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Producing volatile fatty acids and polyhydroxyalkanoates from foods by-products and waste: A review

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HIGHLIGHTS

- Cheese whey, olive oil wastes and winery wastewaters are about 300 M tons worldwide.
- About 85 kg of food wastes are annually produced by each people in the world.
- VFA and PHA conversions can reach 0.9 gVFAs/gCOD and 0.7 gPHA/gVSS, respectively.
- Wine wastes have the highest PHA yield (0.7 gPHA/gVSS), olive ones the lowest (0.3)
- These yields allow to estimate the global annual PHAs production of about 260 M tons.

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ABSTRACT

Dairy products, extra virgin olive oil, red and white wines are excellent food products, appreciated all around the world. Their productions generate large amounts of by-products which urge for recycling and valorization. Moreover, another abundant waste stream produced in urban context is the Organic Fraction of Municipal Solid Wastes (OFMSW), whose global annual capita production is estimated at 85 kg. The recent environmental policies encourage their exploitation in a biorefinery loop to produce Volatile Fatty Acids (VFAs) and polyhydroxyalkanoates (PHAs). Typically, VFAs yields are high from cheese whey and OFMSW (0.55–0.90 g_{COD_VFAs}/g_{COD}), lower for Olive Mill and Winery Wastewaters. The VFAs conversion into PHAs can achieve values in the range 0.4–0.5 g_{PHA}/g_{VSS} for cheese whey and OFMSW, 0.6–0.7 g_{PHA}/g_{VSS} for winery wastewater, and 0.2–0.3 g_{PHA}/g_{VSS} for olive mill wastewaters. These conversion yields allowed to estimate a huge potential annual PHAs production of about 260 M tons.

1. Introduction

Cow milk, grapes and olives represent the fundamental commodities for cheese, wine and olive oil productions, which are among the three of the most appreciated food products worldwide. These three food commodities, especially grapes and olive, are mainly located in the area of the Mediterranean Sea, and in particular in France, Greece, Italy, Spain and Tunisia (FAO, 2019). Their conversion into final food products generates large amount of residues, by-products and wastes: Table 1 summarized the abundance of cow milk, olive oil and wine industries' by-products. Cow milk, olive oil and wine lead to the productions of large amounts of Cheese whey (CW), Olive Pomace (OP) and Olive Mill Wastewaters (OMWW) and Winery Wastewaters (WW), respectively. The recent European and national policies on circular bioeconomy encourage their usage as secondary raw materials for the transition from a linear to a circular economy and the increasing of the sustainability of the food supply chain.

This review aims to discuss the exploitation of the organic matter content in wastes and by-products from milk, olives and grapes conversions in a biorefinery loop for the sequential production of Volatile Fatty Acids (VFAs) and polyhydroxyalkanoates (PHAs). Organic Fraction of Municipal Solid Wastes (OFMSW) was also considered in this

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Table 1
Amounts of food wastes, OP and OMWW, CW and WW around the world and in some Mediterranean Countries (France, Greece, Italy, Spain and Tunisia). * Average value obtained from the 28 Countries considered by Statista, 2020 data.

	CW (M tons)	OP and OMWW (M tons)	WW (M tons)	Annual Food waste (kg/ capita) (United Nations, 2021)
World	180.00–190.00 (Mollea et al., 2013)	16.02 (Statista, 2020)	80–90 (Bolzonella et al., 2019)	85*
France	18.17 (Traversi et al., 2013)	0.01–0.02 (Roussos and Gaime, 2006)	10.00–14.00 (Bolzonella et al., 2019)	85
Greece	0.46 (Siafakas et al., 2019)	6.06 (Aravani et al., 2022)	0.95 (Vlachos, 2017)	142
Italy	9.50 (Statista, 2020)	2.20 (Batuecas et al., 2019)	10.00–14.00 (Bolzonella et al., 2019)	67
Spain	7.20 (Statista, 2020)	5.55 (Statista, 2020)	10.00–14.00 (Bolzonella et al., 2019)	78
Tunisia	Not available	1.39 (Statista, 2020)	Not available	91

review, being the most abundant wastes stream produced at urban level. Its annual production was estimated at 85 kg per person worldwide, even if it changes deeply in the different Countries (United Nations, 2021). In particular, its abundance depends on the evolution of the environmental policy (at European and national level), which in the last decades encouraged the separate recollection of Municipal Solid Waste, leading to the increasing of the source sorted OFMSW, and consequently, opening new perspective for the biological valorization of such source.

VFAs production are organic compounds which serve well in the chemical industry, as they are the precursors for bioenergy production and for the synthesis of a variety of products, such as PHAs, which represent the monomers for the synthesis of biodegradable bioplastics. In the context of waste utilization, PHA production can start from Microbial Mixed Culture (MMC) and can be easily integrated into existing infrastructures adopted for the biological treatment of organic waste residues and wastewaters (Morgan-Sagastume, 2016). In the last two decades, different research groups contributed to the scaling-up of the process to pilot-scale facilities (Conca et al., 2020; Matos et al., 2021; Tamis et al., 2018; Valentino et al., 2018). Independently from the adopted process configuration, the microbial composition of the sludge needs to be selectively enriched in microorganisms with high ability into PHA synthesis. The most applied scheme for the synthesis of PHA by MMC includes a sequence of elements consisting of aerobic and anaerobic units. The first step involves a dark acidogenic fermentation of the waste to obtain a stream rich in VFA. The produced VFA-rich stream represents the readily biodegradable COD for the following aerobic stages: a first sequencing batch reactor (SBR) for the MMC selection/ enrichment of PHA-accumulating microorganisms under feast-famine regime, and a second fed-batch reactor for the accumulation of PHA within cellular walls.

The following examples of PHA production from organic waste refer to the most applied scheme briefly discussed above. The utilization of food waste or CW as carbon source for PHA synthesis led to the most significative examples of MMC-PHA technology's development, with some pilot scale prototype already designed and operative. Regarding the olive waste utilization, even though the research cases have been similarly conceived to the use of food waste and CW, the available results show lower performances; probably, some technical issues (briefly described below) or the lack of interest from the olive waste producers strongly limited further advancements. On the contrary, the waste from winery sector is still poorly investigated as carbon source for PHA production. The literature furnishes examples where pure culture system are utilized; hence, the required process scheme is different from that one described above for MMC. However, the winery-related examples here reported are promising in terms of PHA-related performances.

2. Volatile Fatty acids production from cow milk, olive oil, wine's by-products and OFMSW

2.1. Cheese whey

Dairy products represent a very large sector in food industries around the world. According to the most recent FAO estimation, the production of cow milk was of 843 M tons in 2018. India is the world's largest milk producer, accounting for the 22 % of the global production, followed by the United States of America, China, Pakistan and Brazil (FAO, 2018). Considering the European Union, the average annual production of cows' milk is about 135 M tons and showed a stable trend in the last ten years. The two main cow milk producers are Germany and France with the 21 and the 17.2 % of the total EU cows' milk production, respectively (Traversi et al., 2013). EU cows' milk is exploited to obtain different products: more than 30 % of it is treated to be used as drinking milk, another 38 % and 16 % are transformed in cheese and butter, respectively.

From the sterilization and transformation of cow milk into milk-based products, about 180–190 M tons of CW are annually produced at international level, making of CW one of the most abundant wastes generated from agro-food industry (Mollea et al., 2013) (Table 1). These wastes are highly contaminant, mainly due to their high organic load and of the acidic pH (5.0–6.5). The typical chemical composition of CW is showed in Table 2. The physical and chemical features of CW can cause an excess of oxygen consumption, impermeabilization, eutrophication, toxicity in the receiving environments (Prazeres et al., 2012). The high organic load and the high fermentability of its compounds make CW interesting for biorefinery application and, in particular, for VFAs production.

The high fermentation potential of CW was demonstrated by Lagoa-Costa et al. (2020). They explored the production of VFA from CW using an Anaerobic Sequencing Batch Reactor (SBR), working at mesophilic temperature (30 °C) and under a gentle agitation of 80 rpm. The SBR was inoculated with the effluent of another reactor producing VFAs from CW, which assured the MMC presence. Different Hydraulic Retention Time (HRT) and Solid Retention Time (SRT) were tested to optimize the fermentation's performance. They observed a different influence of SRT and HRT in VFA productivity. Considering the SRT, the degree of acidification (DA) improved from 0.73 to 0.83 when it passed from 5 to 15 days, while an opposite trend was observed with HRT. The DA increased from 0.79 to 0.83 when lowering the HRT from 3 to 1 day. Under these conditions, the acidification yield reached 0.87 and 0.90 $g_{COD\text{-}VFA}/g_{COD}$ in correspondence of the SRT of 15 days and the HRT of 1 day, respectively. The manipulation on the SRT and HRT had influence on the microbial community too: hydrolytic bacteria dominated at shorter SRT and acidogenic/acetogenic bacteria were more abundant at larger SRT. It is important to remark that, even if the final VFAs yield was very high, the highest VFAs concentration was only around 8.5 g/L, as effect of the low solid charge into CW. Another research group worked even at lower HRT, in a range of 1–4 h, adopting an Anaerobic fluidized bed reactors (AFBR) (Rosa et al., 2014). They concluded that the best HRT was of 4 h as lower values favored the washout of the reactor. Then, from the scientific literature data, it is possible to assume that an optimal acidogenic fermentation of CW should be comprised in a HRT range of 4–24 h.

