Production of ethyl esters of volatile fatty acids from food waste

C. Pastore[1], L. di Bitonto[1], F. Valentino[2], G. Moretto[3], M. Gottardo[5], G.A. Martinez[4], S. Notarfrancesco[4], E. Morselli[4], L. Bertin[4] P. Pavan[3], D. Bolzonella[5], M Majone[2]

[1]Water Research Institute, National Council of Research, Viale De Blasio 5, Bari, 70132, Italy
[2]Department of Chemistry, "La Sapienza" University of Rome, P.le Aldo Moro 5, 00185, Rome, Italy
[3]Department of Environmental Science, Informatics and Statistics, Via Torino 155, 30170, Venezia Mestre, Italy
[4]Chemical Engineering Department, Alma Mater Studiorum University of Bologna, Bologna, 40126, Italy
[5]Department of Biotechnology, University of Verona, Strada Le Grazie 15, 37134, Verona, Italy
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Presenting author email: carlo.pastore@ba.irsa.cnr.it

Introduction

With the development of the global economy and the increment of population, the generation of food waste (FW) has been continuously increasing. The production of FW in EU27 accounts for 90 million tonnes per year and will reach 126 million tonnes per year by 2020 (Web reference, 2019). The corresponding CO_2 emissions are estimated in 170 million tonnes of CO_2 eq. emitted/year. The problem of global warming due to the increase of emission of greenhouse gases in the atmosphere encouraged the development of "biorefineries", in which waste materials can be used to fix carbon into organic molecules for the production of biofuels and high added value bioproducts. Volatile fatty acids (VFAs) production from acidogenic fermentation of waste streams is getting attention due to increasing market demand and wide range usage area in food, pharmaceutical and chemical industries, as well as its cost-effective and environmentally friendly approach (Valentino *et al*, 2019). Produced VFAs can then be used for the production of alkyl esters to be added to gasoline (for their high octane number), used as biosolvents to produce chemicals (alcohols, ketones, aldehydes and esters; Agler *et al*, 2011), or as a low cost carbon source for the production of biopolymers, like PHAs (Dionisi *et al*, 2004).
In this work a three step process has been proposed and tested for the production of ethyl esters of VFAs from food waste and biological sludge mixture: i) acidogenic fermentation of biowaste mixture to produce VFAs, ii) recovery of VFAs from an aqueous media into an ethanolic solution through a Solid Phase Extraction (SPE) and iii) a promotion of reaction of VFAs and ethanol to produce the target products and their isolation and purification.

Material and methods

Feedstock characteristics

The feedstock was weekly collected inside the Treviso municipal WWTP facility and it was composed by a mixture of the excess secondary sludge (SS) and the liquid fraction from solid/liquid separation after squeezing of OFMSW (abbreviated as "OFMSW" in the following). The source-sorted collection of OFMSW was made throughout the whole Treviso municipality and transferred to the full-scale WWTP after its squeezing and homogenization in a dedicated plant. A small aliquot of the squeezed OFMSW slurry was diverted to feed the acidogenic fermenter along with the sludge, separately collected after secondary settling and thickening in the same WWTP.

Acidogenic fermentation

The acidogenic fermentation step has the objective of hydrolyzing and fermenting the organic content of SS-OFMSW mixture into mainly volatile fatty acids (VFA); it includes an anaerobic batch reactor (V=380 L) and a centrifugation unit. The anaerobic reactor consisted in a Continuous Stirred Tank Reactor (CSTR), mechanically stirred and under temperature control by using a thermostatic jacket. The HRT (equal to SRT) was set at 6 days. The CSTR was not equipped with pH control, since the alkalinity of the feedstock ensured enough buffer capacity during the acid production process (pH range 5.0-5.5). The centrifugation unit was used for solid/liquid separation after fermentation. It is composed of coaxial centrifuge filter equipped with 5-10 μm porosity nylon filter bag, allowing the removal of 80% of total suspended solids approximately. This step was crucial for obtaining a cleaner fermented stream, although with a solid level still high at around 10.0 g/L, to be used for the following aerobic selection step. Acidogenic fermentation has been conducted in continuous mode, by investigating different mixture composition and/or different temperature.

