Volatile fatty acids production from organic waste for biorefinery platforms

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Abstract

Short chain volatile fatty acids can be produced through the acidogenic fermentation of organic waste of different origin. These compounds are extremely useful as starting compounds for the chemical industry of biopolymers, such as PHAs, reduced chemicals and derivatives. The aim of this paper is to collect and review the data obtained within twenty years of research on anaerobic fermentation of the organic fraction of municipal solid wastes, fruit/vegetable wastes, waste activated sludge and agrowaste, carried out by the same research group, so to generalize the obtained results and compare those with literature data obtained in similar conditions. The yields in terms of volatile fatty acids production per kg of organic matter (as chemical oxygen demand) were evaluated and compared, considering process parameters such as hydraulic retention time, organic loading rate, and temperature.

1. Introduction

Significant efforts have been made over the last few years to achieve an appropriate transition towards a biobased economy, aiming to replace fossil-derived fuels and chemicals with new sustainable biofuels and value-added bioproducts respectively. The first generation biorefineries, which used crops as feedstock, raised an ethical debait known as "food/feed vs. fuel" (De Jong & Jungmeier, 2015; Tomei & Helliwell, 2016). In order to overcome this disagreement, the new-generation biorefinery platforms encourage a multi-feedstock input, in other words, the use of wide available organic waste, by-products and residues that are not directly used for feed/food purposes (including agricultural, municipal, industrial wastes) to be converted in a complete portfolio of different intermediates, biobased compounds and biofuels (Koutinas et al., 2014; Galkin et al., 2016; Nizami et al., 2017).

In this scenario, organic carboxylic acids, particularly Short Chain Volatile Fatty Acids (SC-VFAs), i.e., C<5, are of great interest as they constitute a group of functional molecules, which serve as starting material for the chemical industry (Martinez et al 2016). SC-VFAs are linear short-chain aliphatic carboxylate compounds with a carbon chain consisting of C2 (acetic acid) to C5 (valeric acid). Because of their functional groups, SC-VFAs are extremely useful as represent suitable precursors for production of biopolymers, such as polyhydroxyalkanoates (PHAs), reduced chemicals and derivatives (esters, ketones, aldehydes, alcohols and alkanes) as well as biofuels like CH_4 and H_2 (Raganati et al 2014).

Conventionally, SC-VFAs are produced biologically via fermentation pathways, using pure culture of specific anaerobic bacterial strains, achieving high SC-VFAs yields. Nevertheless, to make economically viable the production of SC-VFA from organic wastes, the use of mixed microbial cultures (MMCs) is particularly attracting (Bhatia and Yang, 2017). Although MMCs performance may leas to lower yields in terms of SC-VFA, they have several advantages, since non-sterile conditions are needed, and risk of contamination is decreased. At the same time, MMs can be able to metabolize a wide spectrum of organic waste, such as agricultural or urban wastes like wastewater sludge and food waste. (Jankowska et al., 2015).

However, in order to strengthen the potential of MMCs fermentation in terms of SC-VFAs production, it is necessary to pay close attention to process parameters and operational conditions during the experimental setup. In fact, different hydraulic retention time (HRT), organic loading rate (OLR), temperature, and pH, may lead to fermentation end-products other than SC-VFAs, such as longer chain fatty acids, alcohols, biohydrogen, biomethane, esters, and other intermediates (Venkata Mohan et al. 2016).

This paper review the results we obtained in studies about the production of SC-VFAs by MMCs working either in mesophilic or thermophilic environment, and metabolizing different type of organic wastes. Results

are then compared with literature data to generalize the observed results and fix the ranges of best operational conditions.
Bottlenecks and future perspective for the process improvement are also emphasized in the paper conclusions.

2. Feedstocks for VFA production

A large variety of organic waste streams for SC-VFAs production were collected and studied in regards to their degradation potential and conversion into SC-VFAs. They include both solid and liquid wastes, particularly the organic fraction of municipal solid waste (OFMSW), sludge (both primary- and waste activated sludge), food waste, and livestock effluents of different origins (agricultural, dairy, pulp and paper industries). Furthermore, various mixtures of different organic wastes had also been studied aiming to promote a higher production of SC-VFA (Lee et al., 2014). The diversity among organic wastes, in terms of solids, chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), and total phosphorus (TP), is presented below.

