45] who found increased OLRs in sewage sludge fermentations increased VFAs concentrations. The effect of OLR on acidogenic fermentations co-digestion of sewage sludge and WAS were investigated [46]. Mesophilic, 4.5 L continuously stirred tank reactors (CSTRs) at pH 5.2 had OLRs of 1.65, 2.74, 4.12, 8.23, and 32.9 g$_{vs}$/Ld. Peak VFAs concentrations occurred at 2.74 gCOD/Ld with a total VFAs concentration of 12.21 g/L, and suppressed acetic acid production, which accounted for 2 % of total VFAs. This is consistent with Gu et al. [43] who noted acetic acid suppression at higher OLRs. These studies illustrated how OLRs influence acidogenic metabolic pathways, however it's unclear that increased OLRs are industrially applicable.

The effect of pH on VFAs production has been studied. Cabrera et al. [47] undertook mesophilic batch fermentations of olive-mill waste in 1.7 L bioreactors for 42 days at pH 5 and 9. At pH 5, VFAs concentrations were 2.34 g/L, consisting of acetic (1081 mg/L), propionic (604 mg/L), butyric (455 mg/L), and valeric (204 mg/L) acids. At pH 9, this increased to 4.25 g/L, largely owing to increased acetic acid production from 1.08 g/L at pH 5–3.13 g/L at pH 9, probably by alkaline suppression of methanogenesis. Esteban-Gutiérrez et al. [48] investigated the effect of temperature and pH on acidogenesis in 10–day sewage sludge fermentations at pH 5.5/35 °C, pH 5.5/55 °C, pH 10/35 °C, and pH 10/55 °C. Optimum VFAs-producing conditions were pH 10/55 °C, with concentrations of 5.55 g/L. Moretto et al. [31] studied VFA production from mixed urban biowastes, in 0.75 L bioreactors for ten days under the following conditions: 37 °C/pH 5, 7 and 9; 55 °C/pH 5, 7 and 9; and with thermal feedstock pretreatment at 72 °C, before fermentations at 37 °C/pH 5, 7 and 9. Optimal acidogenic conditions were alkaline and mesophilic with thermal pretreatment. These conditions were then applied to a 6 L CSTR at OLRs of 7.7, 9.3 and 11.3 kg$_{vs}$/m^{3}d. In all repeats, acetic and propionic acid were the dominant VFAs, accounting for 22–25 % and 22–28 % of total VFAs, respectively. Butyric and valeric acids accounted for 20–22 % and 10–13 %. Peak VFAs concentrations occurred at lower OLRs, with 39 $\pm$ 3 g COD/L at an OLR of 7.7 kg$_{vs}$/ m^{3}d.

5. Electro-driven approaches to control VFA production and separation during fermentation processes

Electro-driven approaches employing polarized electrodes have been investigated to favor the production of desired VFAs or to enhance acids separation from the fermentation broth. These approaches are referred to as electro-fermentation or electrodialysis, respectively.

5.1. Electro-fermentation

Electro-fermentation (EF) is a novel and emerging strategy to control the metabolic pattern of either pure or mixed microbial cultures (MMC)
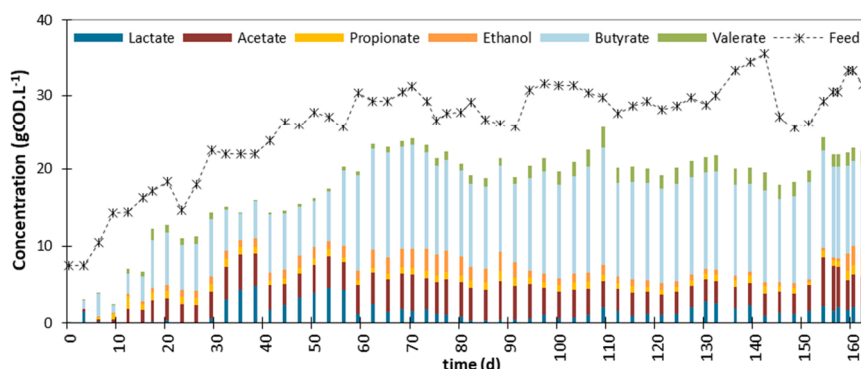

Fig. 2. Trends of COD concentration in the feed and VFAs concentration in the effluent obtained from the acidogenic reactor.

with the aim to enhance the production of specific compounds during the fermentation process. In particular, EF relies on the use of polarized electrodes to exchange electrons with the microbial culture or to simply modify the oxidation-reduction potential of the reaction medium, in order to affect the intracellular reduced/oxidized NAD balance [49,50].

Here, EF tests were carried out in lab scale, batch bio-electrochemical reactors (BES) made of either one or two chambers. The latter consisted of two gastight borosilicate bottles (each one having a total volume of 270 mL) which were separated by a proton exchange membrane (Nafion 117®). A graphite rod was placed in each chamber functioning as the working (cathode) or the counter (anode) electrode, respectively. Both the anodic and cathodic chambers contained mineral medium whereas organic substrates and MMC (as inoculum) were only added in the cathode chamber. Two inocula were used, both consisting of anaerobic sludge collected from the mesophilic pilot-scale anaerobic digester located in Treviso (Italy) operated to treat food wastes (as previously described), whereas the organic substrate consisted of a synthetic solution of glucose (chosen as a key component of carbohydrates contained in the OFMSW).