Another important parameter affecting the VFAs production is the Organic Load Rate (OLR). Acidogenic fermentation is usually favored by high OLR (around 7.5–10 gCOD/Ld), while lower values are more

Table 2
Typical chemical composition of CW (Johansen et al., 2002; Lagoa-Costa et al., 2020), of OPII, OPIII and OMWW (Battista, 2014; El-mrini et al., 2022) and of WW (Bustamante et al., 2005; Ngwenya et al., 2022).

	CW	OPII	OPIII	OMWW	WW
Density (kg/m^3)	1,020–1,030	980–1,010	960–990	985–995	970–990
pH	5.0–6.5	5.5 – 6.5	5.0–6.5	4.5–5.5	4.10 – 8.20
TS content (g/l)	60.0–65.0	255.0–275.0	300.0–340.0	12.0–40.0	18.6–60.6
vS content (g/l)	58.8–64.5	235.0–255.0	280.0–320.0	7.0 – 25.0	10.0–44.5
LHV (kJ/g)	Not available	20–25	20–25	Not available	Not available
Nitrogen content (% w/w)		1.10–1.30	0.80–1.00	0.02–0.05	0.005–0.04
Polyphenols Content (mg gallic acid/l)	Normally not present	120.0–140.0	70.0–90.0	200.0–300.0	140.0 – 170.0
Total proteins (% w/w)	0.7–0.9	Not available	Not available	Not available	Not available
Whey proteins (% w/w)	0.4–0.6	Normally not present	Normally not present	Normally not present	Normally not present
Lactose (% w/w)	4.5–5.5	Normally not present	Normally not present	Normally not present	Normally not present
Fats (% w/w)	0.05–0.35	Not available	Not available	Not available	Not available

indicated for the VFAs conversion into biogas (Strazzera et al., 2018). Calero et al., (2017) studied the influence of the OLR adopting two different reactor's configurations: a laboratory upflow anaerobic sludge blanket (UASB) reactor and a discontinuous SBR. The predominant products in the acidogenic process in both reactors were: acetate, propionate and butyrate. The maximum DA obtained was 98 % in an SBR at OLR of 2.7 g COD/Ld. A similar result (97 %) was obtained in the UASB under an OLR of 15.1 g COD L/d, demonstrating the better performances of the UASB reactor over the SBR at high OLR. The lower performance in VFAs production when working at high HRT and low OLR was observed by Lara-Musule et al., (2021). They worked on the acidogenic fermentation of raw CW in a 3.5L anaerobic SBR under the following operational conditions: OLR = 3.6 gCOD/L and HRT of 30 days. The final VFAs concentration varied from 20 to 25 $g_{COD\text{-}VFA}$/L corresponding to a VFAs yield of 0.18–0.23 $g_{COD\text{-}VFA}/g_{inletCOD}$, explainable with the conversion of the produced VFAs into biogas. But Lara-Musule et al., (2021) work is very interesting as it shows how different temperature and pH conditions can affect the final concentration and composition of the VFAs. Neutral pH (7.5) and a higher mesophilic temperature (40 °C) seemed favoring a better final VFAs concentration in the reaction medium of 25 g/L over the 18–20 g/L achieved by slightly acidic pH of 5.5 and a slightly lower temperature of 35 °C. These latter conditions were particularly interesting as they increased the concentrations of caproic and valeric acids known to be economically more appreciated than butyric and acetic acids (Veluswamy et al., 2021). The caproic acid passed from the 4 % w/w of the total VFAs at pH 7.5 and 35 °C, to 30–35 % w/w at pH 5.5 and 40 °C.

Finally, the effect of adopting inocula from different origins was investigated too. The scientific literature highlights various inoculum sources at a controlled pH may led to different metabolites produced, such as acetate and ethanol, as well as to the consumption of different organic compounds (Tang et al., 2008). Rosa et al., (2014) fermented CW adopting two sources of inoculum, swine wastewater and poultry slaughterhouse wastewater, for hydrogen and VFAs production in an AFBR. The VFAs yields was 30 % higher from AFBR inoculated with poultry slaughterhouse wastewater. The VFAs yield was of about 1.7 mol VFAs/mole lactose against the 1.1 mol VFAs/mole lactose produced by the AFBR inoculated with swine wastewater. The lower VFAs amount from swine wastewater inoculated reactor favored the formation of other typologies of biological precursor, ethanol and methanol. The PCR/DGGE analysis allowed to observe a high similarity degree in the microbial communities of the two reactors but the concentrations of *Selenomonas, Clostridium, and Methanobacterium*, related to the formation of acetic, propionic, lactic acid and hydrogen productions, were higher in the AFBR inoculated with poultry slaughterhouse wastewater.

2.2. Olive milling by-products

The gentle taste and the beneficial properties on diet make olive oil one of the most appreciated sauces around the world. Over the 95 % of the world olive oil production is concentrated in the Mediterranean area. It has been estimated more than 2,486,000 and 1,176,000 ha are dedicated to the olive trees cultivation in Spain and Italy, respectively, the two main olive oil worldwide producers (Statista, 2020).

The modern technology to extract olive oil adopts industrial centrifugal decanter to separate the different phases (oil, liquid and solid) in olive. The olives are crushed to a fine paste by a hammer crusher, disc crusher, depicting machine or knife crusher. The resulting paste is left to rest from 30 to 60 min to favor the agglomeration of the olive oil droplets. Then, the paste is pumped to the industrial decanter, which generally consists in a large capacity horizontal centrifuge. The decanter allows the separation of the paste into three different phases: the olive oil and the two main by-products resulting from the olive oil production: the OP and the OMWW, whose annual amounts were reported in Table 1 (Batuecas et al., 2019; Statista, 2020). OP is the solid rich residue remaining after olive oil extraction, whose chemical and physical features depend on the technology used during olive oil production processes, which can involve a three-phase centrifugation (OPIII) (oil phase 20 % *w/w* olive, aqueous phase 50 % *w/w* olive and 30 % *w/w* as solid phase), or a two-phase centrifugation (OPII), which generates a "wet OP'' with a water content up to 65 % *w/w*. In both cases, OP present high organic concentration (COD greater than 250 g/L), high electrical conductivity, a high concentration of polyphenols (0.1–5 g/L), and low pH (4–6) (Table 2).

OMWW represents the liquid phase by-product from olive oil production, deriving both from water used for the olives washing before the oil extraction, and from the water content in olives' drupes. OMWW is characterized by acidic pH, a brown – black coloring, a very low TS and COD concentrations. OMWW is particularly interesting because of its high polyphenols' concentration. Polyphenolic compounds are a large and complex family of substances, characterized by the presence of large multiples phenol structural units, synthesized by the olive plants as a defense against pathogens and insects. Due to their high solubility in water, polyphenols are more concentrated in OMWW than OP (Table 2).

Despite their characteristics make them very polluting wastes, OP and OMWW are often simply disposed on soil for irrigation and fertilization scopes. It is also the consequence of the lack of a specific European provision for olive oil wastes. Hence, each country has developed its national legislation (Batuecas et al., 2019). With respect to the Italian regulations, the maximum amount of olive waste allowed for the release on soil is 30 m^3 ha/year (parlamento.it (1996)).