2.1 Organic Fraction of Municipal Solid Waste

Organic solid waste are largely and constantly present in urban areas (Cadena et al., 2009). In this light, the valorization of OFMSW into bio-based compounds via fermentation may be extremely advantageous. OFMSW comprises household food waste, residues from markets, restaurants, canteens, company cafeterias, etc., and generally shows a high biodegradability and moisture degree. Although the composition of OFMSW strongly depends on period of collection, also on specific municipality or area (Alibardi & Cossu, 2015). For this reason, a classification of OFMSW according to its collection scheme may be useful tool to allow data comparison: SS-OFMSW, for source-sorted organic fraction of municipal solid wastes, that is food waste originating from markets or canteens; SC-OFMSW, for separately collected organic fraction of municipal solid wastes, that is segregated food waste originated at household level; MS-OFMSW, for the mechanically selected organic fraction of municipal solid wastes. Table 1 provides the average physico-chemical characteristics of different kind of OFMSW, used as feedstock in various experimental works.

2.2 Wastewater sludges

Wastewater treatment generates large amount of both primary and secondary (biological) sludge.
Sludges are rich in organic matter as well, with a COD varying from 14,800 mg/L to 23,000 mg/L (Lee et al., 2014). Anyway, the soluble COD of sludges is usually extremely low, making difficult the production of VFA. In fact, the hydrolysis is the rate-limiting step of the whole fermentation process of sludges. To enhance the hydrolysis, sludges can be pretreated before the anaerobic downstream process or, alternatively, they can be co-digestated with other substrate, for examples waste activated sludges or agro-wastes. Indeed, co-digestion promotes hydrolysis of organic matter of the sludges thanks to synergistic effects, leading to a greater VFA production (Xie et al., 2017). For example, co-digestion of starchy industrial wastewater with primary sludge gained a greater production from 31 mg VFA/g VSS/day to 45 mg VFA/g VSS/day (Maharaj & Elefsiniotis, 2001).

2.3 Agro-waste and livestock effluents

Due to their great organic content agro-wastes are characterized by a high COD. For example, sugarcane bagasse and wheat straw show a COD of 1150.40 $g \cdot kg^{-1}$ and 1188.85 $g \cdot kg^{-1}$ respectively (Bolado-Rodríguez et al., 2016). On the other hand livestock effluents show lower COD contents. Their level is comparable with the organic content of other wastes described so far. For example, cow manure shows a COD of 882 $g \cdot kg^{-1}$ (Cavinato et al. 2017). Despite these differences in terms of COD, both agro-wastes and effluents may be interesting for fermentative SC-VFA production. Nevertheless, these substrates impose some critical technological challenges, due to their chemical composition. For instance, agro-wastes and livestock effluents as cow manure are rich in lignocellulosic matter (straw), whose hydrolysis is a limiting step for the whole process (Chatellard et al., 2017). Different effective pre-treatments were developed to enhance hydrolysis of lignocellulosic fraction, using both physico-chemical and biological strategies, but their cost decrease the economic sustainability of the whole process (Carrere et al., 2016). Furthermore, some animal by-products, as chicken manure, show a high proteinaceous content, which lead to an unbalance C/N ratio. This makes those wastes less appealing also for conventional anaerobic digestion. In fact, free ammonia derived from protein degradation causes inhibition of methanogenesis. For this reason, livestock effluents are conventionally co-digested with other wastes rich in carbon, such as straw from different sources (Wang et al., 2012).

The characteristics of the organic waste used in the different experimental trials are reported in table 1.

Table 1: Characterisation of the organic waste used for VFAs production.

Origin of waste	Type of waste	TS $g \cdot kg^{-1}$	TVS $g \cdot kg^{-1}$	TVS/TS %	COD $g \cdot kg^{-1}$	TN $g \cdot kg^{-1}$	TP $g \cdot kg^{-1}$	References
SOLID WASTES								
OFMSW	SS-OFMSW	288	228	80	347	28	2.4	(Bolzonella et al. 2005)
	SC-OFMSW	88	80	91	102	23	3.7	(Traverso et al. 2000)
	MS-OFMSW	647	301	45	510	14	14	(Sans et al 1995)
	Food waste	260	216	83	954	7.5	0.8	(Micolucci et al. 2014)
AGROWASTE and LIVESTOCK EFFLUENT	Wheat straw	940	871	92.7	1081	N.A	N.A.	(Sambusiti et al 2013)
	Ensiled Sorgum Forage	930	805	86.6	1125	N.A	N.A.	(Sambusiti et al 2013)
	Maize silage	333	313	94	996	14.2	3.1	(Cavinato et al. 2017)
	Cow manure	207	169	82	882	27.8	4.7	(Cavinato et al. 2017)
LIQUID WASTES								
Origin of waste	**Type of waste**	**TS $g \cdot L^{-1}$**	**TVS $g \cdot L^{-1}$**	**TVS/TS %**	**COD $g \cdot L^{-1}$**	**TN $g \cdot L^{-1}$**	**TP $g \cdot L^{-1}$**	**References**
SLUDGE	Waste activated sludge	37	30	79	33	1.8	0.5	(Bolzonella et al. 2007)
	Waste activated sludge	62	43	68	48	3.1	0.9	(Leite et al. 2016)
	Sewage sludge (primary and secondary)	19	15.6	81	18	0.8	0.3	(Longo et al. 2015)