The effect of the presence of a polarized electrode on the distribution of products deriving from the acidogenic fermentation of glucose has been tested either in the absence (unmediated tests) or in the presence (mediated-tests) of exogenous redox mediators (RM), which sustain both the extracellular electron transfer with electrodes and the interspecies electron transfer in the microbial culture. RM used in the study were anthraquinone-2,6-disulfonate (AQDS) and 3-amino-7- dimethylamino-2- methylphenazine hydrochloride (Neutral Red, NR). Each operating condition was tested both in absence (OC test) and in presence (EF test) of electrode polarization. In unmediated EF tests, the cathode electrode was set at -700 mV (vs. the Standard Hydrogen Electrode, SHE), whereas in mediated-tests the electrode potential was controlled at a value of -300 mV (vs. SHE) or -700 mV (vs. SHE) when AQDS or NR were used, respectively. A detailed description of the experimental setup as well as of the analytical methods adopted to analyse the liquid phase (in terms of glucose and all fermentation products) and the headspace of each BES is reported elsewhere [51]. Interestingly, irrespective of the used inocula, unmediated EF experiments resulted in a higher yield of butyrate (as the sum of i-butyric and n-butyric acid*)* production (up to 0.60 mol/mol, corresponding to ca. 0.50 $g_{COD-Butyrate}/g_{COD-Glucose}$) compared to OC tests, when glucose was supplied in presence of its fermentation products (i.e., acetate and ethanol). No difference in the yield of acids production was initially detected between EF and OC tests, when glucose represented the only carbon source in the reaction medium, and this is fully in agreement with what observed in previous experiments [52]. However, in mediated experiments, an evident enhancement in the production of C4 compounds in the EF tests appeared also when glucose was fed as single substrate. With both tested RM, only the n-butyrate isomer was produced indicating a high selectivity of the used mediators towards this specific compound. Indeed, even though the use of mediators is practically feasible only if they are immobilized on the electrode surface, the possibility to combine the simultaneous effect of these compounds and electrode polarization to enhance the production of a specific acid during fermentation, for an ad hoc application, is particularly appealing.

As for EF experiments in single chamber BES, these have been performed in reactors consisting of membrane-less glass bottles (total volume of 100 mL) sealed with a rubber stopper equipped with two graphite rods and a tygon (non-permeable to oxygen) sampling tube closed by plastic clamp. The two rods (i.e., the anode and the cathode electrode) were externally connected by means of a stainless-steel wire. Two MMCs, collected from two anaerobic digesters located in Cardiff (South Wales, United Kingdom), were used as inocula. The membrane-less configuration allows, in principle, to reduce potential losses and capital costs as well as to simplify the reactor design with respect to the two chambers reactors whose utilization, however, reduces the crossover of bacteria and compounds between the compartments holding the

working and counter electrode (where oxygen or other products inhibiting the microbial activity could be developed). With this simplified reactor design, experiments were carried out by using, as organic substrate, glucose supplied individually or mixed with ethanol and acetic acid. A fixed voltage difference was applied between the anode and the cathode electrode, with ten values ranging from -0.6 V to -1.5 V, as detailed elsewhere [53]. The simultaneous presence of an applied voltage and the ternary mixture of substrates as feedstock, boosted butyrate production with a fold of increase from 1.3 to 2.7 with respect to open circuit potential experiments.

Importantly, in all the investigated operating conditions, the pH of the medium was buffered at 5.5 and no methane was detected throughout the experiments.

Taken as a whole, the results obtained with both single- and two-chamber BES clearly indicates the possibility to use polarized electrodes to control the distribution of products deriving from MMC fermentation of glucose, independently from the origin and composition of the microbial culture and of the reactor configuration and operating conditions (e.g., applied electrode potential or voltage difference). Also, in all cases a low value of current flowing in the system was detected (in the order from few to hundred µA). This aspect reflects into a low energy consumption associated to the enhanced generation of a specific compound and it is thus of particular interest in the perspective of upscaling of the technology, that is still admittedly in its infancy. However, further investigations are required to test the effectiveness of the EF process in particular when dealing with real feedstocks, as urban wastes previously described in conventional fermentation studies.

5.2. Electrodialysis

Electrodialysis has been used to encourage acidogenesis by alleviating end-product inhibition and arresting VFAs consumption during methanogenesis. Hassan et al. [54] recovered acetic and butyric acid from a 3 L continually-fed food-waste fermentation using electrodialysis coupled with microfiltration to protect electrodialysis membranes. After 100 h, a VFAs solution of 2.94 g/L was recovered externally into solution. On larger scales, filtration-electrodialysis systems have recovered VFAs from a 100 L, 1 % Total Suspended Solids (TSS) food-waste fermentation, operated at a 10–day HRTs [19]. VFAs were recovered in a solution approaching 4.00 g/L, arresting methanogenesis and increasing VFA production rates from 4 to 35 mg_{VFAs}/gVS d. Applying the same methodology to a 5 % TSS grass fermentation, methanogenesis was suppressed, VFAs yields increased from 0.29 to 0.40 $g_{VFA-COD}/g_{COD}$, and a concentrated VFAs solution of 4.80 g/L was produced [55].

Electrodialysis however targets recovery of all ionic molecules from solution, including important nutrients for fermentation such as phosphates, nitrates and ammonium, which would also be considered impurities in VFA solutions. Including pervaporation upstream of electrodialysis has excluded nutrients from electrodialysis [56], and increased VFA yields from 0.71 to 0.88 $g_{VFA-COD}/g_{COD}$ in another 5 % TSS grass fermentation in an 83 L bioreactor over three, seven-day, HRTs. This yielded a solution of 4.5 g/L VFAs, free from nutrient impurities. In all VFA recovery studies, substrate utilization rates were enhanced, an important consideration for wastewater remediation. Significant VFA concentrations were unrecovered however, providing headroom for intensified VFA recovery, and increased yields and substrate utilization rates.

