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Volatile Fatty Acids Production from Household Food Waste

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The present study aims at determining key factors and current constrains of household food waste (HFW) fermentation process and its large-scale implementation within the frame of biorefinery concept. The production of Volatile Fatty Acids (VFA) from HFW by a mixed microbial culture fermentation (MMC) was studied in both, batch and semi-continuous scale reactors.
Results from batch scale trials without pH control pointed out that highest conversion yield obtained, 111 ± 20 mg of chemical oxygen demand, as VFA, per gram of volatile solids fed to the system, was reached after 6-7 days of fermentation. Moreover, during semi-continuous fermentation at uncontrolled pH and hydraulic retention time (HRT) of 6 d, was observed a VFA production of 3.3 ± 0.8 $g \cdot L^{-1}$ on average, being increased up to a maximum of 30.1 $g \cdot L^{-1}$ when pH was controlled at pH 5.5.
In light of the results obtained, HFW should be considered a promising feedstock for the production of chemical intermediates like carboxylic acids and platform chemicals in general. Nevertheless, best optimal operational conditions have not been still properly deciphered and further research must be done to foster economic viability of VFA production in future urban biorefineries.

1. Introduction

The increment of urban wastes generation has become a burning issue in recent years. According to Stenmarck et al. (2016), each person generates annually 179 kg of food waste accounting for a total of 88 million tonnes generated across the European countries. Household generation of organic waste is the major contributor (53 %).
According to Lin et al. (2013), most of the biodegradable wastes are landfilled or used for first generation recycling practices such as compost and biogas or animal feed (where possible), leading to both, socio-economic and environmental impacts related to the emission of pollutants to soil, air and water. It was estimated that 4.2 tons of carbon dioxide (CO_2) are released from decomposition of every single ton of biodegradable waste landfilled, accounting to 3 % of total global greenhouse gas (GHG) emissions (Segrè and Falasconi, 2011). Moreover in 2012, the costs associated with household food waste management in EU-28 were 98 billion € (Stenmarck et al., 2016).
The uncontrolled disposal of food waste in landfills generates environmental issues like GHG emissions and leachate formation on one hand, and close the opportunity to use it as a feedstock in proper value chains on the other hand. Also, the European and National legislations are trying to move this stream of material from massive disposal (landfilling) to virtuous recycling systems where this organic waste is properly valorised (Circular Economy Action Plan, January 2017). Italy, for example, is making good progress towards tackle the environmental burden of conventional HFW disposal by reducing the amount of organic waste landfilled from 82 % in 1995 to 54 % in 2010 (Ferraris and Paleari, 2013) due to a strong implementation of a separate collection scheme, which involved the increase of taxes on waste disposal by 70% in the last 10 years (Colombo et al., 2017).
Apart from the demanding regulatory requirements, new innovative approach strategies are gaining importance as a promising drive forward to foster valuable products recovery from organic fraction streams. It is widely reported that HFW could be considered a suitable source of ready biodegradable compounds, which can be converted into valuable products such as volatile fatty acids (VFA), lactic acid, citric acid, succinic acid, single cell oils, enzymes and biopolymers. In particular VFA have wide range of applications such as biological

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nitrogen removal (Lim et al., 2006), production of biodiesel (Fei et al., 2011), generation of electricity through microbial fuel cells (Chen et al., 2013b), and advanced bio-based products such as polyhydroxyalkanoates (PHA) (Chen et al., 2013a).

Regarding PHA production, its final composition is strongly affected by the kind of VFA used for their synthesis. For instance, the poly-3-hydroxybutyrate (P3HB) is produced from acetic and butyric acids, whereas propionic and valeric acids are needed for poly-3-hydroxyvalerate (PHV) production (Albuquerque et al., 2007). VFA production from organic wastes using Mixed Microbial Cultures (MMC) is particularly cost-attractive, since non-sterile conditions are needed, and there is low risk of contamination (Bhatia and Yang, 2017).

Considering the existing literature, experimental data about VFA production yield at large scale using MMC is sparse. Bolzonella et al. (2005), observed VFA yields of 40 mg VFA·gVS $^{-1}$ in a 3 m^3 pilot scale reactor operated in batch mode (tª 14-22 ºC; pH 4-5; HRT 4-4.5 d). In another similar study, Sans et al. (1995), observed a VFA concentration of 23 g VFA·L^{-1} in a plug flow reactor (80 L) which was operated at pH 6 (tª 37 ºC; HRT 6 d, OLR 38.5 kg VS·m^3·d^{-1}). In both studies the substrate employed was organic fraction of municipal solid waste (OFMSW) generated in the north of Italy and collected in different modes and periods of the year.