N.A.= not available

3. Reactors configuration

The process adopted and the consequent reactor configuration focused on the hydrolysis and acidogenic steps of biomass conversion: these are the first stages of a complete anaerobic process where the energy recovery as biogas and the consequent stabilization of the organic matter is the main aim.
Shifting the interest from biogas to volatile fatty acids production, the reactor configuration was splitted into two rectors, in order to enable the hydrolysis and acidogenic reactions in the first reactor, and methanogenic reactions in the second one (Figure 1).
The feeding system was a semi-continuous approach, once per day.
Temperature ranges (T) tested were mainly mesophilic (35-37 °C) and thermophilic (55 °C). Psychrophilic temperature (23 °C) was tested only by Cecchi et al. (1994) in order to face up the energy consumption problem, while the extreme-thermophilic temperature was adopted by Bolzonella et al. (2007) treating waste activated sludge; this option makes sense considering the difficulty of anaerobic digesting this type of substrate.
Hydraulic retention times (HRT) applied ranged from 1 day to about 6 days; just in one case was tested a longer HRT (11days), but the best yields were observed below 6 days of hydraulic retention time. Even the organic loading rate (OLR) range was wide, depending on the organic waste physical-chemical characteristics and HRT; values from 4 to 102 kgVS $m^{-3}d^{-1}$ was tested for OFMSW and food waste, and from 1.2 to 28.9 kgVS $m^{-3}d^{-1}$ for waste activated sludge.

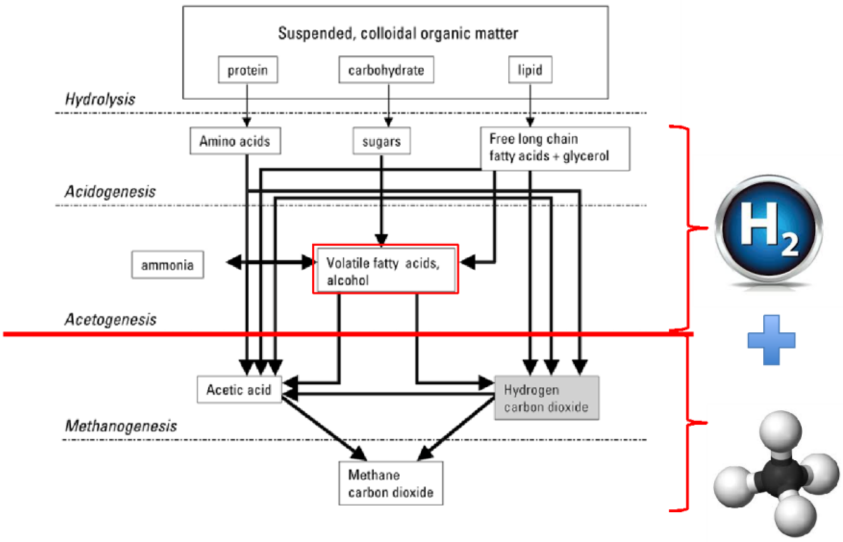

Figure 1: products cascade of anaerobic digestion biological process: phase separation to obtain volatile fatty acids.

4. Volatile fatty acids yields and composition

Table 2 shows results obtained from different experimental tests, the operational conditions (HRT, OLR, T) used, the yields and the total and single SC-VFA concentrations achieved. Although those experimental works were carried out in different years, using different size reactor and type of substrate, they were characterized by almost similar feeding approach and analytical methods, making possible a comparison among them.
Results obtained in our studies are also compared with other similar studies reported in the same table so to generalize the obtained results.

Table 2: VFAs production yields obtained.