As the focus of fermentation shifts from biogas to VFA production, a consensus for optimum VFA production conditions is becoming established. These include thermal pretreatment, mesophilic temperatures, and alkaline pH levels. Further work is required in which selective VFA recovery combined with optimal VFA production conditions. Such combinations could maximize VFA yields and substrate utilization rates with industrial scale volumes of recalcitrant substrates as feedstocks.

6. Comparisons of the VFAs yields and profile from urban wastes

The most abundant urban wastes: TPS, sewage sludge and OFMSW were fermented under different pretreatments and operational conditions to maximize the VFAs production. The VFAs yields from the urban wastes adopted along Res Urbis project are summarized in Fig. 3.

Even if TPS emerged as one of the most recalcitrant substrates, it demonstrated good VFAs production potential when previously hydrolyzed at 60 °C, pH 10 for 6–10 h. Under these conditions, the degree of solubilization increased from around 5–35 %, allowing a higher organic matter conversion into VFAs. The final VFAs yield was about 0.50 $g_{VFA-COD}/g_{COD}$.

OFMSW is the other abundant substrate produced in the urban context. Unlike TPS, sewage sludge, and sewage biosolids, OFMSW has a higher content of different carbon compounds, which can be potentially converted in VFAs. It is important to note that OFMSW is often poor in nitrogen and phosphorus compounds, which play a double role in acidogenic fermentation for VFAs production: providing essential macronutrients to the microorganisms and buffering the system. This latter role is fundamental as it avoids the decreasing of the pH under the inhibiting level of 4.5. It is not surprising that OFMSW having a higher protein fraction showed better VFAs yields than OFMSW with higher starch, lipids and carbohydrates' fractions. The batch tests treating synthetic OFMSW with higher concentrations of proteins had a VFAs yield of 0.80 $g_{VFA-COD}/g_{COD}$. The same synthetic OFMSW in continuous mode (T = 55 °C, HRT=6; OLR=11 g_{VS}/Ld) achieved a good VFAs yield of 0.38 $g_{VFA-COD}/g_{COD}$, with a high concentration of butyric acid (60 % w/w) followed by valeric and acetic acids accounting for the 14 % and 7 % w/w, respectively. Tests on an actual OFMSW stream, having lower protein fraction than synthetic OFMSW, showed lower VFAs yields. Batch tests had a performance of 0.25–0.30 $g_{VFAs-COD}/g_{COD}$, showing a different VFAs composition with lower valeric acid concentration and higher acetic acid one. Continuous tests on OFMSW were favored by the adoption of a two stage AD process with the recirculation of a digestate fraction from the second methanogenic reactor, rich in ammonia from the proteins' degradation, which prevents the system's acidification. The VFAs yield under continuous condition was of 0.35 $g_{VFAs-COD}/g_{COD}$, lower than the obtained in batch experiments (0.55 $g_{VFAs-COD}/g_{COD}$) This value was almost the same of the VFAs yield from synthetic OFMSW, operated in continuous mode and demonstrated that a minimal protein and ammonia amount assured good performances of conversion into VFAs. The resulting VFAs profile was represented by acetic, propionic and butyric acids in concentration of 25 %, 19 % and 33 % w/w, respectively. Another strategy to guarantee a successful acidogenic fermentation was the ammonia stripping, which allowed the increment of the 13 % of the VFAs yield and the adoption of sewage sludge in co-fermentation.

The utilization of sewage sludge with the OFMSW in fermentation process allows to obtain a better stability, which is extremely important for the quality of the final fermentation liquids. Sewage sludge increases the mixture alkalinity (which is very low in the OFMSW); this parameter needs to be high enough to balance the acidification, especially when a highly biodegradable substrate is present, such as OFMSW. This benefit is also better exploited under mesophilic condition (37 °C), when the acidification mechanisms are characterized by lower specific rates, compared to thermophilic environment (55 °C). Hence, a controlled fermentation process without any chemicals' addition is the preferable way to sustain a stable and prolonged VFAs production; this is easily accomplished with the mixing of sewage sludge (source of nutrients and alkalinity) with the OFMSW. In addition, as demonstrated in the last works depicted in this review, thermal pretreatment can facilitate the acidification process, leading to a substantial increase of the fermentation yield (higher than 0.60 $g_{VFA-COD}/g_{COD}$) and the $COD_{VFAs}/sCOD$ ratio (between 0.80 and 0.90, COD basis).

Finally, another specific FW typology was considered, the fruit residues. Acidogenic fermentation of fruit waste was also very effective: the conversion of this food industry residue into VFAs reached the very high yield of 0.72 $g_{VFA-COD}/g_{COD}$, essentially composed by butyrate (41 %, gCOD-basis), acetate (13 %, gCOD-basis) and valerate (5 %, gCOD-basis).