Moreover, several authors studied the optimization of mesophilic fermentation of similar substrates concluding that VFA yield was optimized at pH between 5 and 7. For example, Zhang et al. (2005) observed VFA yield of 0.27 g·g TS^{-1} from kitchen waste fermented at batch scale and pH 7. Other authors reported VFA yields of 0.47 g·g VS^{-1} from simulated food waste fermented at pH 6 (Jiang et al., 2013). The variability observed in the reported results indicate that VFA yield is highly dependent on the characteristics of the inoculum employed, operating conditions, and intrinsic heterogeneous composition of the substrate employed. In particular, HFW composition varies greatly depending on period and collection system, municipality, area, and socio-economic groups (Alibardi and Cossu, 2016). As a conclusion, it seems essential to determine VFA production yield from HFW generated in European countries aiming to contribute to a better understanding of the process and to foster real implementation of HFW fermentation at large scale.

The scope of the present study is to determine HFW suitability as source of carbon and microorganisms for VFA production as well as key factors and current constrains of large scale implementation of the fermentation process. After a complete characterization of HFW, fermentation experiments were carried out at batch scale without exogenous inoculum neither pH control. Then, in order to mimic a large-scale integration of the process, semi-continuous stirred tank reactor (SCSTR) was operated at uncontrolled pH and at pH fixed at 5.5, aiming to determine best operational conditions of VFA production from HFW.

2. Materials and methods

2.1 Substrate

In order to ensure reproducible conditions and limit the intrinsic composition variability of HFW, a model substrate with average chemico-physical characteristics of HFW generated in Mediterranean countries was prepared in the laboratory. Food products were gathered from local markets. Then were homogeneously mixed in a cutter mixer and stored in the frozen (-20 ºC) before experiments.

The characterization of the feedstock employed, Table 1, was in line with composition of real HFW samples reported in literature (García et al., 2005; Matsakas et al., 2014; Alibardi & Cossu, 2016).

Table 1: Physico-chemical characteristics and macromolecular composition of HFW.

Parameter	Value	Parameter	Value
pH	5.7 ± 0.2	Proteins (% TS)	23.9 ± 1
Total solids, (g TS·kg^{-1})	257 ± 13	Carbohydrates (% TS)	21.1 ± 0.6
Total volatile solids, (g TVS·kg-1)	254 ±11	Lipids (% TS)	15.6 ± 1
Chemical oxygen demand, (g COD·kg^{-1})	314 ± 6	Fibers (%TS)	31.6 ± 0.5
Soluble chemical oxygen demand (g SCOD·kg^{-1})	57.1 ± 5	Cellulose (% TS)	10.7 ± 0.6
Total Kjeldahl nitrogen (g TKN·kg^{-1})	9.9 ± 2	Hemicellulose (% TS)	10.4 ± 1
Ammonium (mg NH_4^+·kg^{-1})	36.3 ± 7	Lignin (% TS)	10.5 ± 1
Total phosphorus, (g P·kg^{-1})	1.4 ± 1	Sugars (% TS)	30.2 ± 1
Carbon to nitrogen ratio (C/N)	15.6		

2.2 Batch trials

This first experimental part was carried out in duplicate using glass bottles operated without pH control in batch mode for 8 days. Reactors were inoculated with fermented HFW. The inoculum was acclimatized 24 h before to start the experimental trials at working temperature. The substrate to inoculum ratio (S/I ratio) was 7:1 on volatile solid basis following optimal S/I ratio reported by Pan et al. (2008) and Nathao et al. (2013). The working volume was adjusted at 0.5 L with tap water in order to reach homogeneous mixing. Reactors were sealed with chloro-butyl caps and shaken manually once a day. PH, soluble chemical oxygen demand (SCOD), volatile fatty acids (VFA) and lactic acid (LA) concentration were daily monitored.

2.3 Semi-continuous trials

Semi-continuous fermentation of HFW was performed during 115 days without exogenous inoculation in a semi-continuous stirred tank reactor, SCSTR with 4.2 L working volume. Temperature was maintained constant at 37 ± 1 °C by a thermostatic bath. Feedstock was diluted in a ratio of 1:2 (v/v) with tap water in order to reach homogeneous mixing. Reactor was feed once per day, the organic loading rate (ORL) was 20.8 ± 1 kg $VS \cdot m^3 \cdot d^{-1}$ and the hydraulic retention time (HRT) was kept at 6 days following the configuration employed by Sans et al. (1995). Concentrations of total solids (TS), volatile solids (VS), total chemical oxygen demand (COD), ammonium (NH_4^+), SCOD, VFA, LA, and pH, where monitored in the fermented effluent during all the experimental period. Moreover, the reactor operation was divided in two different periods. During the first period, fermentation was performed without pH control for 80 days. In the second period, pH was fixed at 5.5 until the end of the experiment using a sodium hydroxide solution.