The high content of organic matter in olive by-products encouraged their usage as substrates for VFAs production by acidogenic fermentation. In particular, Ouazzane et al., (2017) remarked the OP is very interesting at this scope for the equilibrate concentrations of polysaccharides, proteins, fats, polyphenols even if the high content of lignocellulosic materials, such as cellulose and lignin, can reduce the potential in VFAs productivity. Thus, the hydrolysis of lignocellulosic compounds in OP represents a challenge to maximize the VFAs yield. Different pretreatments (steam explosion or chemical-thermal treatments) have been largely applied in order to enhance the breakdown of fiber structures (Ruggeri et al., 2015) (Serrano et al., 2017). Despite the good solubilization degree, the adoption of thermal pretreatments are not best energetic options, considering the high moisture content of OP. Chemical pretreatments are a more suitable alternative. Ruggeri et al., (2015) tested the efficacy of the alkaline pretreatment on the lignocellulosic degradation of the OP. The pretreatment, performed in batch condition on an OP-OMWW mixture having a TS content of 10 % w/w by the addition of 2 M NaOH solution until the reaching a pH of 12 for 24 h, improved VFAs concentration of more than 5 times, reaching a final level of about 6.0 g/L. More recently, Cabrera et al., (2019) pH-controlled fermentation was carried out at acidic (pH = 5), neutral (pH ≈ 7) and alkaline (pH = 9) operating pH levels. When processed at neutral pH, the tests achieved a conversion of 93.5 % of fed COD to methane. Instead, fermentations at pH 5 and 9 resulted in the inhibition of the methanogenic activity. The best VFA production reached its maximum concentration of 3.7 g COD-VFA/L, where acetic acid represented up to 79.3 % of the total VFAs. The good performance of alkaline action appears to be caused by an increased porosity of the lignocellulosic materials, caused by an increased internal surface area, a decreased degree of polymerization and crystallinity, and a destruction of the structural links between the carbohydrates and lignin (Fan et al., 1980). Lignocellulosic compounds' treatment was also faced by Dionisi et al., 2005), which tested a physical pretreatment, the centrifugation, in order to remove the most recalcitrant solid fraction of the OP. The final VFAs concentration passed from 9.0 to 13.0 g/L, allowing an increasing of the VFAs yield (COD based) from 25 % w/w to 35 % in correspondence of no-pretreated and centrifugated pretreated Centrifugation determined also a different VFAs profile. Acetic acid was the predominant acid in absence of any pretreatment (40 % w/w). The same percentage belonged to butyric acid when OP was firstly pretreated. It is important to remark that centrifugation consisted in a simple removal of the recalcitrant lignocellulosic materials, which require further specific waste management operations.

If the presence of lignocellulosic materials decreases the acidogenic potential of olive oil by-products, polyphenols have the opposite effects. The high polyphenol content of the OP and, especially, of OMWW inhibited the methanogenic bacteria activity, favoring the acidogenic accumulation (Battista et al., 2014; Obied et al., 2005; Ramos-Cormenzana et al., 1996). Consequently, the pretreatments of OP-OMWW with flocculant salts ($FeSO_4$, $FeCl_3$, $MnSO_4$) should be avoided as they are able to favor the precipitation of polyphenols, activating the VFAs consumption for methane production (Battista et al., 2014).

The inhibition of methane production can be also favored by the adoption of high organic content, especially when fermentation is performed in continuous mode. Rincón et al., (2008) investigated the effect of the OLR and of HRT on acidogenic fermentation of OP derived from a two-phase centrifugation. In particular, they carried out eight experimental runs corresponding to OLRs of: 3.2, 5.6, 7.4, 9.6, 11.0, 12.9, 14.0, and 15.1 g COD/L d, which were equivalent to HRTs of 50.0, 28.8, 21.8, 16.9, 14.7, 12.4, 11.5 and 10.7 d, respectively. It was demonstrated that the VFAs concentration increased with the OLR, achieving the maximum value of about 16.5 g/L at the OLR of 12.9 g COD/L d, while higher OLR inhibited the process. The profile of the produced VFAs was also influenced by the OLR: acetic and propionic acids were the predominant VFAs, representing the 50 % and 30 % w/w of the total VFAs at OLR of 12.9 g/Ld. In particular, the concentration of propionic acid was significantly lower than acetic acid concentration except for an OLR of 3.2 g COD/L d. The concentration of butyric acid also increased with the OLRs but reached its peak at a lower OLR value (9.6 g COD/Ld). Finally, the concentration of valeric acid was always low for all the OLRs, showing a peak of 2.5 g/L in correspondence of high OLR (14 gCOD/Ld), when the decline of the other VFAs occurred. The positive effect of high OLR was also demonstrated by Azbar et al., 2009), who used a UASB reactor for OMWW acidogenic fermentation at different OLRs (0.45 and 32 g COD/L d) for 477 days. The results demonstrated that the UASB reactor could tolerate high influent COD concentrations, with VFAs concentration which increased from 0.35 to 2.4 g/L, reaching the peak in correspondence of the OLR of 20 gCOD/Ld. Even in this case, acetic and butyric acids were the most abundant acids.

2.3. *Winery wastewater*

One of the most economically profitable sectors in food industry is represented by wine production, whose international amount reached 29 M tons of produced wine in 2014 (Bolzonella et al., 2019). Wine production is mainly located in European Union where is concentrated more than the 61 % of the international wine production. Italy, France, and Spain are the leading Countries in wine production with a similar production of about 4–5 M tons in 2020 (Statista, 2020). The wine production generates large amount of wine wastewaters (WW): 0.2–4 L of WW for liter of wine produced (Bolzonella and Rosso, 2013). Considering these numbers, it is possible to estimate the WW annual production both at international level and for the main producing Countries (Table 1). WW derives from all the operations of the wine production which includes: i) the stemming, or rather the separation of grape stalks; ii) the crushing of grapes to release the juice; iii) the fermentation of the liquid phase from grapes' crushing; iv) the solid/liquid separation after fermentation and v) the clarification and stabilization of the produced wine (Bolzonella et al., 2019). The main chemical and physical characteristics of WW are reported in Table 2. The main chemical compounds in WW are ethanol, glucose, fructose, and tartaric acid (Agustina et al., 2008). WW, especially-one derived from red wines production, contains a great concentration of polyphenols (Table 2): p-coumaric, cinnamic, caffeic, gentisic, ferulic, tannic and vanillic acids. Unlike OMWW and OP, a great part of polyphenols in WW is already removed along the biologic treatments included in the wine production. Consequently, the residual polyphenols concentration in WW is estimated to be in the range 13–700 mg/L, which is usually considered not alarming values for the methane production by anaerobic digestion and even less for VFAs production by acidogenic fermentation.

A first consideration in the approaching to a state of art about the acidogenic fermentation of WW is that this substrate was essentially adopted for biogas production by anaerobic digestion even that for VFAs production. Consequently, the scientific literature includes few papers specific for acidogenic fermentation of WW, at the best authors' knowledge.

Batch acidogenic fermentation of WW was performed by Fernández et al. (2008) at 35 °C and slightly acidic condition (pH 5). They obtained a total VFAs of 4.5 $g_{VFA\text{-}COD}$/L after around 800 h of fermentation, with a VFAs yield of 0.53 referred to the initial glucose concentration. Regarding the VFAs profile the main VFAs was acetic acid (2.5 g/L), followed by butyric and propionic acids (1.5 and 0.5 g/L, respectively). Better results were achieved for longer fermentation time by Esteban-Gutiérrez et al., (2018), who focused on the effect of pH (5.5 and 10) and temperature (35 and 55 °C) on VFAs yield. They demonstrated that alkaline pH (9) and thermophilic temperature (55 °C) maximized the VFAs concentration at about 11.5 $g_{VFA\text{-}COD}$/L, corresponding to a VFA yield of 0.25 g/gCOD. Butyric and acetic acids were the main produced VFAs with 6.5 and 3.0 g/L, respectively.

The effects of different parameters were investigated on the VFAs production from WW. Petropoulos et al., (2016) evaluated the variation of OLR, one of the most impacting parameters in VFAs and methane productions, affected the process yields. They applied OLR from 2 to 80 gCOD/Ld to a 135 L expanded granular sludge bed (EGSB) pilot-scale reactor, while HRT was kept constant at 26 h.

The methane production was steady until a total OLR of 39 g/Ld with a specific methane production of 310 L/kgCOD. Higher OLR favored the washout of the methanogenic microbial culture and the consequent VFAs accumulation into the reaction medium. The highest VFAs concentration of about 2 g/L was achieved for OLR of 60–70 gCOD/Ld.

Another recent paper confirmed the importance of short HRT and, consequently, of high OLRs for WW acidogenic fermentation. This work studied the effect of different HRT (from 8 to 20 days) on methane production of a 50:50 v/v mixture composed by WW and sewage sludge. The highest VFAs concentration of 0.8 g/L was achieved at the lowest HRT of 8 days, when a first decline in methane production was recorded. This VFAs concentration was very low and can be explained considering the process was not designed to optimize the VFAs yields, which usually requires lower HRT (Strazzera et al., 2018).

In the last years WW increased its appeal in the scientific community for the possibility to produce caproic acid by chain elongation. WW is considered a good candidate at this scope for the simultaneous presence of ethanol and glucose which can be easily degraded in acetic acid. Kucek et al., (2016) adopted a reactor microbiome with continuous in-line extraction, fed with WW and wine lees to produce biomass. A promising biomass productivity of 7 gCOD/L d was achieved by the test, which was mainly composed (70 % of the total biomass) by *n*-caproate producing microorganisms. At the best conditions (OLR of 5.8 gCOD/Ld and semi continuous feeding mode), the caproic acid reached the highest concentration of about 3 g/L, corresponding to yield of 0.7 g caproic acid/gCOD.