This review remarked the high potential of the main wastes derived from urban context, which can be exploited for VFAs production making them interesting secondary raw materials for biorefinery applications. A first consideration is that the mono-fermentation of no pretreated substrates led to lower VFAs yields: OFMSW and TPS achieved a VFAs yields of 0.25–0.30 and 0.50 $g_{VFAs-COD}/g_{COD}$, respectively (Fig. 3). The introduction of ammonia rich substrates or the adoption of a thermal pretreatment, such as SS, led OFMSW to higher VFAs yields as effect of the buffering action and the better solubilization. The combination of thermal pretreatment with co-fermentation of SS and OFMSW allowing the increasing of the VFAs production yield to 0.85 $g_{VFAs-COD}/g_{COD}$.

With reference to the VFAs profile, it was observed that substrates with lower VFAs yield presented a higher concentration of acetic acid, while the improvement of the acidogenic fermentation and, consequently of the VFAs yield, allowed the increasing of propionic and butyric acids (Table 5).
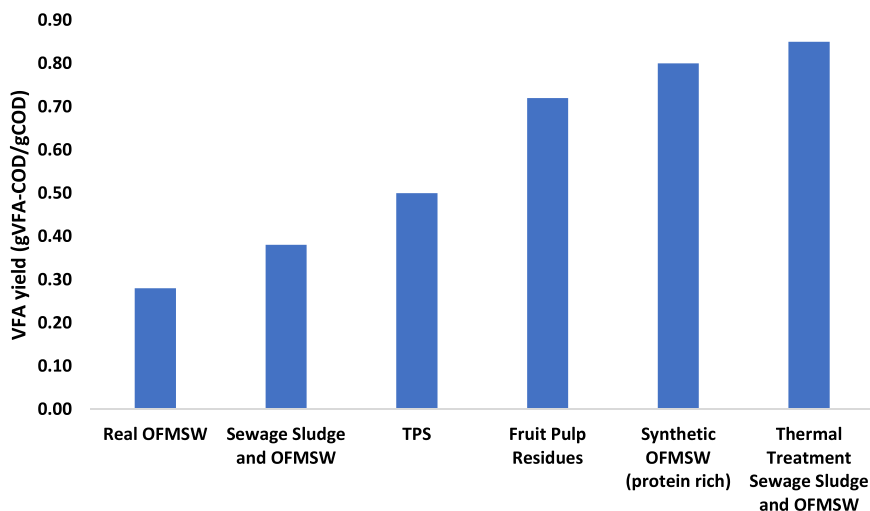

Fig. 3. VFAs yields of the main urban wastes considered by Res Urbis Horizon project.

Table 5

VFAs profile of the urban wastes adopted by Res Urbis project. The operational conditions which led to these profiles were detailed in the review.

% (gCOD basis)	Real OFMSW	Sewage Sludge and OFMSW	TPS	Fruit wastes	Thermal pretreatment Sewage Sludge and OFMSW
Acetic Acid	26–35		35	13	
Propionic Acid	18–28		16	3	
Butyric acid	20–27	28–45	15	41	
Valeric acid	9–15	–	9	5	

7. The current status of the European municipal waste management

The definition of "Municipal Waste" (MW) reflects the different waste management practices adopted by the European countries. Eurostat defined MW as waste mainly produced by households collected and disposed by municipal authorities; the definition also includes waste from the same sources and other waste similar in nature and composition, which is collected directly by the private sector (business or private non-profit institutions). Based on such definition, MW generation in EU28, expressed in kilograms per capita, unchanged from 2005 (506 kg per capita) to 2020 (505 kg per capita), while increased (+8.2 %) from 1995 to 2020. Denmark and Luxembourg were the biggest generators of municipal waste in 2020, with 845 kg per capita and 790 kg per capita, respectively. Malta and Germany also showed values above the average EU28: 643 and 632 kg per capita respectively. The lowest volumes came from Romania (287 kg per capita), followed by Poland and Hungary (346 and 364 kg per capita respectively). The variations reflect differences in consumption patterns and economic wealth, but also depend on how municipal waste is collected and managed [57].

Only seven EU member states created less municipal waste per person in 2020 than in 1995: Bulgaria, Hungary, Slovenia, Romania, Spain, Belgium, and the Netherlands. At the other end of the scale, Croatia generated 90 % more, Latvia and Czech Republic 70 % and 80 % respectively.

The total amount of MW landfilled from 1995 to 2020 has diminished, from 121 to 52 million tons; this corresponds to an average annual decline of 4.0 %. This reduction can partly be attributed to the implementation of European legislation. For instance, the Directive 31/1999 stipulated that Member States were obliged to progressively reduce the amount of biodegradable municipal waste going to landfills, up to 10 % until 2035, encouraging the adoption of biological and incineration process. Within this context, there is no mention about differences between the OFMSW and the green waste (grass or green maintenance area), which should be considered as MW in general. This scenario goes in favor of new technology development for the requalification of MW in a new industrial development based on biological processes.

Sewage sludge is the by-product of wastewater treatment processes, and it can be a mixture of primary sludge (generated from primary settling), and secondary sludge (or WAS), which is the activated waste biomass produced from biological treatments. The annual sludge production into the EU-28 is in the order of 9.0 million tons of dry solids [58] and it has four main destinations: agriculture 49.2 %; incineration 24.9 %; recultivation and land reclamation 12.4 %; landfill 8.7 %; and other destinations for the remaining amount (4.9 %). The use of sewage sludge as a fertilizer in agriculture is the preferred option due to its content of organic substances and nutrients; dewatered sewage sludge contains 50–70 % organic matter and 30–50 % mineral components (including 1–4 % of inorganic carbon), 3.4–4.0 % nitrogen (N), 0.5–2.5 % phosphorus (P), and significant amounts of other nutrients, including micronutrients [59]. However, before use as fertilizer, the sewage sludge should undergo stabilization treatment with the aim of reducing pathogens, eliminating offensive odors, and inhibiting putrefaction potential. The AD of the sludge originated in the WWTPs is the preferred stabilization step for medium and large plants since the produced biogas is a valuable renewable energy source. The technology is mature and widely used, especially in relation to land application. In Europe many WWTPs bigger than 50,000 Personnel Equivalent (PE) are already equipped. Despite of the high biogas production potential from sewage sludge treatment (the EU28 countries produced biogas up to 1.4 Mtoe - million tones oil equivalent [60], the specific gas production (SGP) is relatively low, limiting the possibilities to produce electricity (in the combined heat and power units - CHP) for a less attractive heat sufficiency.