2.4 Analytical methods

Before fermentation experiments were set up, HFW was characterized in terms of total solids (TS), volatile solids (VS), total Kjeldahl nitrogen (TKN), total phosphorus (TP), and chemical oxygen demand (COD) according to Standard Methods (APHA-AWWA-WPCF, 2005). Besides, pH, ammonium (NH_4^+) and VFA were monitored during fermentation reactors operation. pH was determined by using a portable probe (Eutech pH 700). NH_4^+ concentrations were measured by using an ion selective electrode (Orion 9512). VFA concentration was determined by ion chromatography system (Dionex ICS 1100 with AS23 column). Lignocellulosic composition was determined in terms of neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent lignin (ADL) and crude fiber (CF) according to Van Soest and Wine, (1967). Lipids analysis were carried out following method described by Soxhlet (1879), crude protein was determined by the standard Kjeldahl procedure of the Association of Official Analytical Chemists, (1990). Sugars were determined by mass spectrometry (MS) previous sample filtration at 0.20 µm. Finally, lactic acid (LA) was determined using a commercial kit (Megazyme, Bray, Ireland).

3. Results

3.1 VFA yield from HFW fermentation at batch scale

During the batch trials pH dropped down quickly within the first day of fermentation reaction due to both, production of the carboxylic acids and low buffer capacity of the HFW. After that, pH was maintained stable until the end of the experiment at 3.9 ± 0.2. VFA yield increased gradually until 6-7 days of fermentation reaction up to a maximum yield of 111 ± 20 mg $COD\text{-}VFA \cdot g\ VS^{-1}$. The composition of the VFAs produced was mainly acetic acid (>80 %). Propionic acid was also detected in a percentage lower than 15 % of the total VFAs produced. Additionally, it is interestingly relevant the lactic acid (LA) production, which is a well-known precursor of certain VFA, in particular propionic acid (Zhang et al., 2005). The 6^{th} day of experiment LA yield was 2.6 times higher than volatile acids yield (220 mg ±12 $COD\text{-}LA \cdot g\ VS^{-1}$). Results are showed in Figure 1.

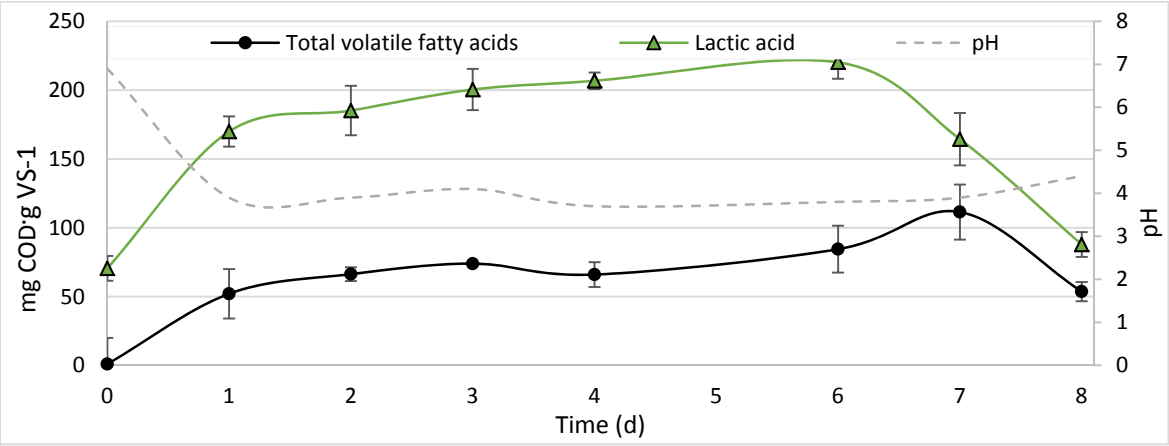

Figure 1: VFA and LA yield during HFW fermentation at batch scale.