2.4. Organic fraction of Municipal solid wastes (OFMSW)

Organic Fraction of Municipal Solid Wastes (OFMSW) represents one of the major waste streams produced annually at urban context. OFMSW is composed by different food wastes (residues of fruits, vegetables, meat, fish, bread, pasta and other carbohydrates wastes) and eventual inert materials (plastic, wood and glass fractions), which are improper throw away with food wastes and, consequently, require a separation step before the OFMSW valorization. The annual amount of OFMSW production is approximately 2 billion metric tons, of which 1.3 billion tons come from Europe and Western countries. This amount corresponds to some 300 g of household FW per capita per day (Battista et al., 2020).

OFMSW quality is strongly favored by an efficient system of source separate collection, which makes it easier to apply biological processes for their treatment. However, even with an ideal food waste management, the current national legislations avoid food waste landfilling, promoting their treatment through thermal and/or biological processes (including incineration); despite of this scenario, the disposal cost of such waste remains high (75–125 €/ton) (Fava et al., 2015). Moreover, OFMSW composition depends on some other factors, such as seasonality, the area of recollection and the regions of provenience. Although these numbers of variables, OFMSW is characterized by a high organic content (around 15–20 % TVS) and of nitrogen and phosphorous (2–15 g/kg and 0.5–1.0 g/kg, respectively), which makes it a good candidate for VFAs production.

A recent work by Strazzera et al. (2021a) studied the effect of the different main carbon fractions (carbohydrates, proteins, lipids, cellulosic compounds, etc.) contained in OFMSW both on the quantity and profile of VFAs production working in batch tests. They demonstrated that the VFAs production was very high from the OFMSW rich in protein with a final VFAs concentration of almost 14 gCOD/L at pH 7, corresponding to a VFAs yield of about 0.8 $g_{VFA\text{-}COD}/g_{COD}$. 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 work highlights also the pH is a fundamental parameter for VFAs productions. The final VFAs yield from OFMSW rich in protein declined to 0.7 and 0.6 $g_{VFA\text{-}COD}/g_{COD}$ in correspondence of a pH of 5.5 and uncontrolled pH, respectively. On the contrary, lower VFAs yield were achieved for OFMWS rich in sugars-fibers and lipids fractions, with a final productivity 0.55 and 0.09 $g_{VFA\text{-}COD}/g_{COD}$, respectively, at pH 7. For slightly acidic pH and uncontrolled pH the yields were even lower. The lower VFAs yields from OFMSW rich in sugars-fibers fraction was explained by the high hydrolysis' kinetics of these substrates which caused a rapid acidification of the reaction medium and, consequently, the inhibition of the VFAs producing microorganisms. While, the low yields from lipids-rich fraction's tests, was due to the high presence of Long Chain Fatty Acids (LCFA), known to damage to cell membranes, to reduce nutrients transport and decrease cell permeability with a consequent fermentation inhibition (Peces et al., 2020). Besides the nature of the carbon fraction, the VFAs production from OFMSW is also influenced by the operational conditions of the acidogenic fermentation, in particular by the OLR, pH and temperature. Strazzera et al. (2021b) tested different OLR, pH and temperature to optimize the VFAs production. The 450 days long experimental campaign saw the adoption of two OLR (22 and 11 gTS/Ld), different pH values (uncontrolled, 5.5 and 7) and at mesophilic and thermophilic temperatures. The best VFAs yield of 0.38 $g_{VFA\text{-}COD}/g_{COD}$, corresponding to a solubilization rate of 0.63 g sCOD/g tCOD was achieved under the following operational conditions OLR of 11 gVS/Ld, pH of 7 and thermophilic temperature. the VFAs profile was characterized by the predominance of the butyric acid, whose concentration accounted for more than the 60 % of the total acids, followed by caproic acid (almost the 20 %). Fernández-Domínguez et al., (2020) tested the effect of a larger temperature range (20–70 °C) on acidogenic fermentation. It was shown that the differences in the maximum VFAs yield were significant only for the test carried out at 70 °C, in which the lowest maximum VFAs yield of 0.45 $g_{VFA\text{-}COD}/g_{COD}$ was reached. The same work analyzed also the effect of pH, testing both slightly acidic pH of 6 and (ii) alkaline pH of 10, keeping constant a HRT of 3.5 d, corresponding to an OLR in the range of 11.9–14.7 kg VS/(m^3.day). The authors observed a better COD solubilization under alkaline conditions, but it did not lead to an increase of VFAs yield, which remained constant at 0.34–0.36 $g_{VFA\text{-}COD}/g_{COD}$. Regarding the VFAs profile, a higher acetic concentration and a lower butyric and valeric acids concentration was detected under alkaline conditions. The performances were slightly better than ones from a previous work by (Lim et al., 2008) who recorded a VFAs yield of 0.26–0.32 $g_{VFA\text{-}COD}/g_{COD}$ when working with a semi-continuous fermenter treating food waste operating under a HRT of 4 days and at 35 °C.

Another study carried out by Valentino et al., (2021) tested the possibility to recirculate digestate to prevents the system's acidification, as effect of the high ammonia content deriving from the proteins' degradation. In particular, they treated screw pressed OFMSW (120 g TS/kg; 107 g VS/kg) in a two stage AD process (mesophilic fermentation at 37 °C + anaerobic digestion 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/m^3d, the fermented OFMSW presented a VFAs yield of 0.33 $g_{VFA\text{-}COD}/g_{COD}$. Under these working conditions, Valentino et al., (2021) found that a 56 % (on COD basis) of the total VFAs was represented by propionic and valeric acids.

Finally, a common strategy to stabilize the acidogenic fermentation consists in the co-fermentation of OFMSW with sewage sludge. Sewage sludge, rich in N and P compounds, can supply fundamental macronutrients to OFMSW (Perez-Esteban et al., 2022). In Valentino et al., (2019a, 2019b) 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/m^3d. 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 both cases, the pH values were not strongly affected by the VFAs increasing since the buffer capacity of the mixed liquor, which comes from the sludge, was high enough to sustain the acidification process. The role of pH on fermentation's performances was investigated in batch tests performed by Moretto et al., (2019). 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. 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).

3. PHAs production from cow milk, olive oil, wine's by-products and OFMSW

3.1. Cheese whey

CW has been found to be efficient as a carbon source to produce PHA (Table 3). Domingos et al. (2018) utilized a pure culture of *Cupriavidus necator* (DSMZ 545) for PHA synthesis from VFA-rich fermented CW. In particular, the authors employed an electrodialysis (ED) step for the

Table 3

Summary of the main PHA-producing bacteria, process performances and PHA composition from food waste, wine, cheese and olive by-products (*pure culture system).

Origin of the substrate	Substrate	Main PHA-producing strains	PHA composition (w/w)	Final PHA biomass content (gPHA/gVSS)	Process productivity and/or overall yield	Reference
Dairy industry	Cheese whey	*Cupriavidus necator* (DSMZ 545)*	6 % 3HV; 94 % 3HB	8–10 %	0.21 g/L/h	Domingos et al., 2018
	Cheese whey and brewery wastewater	–	12 % 3HV; 88 % 3HB	45–50 %	–	Lagoa-Costa, Kennes and Veiga, 2022
	Cheese whey and sugar cane molasses	–	19 % 3HV; 81 % 3HB	65 %	0,56 gPHA/L/h	Duque et al., 2013
	Cheese whey	–	0–40 % 3HV; 60–100 % 3HB	–	1,175–0,454 g/L/h	Colombo et al., 2016
	Cheese whey	–	30 % 3HV; 70 % 3HB	50–60 %	Average of 7.8 g/L/day = 0,325 g/L/h	Carvalheira et al., 2022
	Cheese whey	–	15–17 % HV;	–	–	Valentino et al., 2015
	Cheese whey	–	89–92 % HB 8–11 % HV	14–43 %	0,20 – 0,25 – 0,12 g/L/h	Oliveira et al., 2018
Wine industry	Solaris grape pomace	*Pseudomonas resinovorans* (DSMZ 21078)*	16.3 % 3-hydroxyhexanoate 33.8 % 3- hydroxyoctanoate 30.4 % 3-hydroxydecanoate 10.0 % 3- hydroxytetradecenoate	23.3 %	0.05 gPHA/L/h	Follonier et al., 2014
	Gewürztraminer wine pomace	*Pseudomonas putida* KT2440*	poly(3-hy- droxyoctanoate-*co*-3-hydroxy-10-undecenoate)	40 – 42 %	0.10 g/L/h	Follonier et al., 2015
	Red grape pomace	*Cupriavidus necator**	PHB	63 %	–	Martinez et al., 2015
	Wine lees	*Cupriavidus necator* DSM 7237*	PHB	71.3 %	0.56 g/L/h	Dimou et al., 2015
	Grape pomace extract	*Cupriavidus necator**	PHB	63 %	0.28 g/L/h	Kovalcik et al., 2020
Organic fraction of municipal solid waste	Food Waste	–	12–40 % 3HV; 60–88 % 3HB	16–25 %	–	Amulya et al., 2015
	OFMSW-leachate	*Plasticicumulans acidivorans*	–	78 %	0.48 COD_{PHA}/COD_{SOL}	Korkakaki et al., 2016
	OFMSW	–	43–45 % 3HV; 55–57 % 3HB	47 %	114 g PHA/kg TS	Colombo et al., 2017
	OFMSW	*Acidovorax* spp., *Hydrogenophaga* spp	7–12 % 3HV; 88–93 % 3HB	55 %	37 g PHA/kg TS	Valentino et al., 2018
	OFMSW	–	41–71 % 3HV; 29–59 % 3HB	15–20 %	117–199 g PHA/kg TS	Papa et al., 2020
	OFMSW	–	0–4 % 3HV; 96–100 % 3HB	22–37 %	89–155 gPHA/kg TS	Papa et al., 2022
	Fruit Waste	*Rhodobacter, Amaricoccus, Zooglea*	1 % HV; 33 % 3HB; 66 % HHx.	71.3 %	–	Silva et al., 2022
	OMWW	–	10 % 3HV; 90 % 3HB	54 %	–	Dionisi et al., 2005
	OMWW	*Meganema perideroedes*	–	29 %	–	Beccari et al., 2009
	OMWW	*Pseudomonas putida*	–	9 %	–	Ntaikou et al., 2009
	OMWW	*Pseudomonas putida*	3HB, 3HO	25 %	–	Ntaikou et al., 2014
	OMWW	*Pseudomonas putida*	64–76 % 3HB; 6–22 % 3HV; 8–22 HHx.	9 %	–	Kourmentza et al., 2015
	OMWW	–	6–10 % 3HV; 90–94 % 3HB	30 %	1.50 g PHA/(L d)	Campanari et al., 2014
	OMWW	*Thauera*	14–21 % 3HV; 79–86 % 3HB	–	1.05 g PHA/(L d)	Campanari et al., 2017