Hence, also for sewage sludge, the current disposal and/or valorization technologies still appear limited to exploit this precious and abundant source for new bio-products. Its co-treatment with MW appears a profitable route to follow and to scaled-up within a new-generation biorefinery industry.

8. Conclusions

World human population will reach 10 billion people in 2050. Recent estimations predict that people will be concentrated along the coasts and in big urban contexts. Urban contexts produce annually large amounts of wastes, residues and by-products (sewage sludge, sewage biosolids, OFMSW, park and grass residues) deriving from the most varied anthropogenic activities. The present review gave an overview on the conversion of urban wastes into VFAs, finding encouraging yields both in mono-fermentation and, especially, in co-fermentation conditions.

Being biological precursors of different biofuels and bioproducts, the obtained VFAs can enter and be further transformed into a biorefinery loop. Among the most valuable bio-based products derived from VFAs, there are the PolyhHydroxyalcanoates (PHAs), biobased-plastics, which can contribute to reduce the amount of another waste largely produced and consumed in cities, the fossil-based plastics.

Very recently the scientists are studying the VFAs exploitation for Single Cell Proteins (SCPs) production. SCPs are microbial cells which are grown and harvested to accomplish the food requirement of animals or human due to its high protein content. Moreover, VFAs can be also exploited in chain elongation process to synthesize caproic acid and other medium fatty chain for the production of lubricants, fragrances, paint additives and pharmaceuticals. Finally, the most conventional application of VFAs is represented by biogas production by AD, which can be upgrade into methane and exploited in a cogeneration system for heat and electricity productions.

All these examples demonstrate that a large spectrum of valuable applications for VFAs derived from the urban wastes' conversion. Consequently, cities can become the fundamental actor for the creation of a circular economy model, with the adoption of their main waste streams as secondary raw materials which multiple environmental and economic advantages.

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

No data was used for the research described in the article.

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References

[1] European Commission, 2019. ⟨https://eur-lex.europa.eu/resource.html?uri=cellar:b828d165-1c22-11ea-8c1f-01aa75ed71a1.0002.02/DOC_1&format=PDF⟩. (Accessed 7 February 2022).

[2] EEA, The European environment-state and outlook 2020., 2019. ⟨https://doi.org/10.15196/TS600305⟩.

[3] F. Battista, E.M. Barampouti, S. Mai, D. Bolzonella, D. Malamis, K. Moustakas, M. Loizidou, Added-value molecules recovery and biofuels production from spent coffee grounds, Renew. Sustain. Energy Rev. 131 (2020), 110007, https://doi.org/10.1016/J.RSER.2020.110007.

[4] Horizon2020 Smart Plant project, (n.d.). ⟨https://www.smart-plant.eu/⟩ (Accessed 27 June 27 2022).

[5] Horizon2020 AGROCYCLE project, (n.d.). ⟨http://www.agrocycle.eu/⟩ (Accessed 27 June 2022).

[6] Horizon2020 Circular BioCarbon project, (n.d.). ⟨https://circularbiocarbon.eu/about/project⟩ (Accessed 27 June2022).

[7] Horizon2020 Fit4Food project, (n.d.). ⟨https://fit4food2030.eu/⟩ (Accessed 27 June 2022).

[8] Horizon2020 Decisive 2020 project, (n.d.). ⟨https://www.decisive2020.eu/⟩ (Accessed 27 June 2022).

[9] Food Waste Definition, (n.d.). ⟨https://www.eu-fusions.org/index.php/about-food-waste/280-food-waste-definition⟩ (Accessed 7 February 2022).

[10] G. Strazzera, F. Battista, B. Tonanzi, S. Rossetti, D. Bolzonella, Optimization of short chain volatile fatty acids production from household food waste for biorefinery applications, Environ. Technol. Innov. 23 (2021), https://doi.org/10.1016/J.ETI.2021.101562.

[11] F. Battista, N. Frison, P. Pavan, C. Cavinato, M. Gottardo, F. Fatone, A.L. Eusebi, M. Majone, M. Zeppilli, F. Valentino, D. Fino, T. Tommasi, D. Bolzonella, Food wastes and sewage sludge as feedstock for an urban biorefinery producing biofuels and added-value bioproducts, J. Chem. Technol. Biotechnol. 95 (2020) 328–338, https://doi.org/10.1002/JCTB.6096.

[12] M.T. Agler, B.A. Wrenn, S.H. Zinder, L.T. Angenent, Waste to bioproduct conversion with undefined mixed cultures: the carboxylate platform, Trends Biotechnol. 29 (2011) 70–78, https://doi.org/10.1016/J.TIBTECH.2010.11.006.