Feedstock	HRT, (d)	OLR, $kgVS{\cdot}m^{-3}d^{-1}$	Temperature °C	Yield, $gVFA{\cdot}kgCOD^{-1}$	Conc. VFA $g{\cdot}L^{-1}$	References
OFMSW	6	4.1	23	127	9.5	(Cecchi et al., 1994)
OFMSW	1-6.6	11-66.9	35-37	64-218	7.9-23.1	(Cecchi et al., 1994; Pavan et al., 1998; Sans et al., 1995)
OFMSW	3.5	16	55	263	13.8	(Cavinato et al, 2011)
OFMSW	6.6	21	55	60	8.3	(Cavinato et al., 2011)
OFMSW	1-6.6	15-78.5	55	31-263	2.5-19.6	(Cavinato et al., 2012, 2011; Chinellato et al., 2013; Sans et al., 1995)
Food Waste	3.0-3.3	16.8-17	55-55	221-234	12.3-13.7	(Micolucci et al, 2014) (Giuliano et al., 2014)
Food Waste and Rice Straw	8	4-42.95 ($gVS{\cdot}L^{-1}d^{-1}$)	35	N.A.	~ 5.5-25.0	(Chen et al., 2015)
Synthetic Food Waste	5	5-6 ($gTS{\cdot}L^{-1}$)	35	N.A.	13.27-24.93	(Jiang et al., 2013)
Fruit/Vegetable waste	1-11	11-102	37	33-279	7.6-28.5	(Traverso et al., 2000)
Fruit/Vegetable waste	5	4.8 ($gVS{\cdot}L^{-1}d^{-1}$)	35	N.A.	~ 15	(Zheng et al., 2015)
WAS	4.6-5.9	1.2-1.9	35	207-325	3.2-7.5	(Longo et al., 2015)*

	2	15	55	383	11.4	(Leite et al., 2016)
	1-5	6.5-28.9	70	220-277	6.5-9.0	(Bolzonella et al., 2007)
OFMSW + WAS	3.3	18	55	137	8.1	(Gottardo et al., 2015)
Wheat straw	3-7	8	55-60	NA	1	(Pohl et al 2013)
Corn straw	3	30 (kgVS/m3)	35	NA	6.77	(Dong et al 2016)
Caw Manure-maize silage	2-6	11.9-35.4	37-55	62-183	6.7-14.6	(Cavinato et al., 2017)

* with the addition of NaOH and Wollastonite for pH control
N.A.= not available

It turns out clear from the data presented in table 2 that the different level of biodegradability of the different feedstocks play a major role in the final yield in terms of VFA produced: in particular, highly biodegradable substrates like food waste showed the highest conversion yields and final concentrations while slowly biodegradable organic waste like waste activated sludge and agro-waste rich in straw showed the lowest observed yields. Noticeably, comparing the yields observed for the organic fraction of municipal solid waste, food waste and agro waste it is possible to observe a specific trend, reported in Figure 2. The VFA production obtained could be above 200 gVFA kgCOD^{-1} applying HRT above 3 days when easily biodegradable substrates like food waste are treated.
On the other hand, recalcitrant substrates, like agro-waste rich in lignocellulosic material, showed a limited conversion yield.
This means that short HRT doesn't allow specific acidogenic microorganisms to grow enough to reach an interesting hydrolysed conversion into VFA. In this graph two data were excluded: the one obtained at 23 °C (127 gVFA kgCOD^{-1}) and the data obtained by Cavinato et al (2011) at 6.6 days HRT (60 gVFA kgCOD^{-1}), because it was negatively influenced by digestate recirculation (from methanogenic reactor to acidogenic one).
The yields obtained were sometimes lower if compared with those obtained from other experiences with food waste fermentation reported in literature. For example, Jiang et al. (2013) obtained yields of 379 and 440 gVFA kgVS^{-1} at 35 °C and 45 °C, respectively. Nevertheless, it must be taken into account that in these experimental tests the fermentation was conducted in a semi-continuous way, whereas in most of the extant literature, the reported yields were obtained in batch conditions.
Considering the different experiences with waste activated sludge, it was difficult to find optimal conditions, but considering the yields obtained by Peces et al. (2016) with primary sludge (maximum acidification yield of 143 gVFA kgVS^{-1} at 37 °C and the lowest yield of 23 gVFA kgVS^{-1} at 55 °C), yields above 200 gVFA kgCOD^{-1} could be obtained.