obtainment of a concentrated acidic stream, to be used as feeding solution in the consecutive fed-batch culture system for PHAs production. After 52 h of aerobic fermentation, the culture produced almost 15 g/L of cells with 71 % of PHA content (w/w). The PHA was composed by 94 % of 3-hydroxybutyrate (3HB) and 6 % of 3-hydroxyvalerate (3HV). These results are comparable to those obtained in other experiments performed with a VFAs-water simulating solution and from pure VFAs; meaning that the use of this waste did not cause any inhibition effects.

A deeper analysis of the CW acidogenic fermentation stage was performed by Duque et al. (2014). The authors investigated the fermentation products profile when shifting the feedstock to CW from sugar cane molasses. The CW acidogenic fermentation showed a net dominance of acetic and butyric acids concentration. As a consequence, the MMC selection stage also showed a PHA with different composition compared to the utilization of fermented molasses, being linearly dependent on the concentration of HV and HB precursors produced in the acidogenic stage. The selected culture reached a maximum PHA content of 65 % with fermented CW.

Colombo et al. (2016) showed that the chemical composition of fermented CW affected the PHA composition despite of the utilization of the same pre-selected MMC. The authors investigated the use of two different fermented CW (fCW$_1$ and fCW$_2$). The fCW$_1$ contained lactic, acetic, and butyric acids at 58 %, 16 % and 26 % respectively; the fCW$_2$ was composed by lactic, acetic, butyric, propionic and valeric acid at 6 %, 58 %, 13 %, 19 %, 4 % respectively. The authors quantified an overall yield of the process for both substrates: for fCW$_1$, 60 g PHA/kg TS was achieved; for fCW$_2$, the value was higher and equal to 70 g PHA/kg TS. Qualitatively, PHA from fCW$_1$ was made up exclusively of 3HB, while the PHA obtained from fCW$_2$ was composed of 40 % of 3- HV and 60 % of HB.

Another issue that has been analyzed by Valentino et al. (2015) was the fate and effect of β-hexachlorocyclohexane (β –HCH), a toxic and persistent pesticide utilized in the past in agriculture sector. Contaminated CW was utilized, after acidogenic fermentation, as substrate for PHA production by MMC. The authors did not report any inhibitory effect on the overall process performances by the β –HCH. The level of contamination (from 0.0 to 2.0 mg β –HCH /L) did not affect the final VFA concentration achieved (7.0–8.0 g COD$_{VFA}$/L); in addition, the fed-batch aerobic tests for PHA accumulation showed similar results independently from the initial β –HCH concentration. In view of the utilization of PHA derived from contaminated CW, the authors assessed the β –HCH migration through the whole process. The results showed that around 90 % of β –HCH was adsorbed on CW solids and it was removed in the solid/liquid separation step (after acidogenic fermentation); an additional removal occurred during the PHA purification steps, reaching an overall 99,9% removal of β –HCH content (Valentino et al., 2015).

Nutrients supplementation is another aspect of PHA production that can be detrimental in the technical feasibility of MMC-PHA technology. CW is usually poor in nitrogen content and, in the frame of PHA production, a certain *N*-supply is necessary. In this context Oliveira and colleagues (2018) evaluate CW proteins as a source of nitrogen for PHA-producing MMC, aiming to eliminate or reduce the cost of nutrients supplementation. The decrease on nitrogen supplementation from a C/N ratio of 100/10 to 100/7.5 induced significant changes in the microbial community and reduced their storage yield and PHA productivity by 30 % and 45 %, respectively. Hence, the system needed a supplement of nitrogen at a total C/N ratio of 100/10 to work properly with CW as the carbon source, as a PHA-accumulating MMC capable of using proteins as the only nitrogen source could not be achieved (Oliveira et al., 2018). Going one step beyond, Carvalheira et al. (2022) set the viability of producing custom PHA with different HV content, through manipulation of the acidogenic fermentation step. The best PHA properties and composition for melt processing was obtained with a fermented stream having an HV precursor (propionic, valeric) content of 9–33 wt%. The selected MMC was successfully obtained under the uncoupled C—N feeding strategy, particularly suitable for *N*-poor feedstock like CW. The MMC accumulated PHA up to 60 % g PHA/g VSS. This study showed the validity of the process at pilot scale, hence supporting larger scale applications for custom PHA production (Carvalheira et al., 2022).

Another study investigating the impact of the feedstock shift was firstly addressed in the variation of VFA profile when the feedstock was gradually changed from pure CW to brewery wastewater (BW) and CW mixture, by increasing the amount of BW up to 50 % of the organic content (Lagoa-Costa et al., 2022). The increase of BW content led to a drop of butyric acid from 52 % to 27 % COD basin, while the production of acetic acid increased from 36 up to 52 %. In addition, the gradual BW increase led to a progressive drop in the degree of the acidification yield, from 0.72 to 0.57 COD$_{VFA}$/COD$_{SOL}$. In the second stage of the research, the obtained VFA-rich streams (characterized by different CW and BW content) were used as substrates in PHA accumulation tests. Similar results were obtained in terms of PHA storage ability (46–51 % g PHA/g VSS), but with a slight variation in monomeric composition. The PHA was only composed by HB and HV monomers; higher HB content (up to 88 % w/w) was related to higher level of CW in the feedstock.

3.2. *Olive milling by-products*

Remarkable attention has been dedicated in the last ten years to discovering viable solutions for handling the OMWW with the aim of reducing the organic load of this by-product and its polluting effects. It has to be emphasized that OMWW can be easily fermented in a dark fermentation process to produce VFA, which are the direct precursors for microbial PHA synthesis (Estévez-Alonso et al., 2021). In fact, the lipidic and phenolic substances contained in the OMWWs generally do not inhibit the acidogenic fermentative bacteria, but they have negative effects on the methanogenesis, making such feedstock unsuitable for anaerobic digestion process (Vuppala et al., 2022). The acidogenic fermentation step is crucial for the transformation of carbohydrates into VFA and other carboxylic acids, to be utilized as building blocks by aerobic PHA-accumulating biomass (Garcia-Aguirre et al., 2017). The literature suggests that the carbohydrates content can reach up to 60 % of the OMWW total dry weight (in the range 4–17 g/L) (Blanco et al., 2022). Hence, OMWW need previous acidification and subsequently the effluent of this anaerobic process can be treated aerobically, using selected MMC for PHA production (Table 3). The technology of PHA production from acidified OMWW has been extensively investigated (del Contreras (2020)) and, sometimes, even in combination with energy recovery (Ntaikou et al., 2009).

Dionisi et al. (2005) firstly investigated the feasibility of using OMWW as feedstock for PHA synthesis, including the necessary step of the anaerobic VFA production (discussed in the section 2.2 above).