3.2 VFA production through HFW fermentation in semi-continuous mode

During the first period of operation, the pH was uncontrolled and it reached a value of 3.6 ± 0.2 inside the reactor. The SCOD was 69 ± 19 g SCOD·L^{-1} and the ammonium concentration fluctuated at 123 ± 17 mg NH_4^+·L^{-1}. The average VFA production was in the range of 3.3 ± 0.8 g·L^{-1} composed mainly of acetic acid (83-99 %), (Figure 2). The average VFA yield during this period, 33.9 ± 13 mg COD-VFA·g VS^{-1}, was in line with results reported by Bolzonella et al. (2005). Nevertheless, these values were lower than those obtained in batch trials, a fact that could be related with low pH values and presence of VFA in its undissociated form, which may contribute to inhibit microbial growth by passing through the cell membrane of microbes (Bonk et al. 2017).

In the second period, pH was maintained at 5.5. The SCOD was 84 ± 8.7 g SCOD·L^{-1} and the ammonium concentration was 332 ± 62 mg NH_4^+·L^{-1} in line with previous data from Traverso et al. (2000). The VFA concentration observed was 25.5 ± 4.3 g·L^{-1} with maximum values of 29 - 30 g·L^{-1}, (Figure 2). Results are in line with those obtained by Sans et al. (1995). Moreover, when fermentation operation was controlled at pH 5.5, the maximum yields observed were in a range of 475 - 509 mg COD-VFA·g VS^{-1}. The composition of the VFA produced was 21 - 31 % acetic acid, 26 - 49 % propionic acid and 17 - 36 % butyric acid.

On the other hand, lactic acid concentration during fermentation without pH control was 5,800 ± 800 mg LA·L^{-1} and changed to 23.4 ± 1 mg LA·L^{-1} when pH was fixed at 5.5. The differences in the LA concentration values when fermentation reactor was operated at pH 5.5 could be an indicator of successfully conversion of lactic acid into propionic acid.

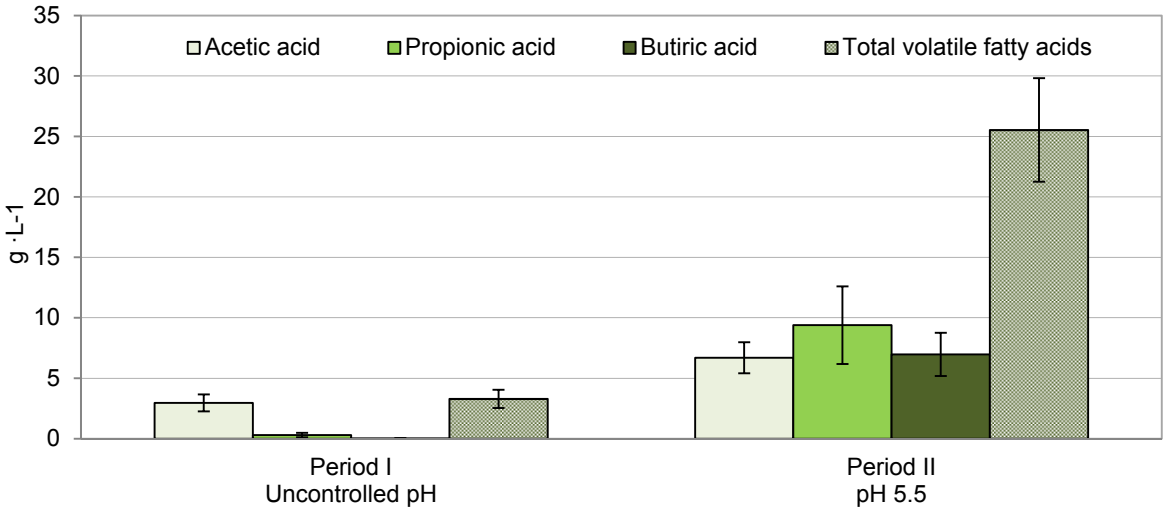

Figure 2: VFA production and composition during semi-continuous fermentation of HFW.

4. Conclusions

According to the experimental results obtained, the following conclusions can be drawn:

- It has been proven that HFW is a suitable source of carbon and microorganisms for VFA production, being required 6-7 days to achieve the highest conversion yields.
- Fermentation pH below 5.5 along with the scarcity of buffer compounds are main limiting factors for maximization of VFA production from HFW.
- pH-Uncontrolled fermentation lead to inhibitory effects on VFA yield related with the presence of VFA in its undissociated form.
- Further research must be done in order to foster the economic feasibility of the HFW fermentation process by taking into consideration cost-saving solutions such as co-fermentation with other organic waste streams.

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