[13] L.D. Nghiem, K. Koch, D. Bolzonella, J.E. Drewes, Full scale co-digestion of wastewater sludge and food waste: bottlenecks and possibilities, Renew. Sustain. Energy Rev. 72 (2017) 354–362, https://doi.org/10.1016/J.RSER.2017.01.062.

[14] G. Strazzera, F. Battista, M. Andreolli, M. Menini, D. Bolzonella, S. Lampis, Influence of different household food wastes fractions on volatile fatty acids production by anaerobic fermentation, Bioresour. Technol. 335 (2021), 125289, https://doi.org/10.1016/J.BIORTECH.2021.125289.

[15] H. Asgharnejad, E. Khorshidi Nazloo, M. Madani Larijani, N. Hajinajaf, H. Rashidi, Comprehensive review of water management and wastewater treatment in food processing industries in the framework of water-food-environment nexus, Compr. Rev. Food Sci. Food Saf. 20 (2021) 4779–4815, https://doi.org/10.1111/1541-4337.12782.

[16] F. Battista, C. Masala, A. Zamboni, Z. Varanini, D. Bolzonella, Valorisation of agricultural digestate for the ammonium sulfate recovery and soil improvers production, Waste Biomass Valoriz. 12 (2021) 6903–6916, https://doi.org/10.1007/S12649-021-01486-Y.

[17] G. Strazzera, F. Battista, N.H. Garcia, N. Frison, D. Bolzonella, Volatile fatty acids production from food wastes for biorefinery platforms: a review, J. Environ. Manag. 226 (2018) 278–288, https://doi.org/10.1016/J.JENVMAN.2018.08.039.

[18] M. Peces, G. Pozo, K. Koch, J. Dosta, S. Astals, Exploring the potential of co-fermenting sewage sludge and lipids in a resource recovery scenario, Bioresour. Technol. 300 (2020), 122561, https://doi.org/10.1016/J.BIORTECH.2019.122561.

[19] R.J. Jones, J. Massanet-Nicolau, R. Fernandez–Feito, R.M. Dinsdale, A.J. Guwy, Fermentative volatile fatty acid production and recovery from grass using a novel combination of solids separation, pervaporation, and electrodialysis technologies, Bioresour. Technol. 342 (2021), 125926, https://doi.org/10.1016/J.BIORTECH.2021.125926.

[20] D. Fernández-Domínguez, A. Sergi, M. Peces, N. Frison, D. Bolzonella, J. Mata-Alvarez, J. Dosta, Volatile fatty acids production from biowaste at mechanical-biological treatment plants: focusing on fermentation temperature, Bioresour. Technol. (2020), 123729 https://reader.elsevier.com/reader/sd/pii/S0960852420310014?token=636BCEC156A9FB63A31EEC0CE39B1922571EB6FA1A16223B8FB4EB4CFA8A912FE5FC75D25A36CC9F73EA70744569D241&originRegion=eu-west-1&originCreation=20220207103904 (accessed February 7, 2022).

[21] C. Cavinato, M. Gottardo, F. Micolucci, D. Bolzonella, P. Pavan, Ammonia concentration and pH control in pilot scale two- phase anaerobic digestion of food waste for hydrogen production: focus on start-up, Chem. Eng. Trans. 49 (2016) 151–156, https://doi.org/10.3303/CET1649026.

[22] Y.K. Cheah, C. Vidal-Antich, J. Dosta, J. Mata-Álvarez, Volatile fatty acid production from mesophilic acidogenic fermentation of organic fraction of municipal solid waste and food waste under acidic and alkaline pH, Environ. Sci. Pollut. Res. 26 (2019) 35509–35522, https://doi.org/10.1007/S11356-019-05394-6/FIGURES/7.

[23] F. Valentino, G. Munarin, M. Biasiolo, C. Cavinato, D. Bolzonella, P. Pavan, Enhancing volatile fatty acids (VFA) production from food waste in a two-phases pilot-scale anaerobic digestion process, J. Environ. Chem. Eng. 9 (2021), 106062, https://doi.org/10.1016/J.JECE.2021.106062.

[24] S.J. Lim, B.J. Kim, C.M. Jeong, J. dal rae Choi, Y.H. Ahn, H.N. Chang, Anaerobic organic acid production of food waste in once-a-day feeding and drawing-off bioreactor, Bioresour. Technol. 99 (2008), https://doi.org/10.1016/j.biortech.2007.06.028.

[25] F. Micolucci, M. Gottardo, D. Bolzonella, P. Pavan, M. Majone, F. Valentino, Pilot-scale multi-purposes approach for volatile fatty acid production, hydrogen and methane from an automatic controlled anaerobic process, J. Clean. Prod. 277 (2020), 124297, https://doi.org/10.1016/J.JCLEPRO.2020.124297.

[26] F. Valentino, G. Moretto, L. Lorini, D. Bolzonella, P. Pavan, M. Majone, Pilot-scale polyhydroxyalkanoate production from combined treatment of organic fraction of municipal solid waste and sewage sludge, Ind. Eng. Chem. Res. 58 (2019) 12149–12158, https://doi.org/10.1021/ACS.IECR.9B01831.

[27] N. Perez-Esteban, S. Vinardell, C. Vidal-Antich, S. Peña-Picola, J.M. Chimenos, M. Peces, J. Dosta, S. Astals, Potential of anaerobic co-fermentation in wastewater treatments plants: a review, Sci. Total Environ. 813 (2022), 152498, https://doi.org/10.1016/J.SCITOTENV.2021.152498.