An olive continuous centrifuge processing plant furnished OMWW with soluble COD 34 of g/L. OMWW centrifugation plus fermentation was the best method for high acidification performances; in addition, centrifugation pretreatment increased the content of VFA with odd number of carbon atoms (propionic and valeric acids) compared to untreated OMWW. The odd VFA led to the formation of the HV monomer in the biopolymer; such characteristic is often required since it improved the thermal and mechanical properties of the PHA. The following PHA-accumulation batch tests (performed with VFA-acclimated MMC) indicated that centrifuged and fermented OMWW did not contain inhibiting compounds (at least at the chosen concentration). The storage yield ($Y_{P/S}^{batch}$) on removed VFAs was close to 1.0 COD$_{PHA}$/COD$_{VFA}$, indicating that PHA can be also produced by readily biodegradable carbon sources other than VFA, usually contained in fermented OMWW. The final PHA content in the biomass was also remarkable (54 % g PHA/g VSS).

Then, the performance of a three-stage PHA production process was evaluated (Beccari et al., 2009). In the first anaerobic stage, OMWW were fermented in a packed bed biofilm reactor; the obtained VFA-rich stream was fed to the SBR. The PHA accumulation capacity of the selected consortia was exploited in the third fed-batch aerobic stage. The

OMWW was taken from a three-phase olive mill in Sant'Agata d'Oneglia (Imperia, Italy) and directly fed to the anaerobic packed bed biofilm reactor (PBBR). The OMWW had the following features: pH 5.5, soluble COD 37.0 g/L, TSS and VSS were 22.6 and 16.6 g/L respectively, TKN 4.97 g/L, total phenolic fraction 1.5 g/L. The PBBR technology was chosen to reduce the risk of shock loading and/or washout problems. The VFA concentration in the effluent was 10.7 gCOD/L, meaning that this stage increased the VFA percentage in the OMWW up to 32 % (COD basis). Acetic, butyric and propionic acid were equal to 62 %, 22 % and 12 % respectively as COD fraction of total VFA. Alcohols were also detected for about 22 % of the overall COD (mainly ethanol).

The aerobic SBR was operated at an overall OLR of 8.5 gCOD/(L d), or 2.7 gCOD/(L d) in terms of VFAs only. Selective pressure on the aerobic culture was successfully maintained: the maximum value of PHA storage yield was 0.36 COD_{PHA}/COD_{VFA}. The SBR stage also allowed a significant reduction of the polluting load of the fermented OMWW, which COD content was removed up to 85 %. The third aerobic fed-batch stage was performed at increased loads compared to SBR, up to 9-fold. The maximum concentration of produced PHA and the polymer content in the biomass increased almost linearly with the amount of fed fermented OMWW. This indicated the possibility to operate the process at relatively high OLR without substantial inhibition phenomena (usually due to lipids and phenolic compounds). The storage yield remained nearly unchanged ($Y_{P/S}^{batch}$, roughly 0.35 COD_{PHA}/COD_{VFA}) compared to the value observed in the SBR. The authors reported clear evidence that a significant contribution to PHA storage was due to substrate other than VFAs, mostly ethanol.

The feasibility of using OMWW as feedstock for combined hydrogen and PHA production, leading to cost effective and environmentally sustainable solution, was demonstrated by Ntaikou et al. (2009). A two stages system consisting of anaerobic continuous stirred tank reactor (CSTR) and aerobic SBR was set up. The anaerobic CSTR was fed with diluted OMWW and operated at different HRT. Hydrogen and VFA production were differently favored by the chosen HRT. The range of 27–33 h as HRT boosted the OMWW acidification, and in particular propionic acid production; hydrogen, butyric and acetic acids production were favored at lower HRT (below 15 h). The CSTR effluent was then collected, filtered, sterilized, and used as substrate for aerobic PHA production. The SBR was characterized by a mixed culture dominated by *Pseudomonas putida* and operated in sequential cycles of nitrogen excess (growth phase) and nitrogen limitation (PHA accumulation phase). The SBR was characterized by an overall cycle length of 3.5 days; in the accumulation phase, butyrate was preferably consumed, indicating that the PHA was dominated by polyhydroxybutyrate fraction. The counted reduction of dissolved COD was higher than the only VFAs uptake, indicating that other substances different from VFAs were also consumed. The level of PHA content showed variations ranging from 4.0 % to 9.0 % g PHA/g VSS; the authors suggested further improvements according to the behavior of the culture (*Pseudomonas putida*), which can accumulate large amounts of PHA under different types of nutrient limitation. In a following study, the double effect of nitrogen–oxygen limitation on PHA production has been investigated, by using both synthetic VFA mixture and OMWW (Kourmentza et al., 2015). PHA production was performed in fed-batch tests using both the enriched mixed culture and isolated strain of *Pseudomonas putida*. The enriched culture showed high PHA production capacity, achieving a PHA content higher than 60 % g PHA/g VSS under nitrogen limitation in the synthetic VFA mixture. However, with the utilization of OMWW, the PHA accumulation significantly decreased to 9 % g PHA/g VSS roughly, even with the dual oxygen–nitrogen limitation. The same behavior was observed with the isolated strains.

In another study by Ntaikou et al. (2014), a two-stage system for PHA production from OMWW (pH 5.5, COD_{TOT} 112 g/L, soluble COD 38 g/L, soluble carbohydrates 17 g/L), obtained from a three-phase olive oil mill process, was conducted at pilot scale. The acidified OMWW (after the dark fermentation step; approximately 8.0 $gCOD_{VFA}/L$) was collected in a sedimentation tank in which partial removal of the suspended solids occurred. Then, it was fed to SBR, where an enriched culture of *Pseudomonas sp.* was used as aerobic inoculum. The clarification of the OMWW with aluminum sulphate to promote a further flocculation and solids precipitation, and its effect on the composition of the acidified OMWW as well as on the PHA yield and properties was investigated. The clarification step had no significant effect on the VFA distribution and on the residual sugars, but only on the values of TSS and COD_T of the acidified OMWW. In addition, the PHA composition and thermal characteristics were also similar for both clarified and not clarified OMWW. However, the clarification step had a positive impact on PHA accumulation, leading to a final content of 25 % g PHA/g VSS. The PHA composition revealed the presence of 3-hydroxybutyrate (3HB) and 3-hydroxyoctanoate (HO) units; the latter was poorly founded in the MMC-derived PHA (Valentino et al., 2017).

In a parallel study, MMC-PHA production has been investigated by using OMWW as no-cost feedstock in a multi-stage process, also involving phenols removal and recovery (Campanari et al., 2014). The typical SBR for biomass selection/enrichment was fed with dephenolized and fermented OMWW, and maintained under an OLR ranging from 2.40 to 8.40 gCOD/(L d). The best selection performances were observed at intermediate OLR (4.70 gCOD/L d), being storage rate and yield equal to 339 $mgCOD_{PHA}/(gCOD_{VSS}\ h)$ and 0.56 COD_{PHA}/COD_{VFA} ($Y_{P/S}^{feast}$) respectively. The applied OLR strongly affected the performance of the fed-batch PHA-accumulating reactor, which was fed through multiple pulsed additions of pretreated OMWW. An overall mass balance (considering the anaerobic fermentation step and the two aerobic steps) has been assessed: the COD abatement was estimated to be 85 % roughly, whereas the conversion of the influent COD into PHA was close to 10 %. The aerobic two-stages PHA volumetric productivity was equal to 1.50 gPHA/(L d).

In a following study, fermented OMWW was subjected to a solid/liquid separation step (centrifugation); the residual solid fraction was utilized for biogas production, whereas the liquid fraction was utilized as carbon source for both biomass selection/enrichment (SBR) and accumulation (Campanari et al., 2017). Considering this liquid fraction, most of the soluble COD (approximately 70 %) was removed in the SBR; in addition, a settling phase was included in each SBR cycle (at the end of the feast phase and before the famine) to uncouple COD feed from nitrogen supply. This strategy allowed to maximize the selective pressure towards PHA-storing microorganisms. In fact, PHA production significantly increased in the accumulation fed-batch reactor, achieving a final concentration close to 2.5 gCOD/L. Finally, the anaerobic digestion tests showed that the residual COD contained in the solid fraction of fermented OMWW, was almost totally converted into methane (up to 100 %), demonstrating the success of the holistic approach for OMWW valorization.

3.3. Winery wastewater

The use of by-products of wine production to obtain PHA has been gaining some interest as it would represent another cheap raw material that would overall highly reduce the cost of PHA production. To the authors' best knowledge, since the use of these by-products is quite recent, only pure culture applications to wine by-products to produce PHA exist, while MCC are still to be implemented (Table 3).

In this context, Follonier et al. (2014) utilized Solaris grape pomace as substrate to produce medium-chain-length (*mcl*) PHA. Different enzyme preparations were tested to convert polysaccharides from the pomace into fermentable monosaccharides. The fermentation experiments were set in a 0.1 L bio-fermenter, with a two-step fermentation with *Pseudomonas resinovorans* as pure culture. The authors reported a high final PHA concentration (21.3 g/L) with a productivity of 0.05 g/L/h.