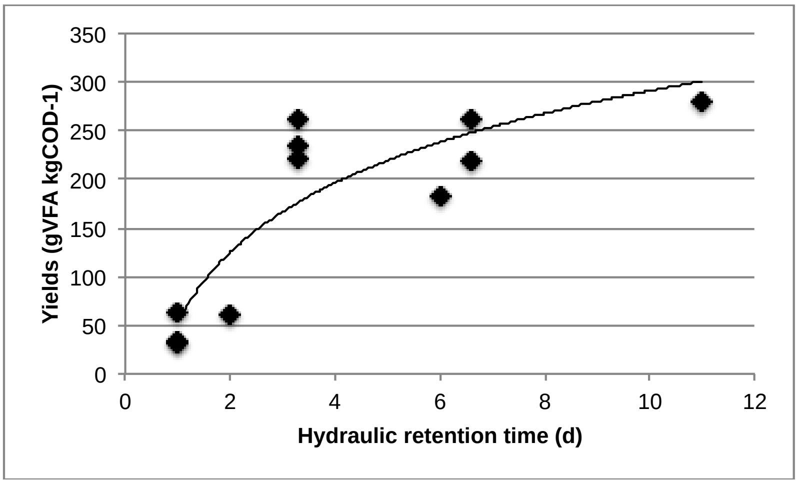

Figure 2: VFAs production using OFMSW/Food waste/Agro waste at different hydraulic retention time.

Considering the organic loading rate (Figure 3) it is possible to obtain interesting yields by applying OLR higher than 15 kgVS $m^{-3}d^{-1}$.

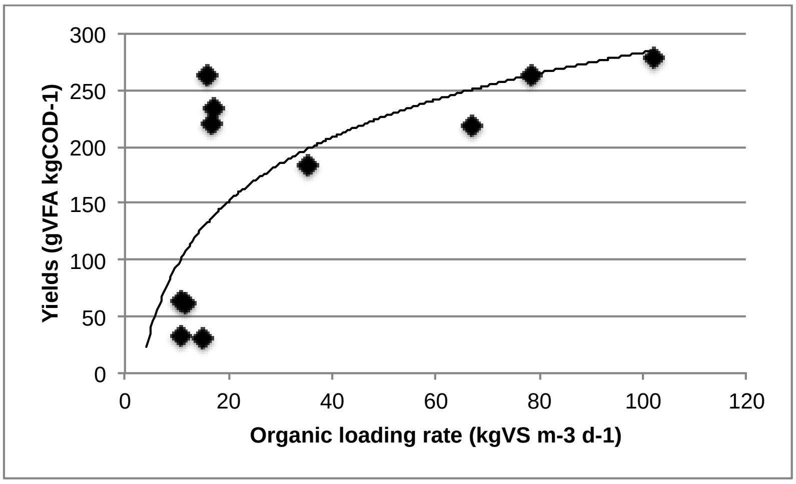

Figure 3: VFAs production using OFMSW/Food waste/Agro waste at different organic loading rate.

Beside VFA production, VFA composition is another important issue. For example, the composition of VFA is very important when the fermentation liquid is used for the production of polyhydroxyalkanoates (PHA). In fact, acetic and butyric acids are used for 3-hydroxybutyrate,whereas propionic and valeric acids are used for 3-hydroxyvaleate. This aspect will be considered in the next future.

In general, acetic acid was dominant in all the tested conditions, however, depending on the type of substrate and applied conditions propionic and butyric acids may increase, decrease or disappear in the final mix composition.

5. Biofuels and biobased products from volatile fatty acids

VFAs can be applied in several applications in food, cosmetics, bioenergy, biomaterials, pharma and textile industry (Bhatia and Yang, 2017).

When considering bio-polymers production PHA is the more promising application. Several microbes can store VFAs into the cell is form of PHA: when acetic acid is dominant 3-hydroxybutyrate (3-HB) is generally dominant, while propionate promotes the formation of 3-hydroxyvalerate (3-HV). The mix composition is therefore essential to tune the final composition of biopolymers which is a prerequisite for bioplastics production of different characteristics (Valentino et al., 2014, Bhatia and Yang, 2017). Another typical application of VFAs mix is the following production of biogas (Leite et al., 2016).

Alkyl esters of VFAs, e.g., ethyl acetate, butyrate and ethyl isobutyrate are applied in the food industry to enhance flavor.

6. Conclusions

Reported results showed that, depending on the nature of the feedstock high conversion yields and concentrations of VFAs can be obtained: in particular, it is possible to reach conversions as high as 0.3 gVFA/gCOD fed and final concentrations as high as 30 g/L. These values are however still low for some applications and higher final concentrations should be reached via concentration process or continuous product removal during the fermentation process.

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