[28] F. Valentino, M. Gottardo, F. Micolucci, P. Pavan, D. Bolzonella, S. Rossetti, M. Majone, Organic fraction of municipal solid waste recovery by conversion into added-value polyhydroxyalkanoates and biogas, ACS Sustain. Chem. Eng. (2018), https://doi.org/10.1021/acssuschemeng.8b03454.

[29] F. Valentino, G. Moretto, M. Gottardo, P. Pavan, D. Bolzonella, M. Majone, Novel routes for urban bio-waste management: a combined acidic fermentation and anaerobic digestion process for platform chemicals and biogas production, J. Clean. Prod. 220 (2019) 368–375, https://doi.org/10.1016/J.JCLEPRO.2019.02.102.

[30] G. Moretto, I. Russo, D. Bolzonella, P. Pavan, M. Majone, F. Valentino, An urban biorefinery for food waste and biological sludge conversion into polyhydroxyalkanoates and biogas, Water Res. 170 (2020), 115371, https://doi.org/10.1016/J.WATRES.2019.115371.

[31] G. Moretto, F. Valentino, P. Pavan, M. Majone, D. Bolzonella, Optimization of urban waste fermentation for volatile fatty acids production, Waste Manag. 92 (2019) 21–29, https://doi.org/10.1016/J.WASMAN.2019.05.010.

[32] F. Morgan-Sagastume, A. Karlsson, P. Johansson, S. Pratt, N. Boon, P. Lant, A. Werker, Production of polyhydroxyalkanoates in open, mixed cultures from a waste sludge stream containing high levels of soluble organics, nitrogen and phosphorus, Water Res. 44 (2010) 5196–5211, https://doi.org/10.1016/J.WATRES.2010.06.043.

[33] F. Morgan-Sagastume, S. Pratt, A. Karlsson, D. Cirne, P. Lant, A. Werker, Production of volatile fatty acids by fermentation of waste activated sludge pre-treated in full-scale thermal hydrolysis plants, Bioresour. Technol. 102 (2011) 3089–3097, https://doi.org/10.1016/J.BIORTECH.2010.10.054.

[34] F. Girotto, M.C. Lavagnolo, A. Pivato, R. Cossu, Acidogenic fermentation of the organic fraction of municipal solid waste and cheese whey for bio-plastic precursors recovery – effects of process conditions during batch tests, Waste Manag. 70 (2017) 71–80, https://doi.org/10.1016/J.WASMAN.2017.09.015.

[35] V. Cabbai, N. de Bortoli, D. Goi, Pilot plant experience on anaerobic codigestion of source selected OFMSW and sewage sludge, Waste Manag. 49 (2016) 47–54, https://doi.org/10.1016/J.WASMAN.2015.12.014.

[36] G. Moretto, F. Valentino, P. Pavan, M. Majone, D. Bolzonella, Optimization of urban waste fermentation for volatile fatty acids production, Waste Manag. 92 (2019) 21–29, https://doi.org/10.1016/J.WASMAN.2019.05.010.

[37] Y.K. Cheah, J. Dosta, J. Mata-Álvarez, Enhancement of volatile fatty acids production from food waste by mature compost addition, Molecules Vol. 24 (24) (2019) 2986, https://doi.org/10.3390/MOLECULES24162986.

[38] L.A. Fdez.-Güelfo, C. Álvarez-Gallego, D. Sales Márquez, L.I. Romero García, Biological pretreatment applied to industrial organic fraction of municipal solid wastes (OFMSW): effect on anaerobic digestion, Chem. Eng. J. 172 (2011) 321–325, https://doi.org/10.1016/J.CEJ.2011.06.010.

[39] F. Silva, M. Matos, B. Pereira, C. Ralo, D. Pequito, N. Marques, G. Carvalho, M.A. M. Reis, An integrated process for mixed culture production of 3-hydroxyhexa-noate-rich polyhydroxyalkanoates from fruit waste, Chem. Eng. J. 427 (2022), 131908, https://doi.org/10.1016/J.CEJ.2021.131908.

[40] A.F. Duque, C.S.S. Oliveira, I.T.D. Carmo, A.R. Gouveia, F. Pardelha, A.M. Ramos, M.A.M. Reis, Response of a three-stage process for PHA production by mixed microbial cultures to feedstock shift: impact on polymer composition, New Biotechnol. 31 (2014) 276–288, https://doi.org/10.1016/J.NBT.2013.10.010.

[41] S. Mateus, M. Carvalheira, J. Cassidy, E. Freitas, A. Oehmen, M.A.M. Reis, Two-stage anaerobic digestion system treating different seasonal fruit pulp wastes: Impact on biogas and hydrogen production and total energy recovery potential, Biomass Bioenergy 141 (2020), https://doi.org/10.1016/j.biombioe.2020.105694.

[42] M. Ye, J. Luo, S. Zhang, H. Yang, Y.Y. Li, J. Liu, In-situ ammonia stripping with alkaline fermentation of waste activated sludge to improve short-chain fatty acids production and carbon source availability, Bioresour. Technol. 301 (2020), 122782, https://doi.org/10.1016/J.BIORTECH.2020.122782.

[43] X.Y. Gu, J.Z. Liu, J.W.C. Wong, Control of lactic acid production during hydrolysis and acidogenesis of food waste, Bioresour. Technol. 247 (2018) 711–715, https://doi.org/10.1016/j.biortech.2017.09.166.