The following year, the same authors obtained a higher volumetric productivity (0.10 g/L/h) by employing a 2-step bioprocess with

Gewurztraminer pomaces as the raw material and *Pseudomonas putida* KT2400 as the chosen microorganism, in a 100 L bioreactor operating in fed-batch conditions. The experiment involved two phases: a batch growth on the extract of the grape pomace, and a fed-batch polymer accumulation phase with a linear feed of 50 mol % octanoic acid and 50 mol % 10-undecenoic acid. With this approach, the authors achieved a final *mcl*-PHA content 41 wt% (5.8 g PHA/L) of poly(3-hy-droxyoctanoate-*co*-3-hydroxy-10-undecenoate) with 53 mol % and 47 mol % of saturated and unsaturated monomers, respectively (Follonier et al., 2015).

Martinez and colleagues developed a multi-purpose four step-cascading biorefinery scheme for the valorization of grape pomace from red grapes *Vitis vinifera L.* varieties.

The processes had multiple aims: i) the recovery of polyphenols by supercritical CO_2 extraction, ii) the production of volatile fatty acids (VFAs) by anaerobic acidogenic digestion, iii) the employment of those VFAs to produce PHAs and iv) the production of CH_4-rich biogas by the anaerobic digestion of solid by-products from the acidogenic process. The authors extracted more than 2.7 g of total polyphenols per 100 g of dry matter, with a high content of valuable proanthocyanidins. The resulting dephenolized material was placed under batch acidogenic anaerobic conditions to obtain a VFA-rich stream at 20 g VFA/L (roughly). Then, a pure culture of a *Cupriavidus necator* strain stored PHA under nitrogen-limiting conditions in 0.5 L-shake flasks with a two-step production. The pre-grown biomass was fed with the acidic effluent and the poly(3-hydroxybutyrate) was accumulated up to 63 % of the cells dry weight. As a circular approach in the utilization of the waste, the authors quantified a production of 113 mL of biomethane per gram of volatile solids (Martinez et al., 2015), in the anaerobic digestion process carried out with the solid by-products obtained from the previous fermentation step.

Kovalcik et al. (2020) utilized grape pomace and fermentable sugars derived from the pomace as carbon nutrient for three different microorganisms, namely *Cupriavidus necator*, *Halomonas halophila* and *Halomonas organivorans* to produce poly(3-hydroxybutyrate) (PHB), with the aim of finding the best PHB-producer. *Cupriavidus necator* proved to be the best one and was employed in a 2-L reactor, obtaining a volumetric PHB productivity of 1.36 g/(L h). In 29.5 h of aerobic cultivation, PHB concentration was 8.3 g/L, and 63 % PHB content in bacteria cell dry mass. The authors discussed the possibility to isolate cellulose, lignin, pigments and phenolic compounds from the same raw materials, under a holistic approach of waste circularity and benefits maximization from waste treatment.

Similarly, Dimou et al. (2015) developed an innovative integrated bio-refinery with wine lees as the raw material able to produce antioxidants, tartrate, ethanol, and the remaining stream was used as a fermentation nutrient supplement for poly(3- hydroxybutyrate) (PHB) production by *Cupriavidus necator* DSM 7237. In this study however, the wine lees were not used as the carbon source but as nutrient-rich supplement medium, while the carbon source was crude glycerol, both in batch and fed-batch fermentations. The culture was able to accumulate PHB up to 71 % w/w; the final PHB content was equal to 30 g PHA/L, with a corresponding productivity of 0.56 g/(L h).

3.4. Organic fraction of municipal solid waste (OFMSW)

More recent and innovative technologies have been aimed to the valorization of food waste into PHA, with many examples that describe the MMC technology applied to the fermented food waste stream and/or food-derived carbon source (Table 3). The achieved results are promising and the direction of the research in this field is currently addressed to the first demonstrative prototypes in Europe.

The first example related to the PHA production from food waste described a multistage process where the first step involved the production of bio-hydrogen via acidogenic fermentation (Amulya et al., 2015). The obtained VFA-rich stream (from bio-H_2 reactor) was subsequently used for the aerobic PHA synthesis, which was carried out according to the typical two-steps described above (MMC enrichment + fed-batch PHA production). Two SBR cycle length were investigated: 12 h and 24 h. The biomass achieved higher performances at the lowest cycle length investigated (12 h). However, PHA production was strongly limited by low VFA concentration of the feed (roughly 6.0 g COD_{VFA}/L); the enriched biomass produced PHA with a relatively low specific rate of 40 mg COD_{PHA}/(g COD_{Xa} h), with a final PHA content of 24 % g PHA/g VSS. The latter was negatively affected by the abundant amount of COD_{SOL} (other than VFA) in the fermented feedstock since the fermentation step was optimized for H_2 production rather than VFA. Despite of these limitations, this study was the first one proposing an integrated multistage process as an opportunity to obtain PHA with simultaneous waste remediation in a biorefinery framework.

In a following study, leachate from the source separated OFMSW was used as a substrate for PHA production (Korkakaki et al., 2016). The authors identified the inhibitory effects of the leachate, giving a practical solution to overcome this problem. The selection/enrichment step (SBR) was firstly conducted on leachate through the typical aerobic feast-famine regime. The maximization of the PHA content of the selected biomass led to a value below 30 % g PHA/g VSS, suggesting that this leachate-based strategy for PHA-producers was unsuccessful. When the substrate for the SBR was switched to a synthetic VFA mixture, the PHA production ability of the microbial community was boosted and in most of the following accumulation tests performed with leachate, the biomass accumulated PHA slightly below the 80 % g PHA/g VSS. The results suggested that the enrichment of a PHA-producing community with a clean acidified stream, and the PHA accumulation with a stream that did not allow for enrichment but enabled high PHA content (the OFMSW leachate), made the overall PHA production process attractive from both technical and economical point of view. The estimated yield in the selection reactor (0.47 COD_{PHA}/COD_{VFA}) has been increased fourfold in comparison to direct use of the complex matrix like the OFMSW-leachate.

Colombo et al. (2016) optimized the OFMSW acidogenic fermentation process in a pilot scale anaerobic percolation biocell reactor (100 L), to produce a VFA-rich percolate from OFMSW, subsequently used for PHA synthesis. The extracted VFA counted for 151 g per kg of fresh OFMSW; the following aerobic PHA line exhibited a yield of 223 g PHA per kg of fed VFA, with a content up to 47 % g PHA/g VSS. The authors gave a first mass balance of the process (even though only the fermentation stage was developed at pilot scale) equal to 114 g PHA/kg TS (from OFMSW). The relevance of this work consists in its usefulness for considering the economic feasibility of PHA production from OFMSW by MMC.

Valentino et al. (2018) added another step compared to the previous work (Colombo et al., 2016). The authors developed a pilot scale integrated-multistage process as a practical example of a biorefinery platform, where the OFMSW (squeezed and mechanical pre-treatment) was used as carbon source for both PHA and biogas production. In this system, the fermentation stage was included in a two-phases anaerobic process, where part of the fermentation effluent was utilized to recover biogas and digestate as fertilizers. Both technical and economical feasibilities have been demonstrated, providing a possible upgrade to traditional OFMSW management practices. The reliable biomass enrichment was demonstrated by a stable feast-famine regime which favored the growth of taxa as *Acidovorax* and *Hydrogenophaga*, usually found in aerobic MMC system under dynamic feeding regime ($Y_{P/S}^{feast}$ 0.41 COD_{PHA}/COD_{VFA}). The selected consortium was able to accumulate PHA up to 55 % g PHA/g VSS. If compared to the benchmark technology (anaerobic digestion) in an urban scenario of 900.000 People Equivalent (PE), the integrated approach for OFMSW valorization is preferable, and it is characterized by an electrical energy production of 85.7 MWh/d, overall PHA yield of 37 g PHA/kg TS and 1.976 t/d as PHA productivity.

In a following work, a simple biorefinery aimed at producing both biomethane and PHA from the OFMSW was described (Papa et al., 2020). The authors proposed the utilization of VFA-rich digestate as substrate for PHA production, starting from the anaerobic digestion process of the OFMSW carried out at different medium–low OLR. The global PHA yield reached almost 200 g PHA/kg TS. By also considering the biogas production of 500–600 NL/kg vS (CH_4 content of 64–67 % v/v), the net energy recovery of this biorefinery was equal to 64 % of OFMSW energy content. Most of the rest was represented by PHA, roughly 30 % of the total energy. To investigate the effect of the solids/liquid separation of the OFMSW on the global performance of the biorefinery approach, the following study was focused on the utilization of OFMSW liquid fraction for PHA synthesis, and biomethane from the OFMSW residual solid fraction (Papa et al., 2020). A complete mass and energy balance have been calculated, with the two major outcomes represented by the global PHA yield (115 g PHA/kg TS) and residual biomethane (219 g CH_4/kg TS). Energy balance indicated that nearly 40 % of OFMSW energy was recovered as bio-products. Compared to the previous study (Papa et al., 2020), the authors judged this approach unsuccessful since the initial anaerobic digestion was performed after the VFA separation. Similar biorefinery approach was also followed by utilizing the squeezed OFMSW in a mixture with sewage sludge (Moretto et al., 2020b, 2020a; Valentino et al., 2019b). It is noteworthy that these examples described a biorefinery platform completely developed at pilot scale. The outcomes of these works revealed a progressive improvement of the performances related to PHA production, for both global yield (from 76 to 110 g PHA/kg TS) and the final PHA biomass content (from 47 % to 59 % g PHA/g VSS). These improvements had a positive impact on the economic evaluation, in turn affected by the hypothetic PHA selling price and by the global mass and energy balance assessment.

As a sub-category of OFMSW, fruit waste was also successfully used for PHA production. Matos et al., 2021) utilized the OLR and pH as tuning parameters in the fermentation reactor to obtain a high VFA yield (0.74 COD_{VFA}/COD_{SOL}). The MMC was highly enriched in PHA-storing microorganisms based on the possibility to operate with the uncoupled carbon–nitrogen feeding. The maximization of the selective pressure allowed to obtain a high storage yield ($Y_{P/S}^{feast}$ 0.98 COD_{PHA}/COD_{VFA}), with a final PHA content close to 80 % g PHA/g VSS. The high global productivity (8.1 g PHA/L d) was due to the notable value of VSS (7.83 g/L) as a response to the high OLR (up to 14.5 gCOD/L d) applied. In addition, the adopted sludge retention time (4 days), which was higher than the HRT (1 day) was a crucial factor to increase biomass productivity as well as the VSS content in the SBR. Also, the PHA storage yield was independent of the SRT, and was directly linked with the abundance of putative PHA-producing microorganism in the MMC. These results demonstrate how a nitrogen-poor feedstock such as the food waste, in combination with different effective strategies to maximize the process performance, can be a promising source for the full-scale implementation of MMC-PHA production technology.

The great part of available literature on MMC processes describes the production of PHA copolymers containing 3HB and 3HV, naturally produced by microorganisms acclimated to different waste. The study by Silva et al. (2022) is particularly relevant since it showed the production of PHA enriched in 3-hydroxyhexanoate (HH) from fruit waste as substrate. Each process stages (acidogenic reactor, SBR and PHA accumulation reactor) was tuned to maximize the process's yield and productivity. In particular, the UASB fermentation reactor was manipulated in its operating conditions (OLR from 5 g COD/(L d) to 28 g COD/(L d), pH kept at 5.0, HRT of 1 d, and temperature of 30 °C as temperature). These conditions enriched the fermented effluents in caproic acid (69 % of the total VFA), with a total VFA concentration of 13.0 g COD_{VFA}/L. The selected MMC (under uncoupled carbon–nitrogen feeding regime) was able to convert caproic acid into HH, achieving a maximum PHA content of 71 % g PHA/g VSS, and a PHA productivity of 3.29 g COD_{PHA}/(L d). Notably, the PHA composition was 33/1/66 as HB/HV/HH % w/w respectively. This work shows values of yield, productivity and HH fraction for the production of a medium chain length (mcl) PHA never reported before, in the frame of MMC process. For this reason, it represents a significant contribution towards upscaling the technology from waste to HH-rich PHA.

4. PHAs potential production from cow milk, olive oil, wine's by-products and OFMSW: A global estimation

The agro-food substrates considered in this review article showed very different VFAs and PHAs production's yields, which were strongly affected both by their chemical compositions, by the operati onal parameters and the reactors configurations. Anyway, considering their annual availability, their solid content (Tables 1 and 2) and the conversion yields into PHAs, the four agro-food substrates have an extraordinary PHAs potential of about 260 M tons/year at worldwide level.

In particular, the best substrate in term of productivity was OFMSW, whose VFAs and PHAs yields were in the range of 0.30–0.45 $g_{VFA\text{-}COD}/g_{COD}$ and of 0.4–0.5 $g_{PHA}/g_{VSS,}$ respectively. Considering the huge annual OFMSW capita production of 85 kg per person (Statista, 2020) and the world human population of about 7,800 M people, the annual potential PHAs production can be estimated at about 240–250 M tons from OFMSW.

CW is another food by-product with a good PHAs yield. Considering it annual production of 180–190 M tons (Table 1), their VSS content (Table 2) and the PHAs yield of 0.4–0.5 g_{PHA}/g_{VSS}, the potential global annual PHAs amount from CW can be of 5–6 M tons. Similarly, it is possible to estimate the PHAs from WW productions. WW showed higher process yield in terms of PHAs (0.6–0.7 g_{PHA}/g_{VSs}), with a consequent PHA potential world annual production of 1.5–2 M tons PHA/year. Regarding the olive by-products, it is necessary to remark that, even if abundant in the national territory, they were few investigated both for VFAs and PHAs conversion. Moreover, the few research papers focused the attention only on the liquid fraction of olive oil production, the OMWW. The OP-OMWW annual production around the world is estimated at 16 M tons (Batuecas et al., 2019). Supposing an equal proportion between OP and OMWW and considering OMWW VSS content and an average conversion yield of 0.2–0.3 g_{PHA}/g_{VSS}, it is possible to estimate an annual global PHA productions of about 500 k-1 M tons.

5. Research needs and future directions

The food wastes' conversion into biofuels and high added value compounds, such as VFAs and PHA, saw a great advance in the last decades thanks to the scientific experimentations and the implementation of research projects, which allowed the reaching of pilot and demonstrative technologies' levels (Battista et al., 2022). Anyway, there are still different technological aspects to be improved for a successful realization of a full scale biorefinery. Even if the VFAs fermentation's knowledge was largely investigated, the main challenge consists in the VFAs separation step from the fermentation medium and their concentration until the reaching of the required industrial-grade concentrations of 70–100 g/L. Many techniques were proposed at this scope: (i) VFA precipitation, (ii) liquid–liquid extraction, where VFAs are separated by organic solvents, (iii) membrane separation, using electrodialysis, where a voltage difference promotes VFA passage through the membrane, (iv) nanofiltration, where the passage is driven by the size or pressure gradient, and (v) adsorption, where VFAs are separated through VFA interactions with the activated sites of a solid matrix (Rizzioli et al., 2021). Even if some encouraging result was achieved, a major part of the investigations was essentially performed at laboratory scale only. Consequently, the scientific community needs to focus its efforts on the scale-up of the VFAs purification's processes in order to have an efficient biobased VFAs' exploitation at industrial level.

Regarding the PHAs, the reported data have shown the technical feasibility of their production and their potential applications from pilot scale demonstrations. However, for the larger scale investigations there are still some fundamental aspects yet to be implemented. As highlighted by Estévez-Alonso et al. (2021), on one hand the upstream processes have been assessed more thoroughly and have provided important information about the feedstock, the yield and how to maximize the production of PHA. On the other hand, the knowledge regarding the downstream processes and the possible final PHA use are still lacking. Regarding the downstream processes, the main challenge is related to the lack of data about the type of PHA composition and polymer properties in scaling-up efforts, in addition to the uncertainty about the demands of molecular mass and purity required for the applications. At the moment, the lack of substantial amounts of the polymer in large prototype plant is the main obstacle in the upscaling efforts, as it doesn't allow the testing of the different types and grades of the MMC-derived material for different purposes, in order to adjust the downstream processes accordingly. To overcome these issues Estévez-Alonso and colleagues (2021) recommend the use of a demo-scale PHA production, to obtain enough waste-derived PHA to be tested as potential marketable products. Parallel to the laboratory research, a precise business evaluation is necessary to assess the economic and commercial scale and growth potential, as well as the best fitting applications in the potential market.

6. Conclusions

The review demonstrated the possibility to exploit OFMSW and the main by-products and wastewaters from the transformation of the most abundant food commodities (cow milk, olive and grapes) for VFAs and PHAs productions according to a biorefinery loop. OFMSW and CW were largely investigated in the last years leading to good performances of about 0.5–0.9 g_{VFAs}/g_{COD} and 0.4–0.5 g_{PHA}/g_{VSS}. WW achieved good yield too (0.6–0.7 g_{PHA}/g_{VSS}), but this substrate was less investigated by the scientific community. Similarly, OMWW was essentially studied for biogas production and the few studies on VFAs and PHAs productions led to lower yields.

CRediT authorship contribution statement

Marco Gottardo: Writing – review & editing. **David Bolzonella:** Supervision. **Giulia Adele Tuci:** Writing – review & editing. **Francesco Valentino:** Conceptualization, Writing – review & editing. **Mauro Majone:** Supervision. **Paolo Pavan:** Supervision. **Federico Battista:** Conceptualization, Writing – review & editing, Supervision.

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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