[44] M.A. Khan, H.H. Ngo, W. Guo, Y. Liu, L.D. Nghiem, S.W. Chang, D.D. Nguyen, S. Zhang, G. Luo, H. Jia, Optimization of hydraulic retention time and organic loading rate for volatile fatty acid production from low strength wastewater in an anaerobic membrane bioreactor, Bioresour. Technol. 271 (2019) 100–108, https://doi.org/10.1016/J.BIORTECH.2018.09.075.

[45] R. Iglesias-Iglesias, S. Campanaro, L. Treu, C. Kennes, M.C. Veiga, Valorization of sewage sludge for volatile fatty acids production and role of microbiome on acidogenic fermentation, Bioresour. Technol. 291 (2019), 121817, https://doi.org/10.1016/J.BIORTECH.2019.121817.

[46] E. Jankowska, A. Duber, J. Chwialkowska, M. Stodolny, P. Oleskowicz-Popiel, Conversion of organic waste into volatile fatty acids – the influence of process operating parameters, Chem. Eng. J. 345 (2018) 395–403, https://doi.org/10.1016/J.CEJ.2018.03.180.

[47] F. Cabrera, A. Serrano, Á. Torres, G. Rodriguez-Gutierrez, D. Jeison, F.G. Fermoso, The accumulation of volatile fatty acids and phenols through a pH-controlled fermentation of olive mill solid waste, Sci. Total Environ. 657 (2019) 1501–1507, https://doi.org/10.1016/J.SCITOTENV.2018.12.124.

[48] M. Esteban-Gutiérrez, J. Garcia-Aguirre, I. Irizar, E. Aymerich, From sewage sludge and agri-food waste to VFA: individual acid production potential and up-scaling, Waste Manag. 77 (2018) 203–212, https://doi.org/10.1016/J.WASMAN.2018.05.027.

[49] R. Moscoviz, J. Toledo-Alarcón, E. Trably, N. Bernet, Electro-fermentation: how to drive fermentation using electrochemical systems, Trends Biotechnol. 34 (2016) 856–865, https://doi.org/10.1016/J.TIBTECH.2016.04.009.

[50] I. Vassilev, N.J.H. Averesch, P. Ledezma, M. Kokko, Anodic electro-fermentation: empowering anaerobic production processes via anodic respiration, Biotechnol. Adv. 48 (2021), 107728, https://doi.org/10.1016/J.BIOTECHADV.2021.107728.

[51] P. Paiano, M. Menini, M. Zeppilli, M. Majone, M. Villano, Electro-fermentation and redox mediators enhance glucose conversion into butyric acid with mixed microbial cultures, Bioelectrochemistry 130 (2019), 107333, https://doi.org/10.1016/J.BIOELECHEM.2019.107333.

[52] M. Villano, P. Paiano, E. Palma, A. Miccheli, M. Majone, Electrochemically driven fermentation of organic substrates with undefined mixed microbial cultures, ChemSusChem 10 (2017) 3091–3097, https://doi.org/10.1002/CSSC.201700360.

[53] P. Paiano, G. Premier, A. Guwy, A. Kaur, I. Michie, M. Majone, M. Villano, Simplified reactor design for mixed culture-based electrofermentation toward butyric acid production, Processes 9 (2021) 417, https://doi.org/10.3390/pr9030417.

[54] G.K. Hassan, J. Massanet-Nicolau, R. Dinsdale, R.J. Jones, M.M. Abo-Aly, F.A. El-Gohary, A. Guwy, A novel method for increasing biohydrogen production from food waste using electrodialysis, Int. J. Hydrog. Energy 44 (2019) 14715–14720, https://doi.org/10.1016/J.IJHYDENE.2019.04.176.

[55] R.J. Jones, R. Fernández-Feito, J. Massanet-Nicolau, R. Dinsdale, A. Guwy, Continuous recovery and enhanced yields of volatile fatty acids from a continually-fed 100 L food waste bioreactor by filtration and electrodialysis, Waste Manag. 122 (2021) 81–88, https://doi.org/10.1016/J.WASMAN.2020.12.032.

[56] R.J. Jones, J. Massanet-Nicolau, R. Fernandez-Feito, R.M. Dinsdale, A.J. Guwy, Recovery and enhanced yields of volatile fatty acids from a grass fermentation via in-situ solids separation and electrodialysis, J. Clean. Prod. 296 (2021), 126430, https://doi.org/10.1016/J.JCLEPRO.2021.126430.

[57] F. Micolucci, M. Gottardo, W.R.M. Leite, Bioprocess network for solid waste management, Optim. Appl. Bioprocess. (2018) 349–382, https://doi.org/10.1007/978-981-10-6863-8_17/COVER/.

[58] Eurostat, Sewage sludge production and disposal from urban wastewater (in dry substance (d.s)), Products Datasets, (2021). ⟨https://ec.europa.eu/eurostat/web/products-datasets/-/ten00030⟩. (Accessed 11 July 2022).

[59] G. Campo, A. Cerutti, C. Lastella, A. Leo, D. Panepinto, M. Zanetti, B. Ruffino, Production and destination of sewage sludge in the piemonte region (Italy): the results of a survey for a future sustainable management, Int. J. Environ. Res. Public Health 18 (2021) 3556, https://doi.org/10.3390/IJERPH18073556.

[60] Euro Obeserver, Biogas Barometer 2020, (2020). ⟨https://www.eurobserv-er.org/biogas-barometer-2020/⟩. (Accessed 11 July 2022).