Recovery of VFAs through SPE

A semi pilot plant was designed and set-up for: (i) lowering the $OFMSW_{Acid}$'s pH and (ii) recovering the organic acids. It consists of two thermostated plexiglass sequential columns, respectively dedicated to the two mentioned aims, each characterized by an empty volume of 760 mL and total length of 130 cm. Two screw caps made of PPS with GL32 thread and a PTFE gasket are placed both on top and bottom of each column while all other connections are in PTFE with GL14 gasket and different shapes (T-shape or L-shape). Two manometers (0-2.5 bar) were installed on top and bottom of the columns to check that the maximum allowed pressure is not exceeded. The pilot plant is equipped with a Masterflex peristatltic pump (2-200 mL min^{-1}) and installed on a

metallic structure. Columns were filled by the cation exchange Lewatit S2568H and the anion exchange Lewatit A365 resins, respectively, and were operated under expanded bed conditions. .

Direct-esterification of VFAs with ethanol using $AlCl_3 \cdot 6H_2O$ as a catalyst

The direct-esterification reaction of VFAs with ethanol was carried out in a glass reactor equipped with a silicone cap that allows sampling throughout the reaction without interrupting, agitation or heating of the system. VFAs were introduced into the reactor with ethanol, and placed into a thermostatic oil bath (343-313 K) and magnetically stirred (250 rpm). Then, a previously prepared ethanolic solution of $AlCl_3 \cdot 6H_2O$ was introduced via syringe into the reactor, to obtain the final VFAs:ethanol:catalyst molar ratio required for the specific experiment. Samples were collected at different reaction time and analysed for any residual acidity and ethyl ester. At the end of the esterification process, a bi-phasic system was observed and the two distinguishable phases were recovered, weighed and analysed for residual acids, ethyl ester, ethanol, water, aluminium and chloride content. Experiments were done in triplicate for an thorough data treatment (di Bitonto et al. 2019).

Results and discussion

Acidogenic fermentation was feasible to a good extent under all the conditions tested. Thermophilic conditions allowed obtaining higher level of average VFA concentration, (23 ± 3 gCODVFA/L), which were mainly composed by acetic (43%), propionic (8%), butyric (20%), valeric (9%) and caproic (18%) and heptanoic (3%) acids. It also contained inorganic anions, mainly Cl^- (1.2 g/L) and PO_4^{3-} (0.5 g/L).

The continuous solid phase extraction process was set up and operated for the recovery and separation of VFAs from the effluent of the acidogenic fermentation processcontained about 25 g/L of VFAs, this representing about 62% of the whole organic soluble fraction. Non-soluble total solids were previously separated by conventional protocols (centrifugation / filtration). The effluent pH was lowered from 5.4 to about 1.5. The adsorbtion column was fed under a flow rate of 40 ml/min, the resin adsorption capacity was exhausted after 11 dimensionless retention times (about 80 minutes). The extraction was carried out by using basified or acidified ethanol to desorb VFAs: more than 90% of the acidic fraction occurring in the initial experimental matrix were recovered in acidified alcohol. Two different set of VFAs solutions were prepared and eluted: VFAs in alkaline (NaOH) and acid (H_2SO_4) ethanol, with VFAs content in the range of 20-60 g/L. VFAs in these two different solutions were actually in different forms: in acid samples VFAs were already dissolved as ethyl esters, whereas in alkaline samples VFAs were in their saline form (as sodium salts). This fundamental difference of the chemical nature of samples, brought to the necessity to define two completely different processes to be realised and optimized to obtain biosolvents. In the case of acid samples only purification of ethyl esters needed to be operated (the yield of ethyl esters were already higher than 75%), whereas in alkaline samples, VFAs needed to be firstly reacted to produce the respective esters and then purified. Pure ethyl esters mixtures were in any case separated and isolated as upper organic layer after the addition of saturated NaCl aqueous solution to the relevant distillate (1:4 volume). Three different biosolvents can be eventually obtained: two from alkaline and one from acid eluates, having different compositions and (for this reason) chemical properties.

Conclusions

In this work a three-step process was proposed to produce ethyl esters of VFAs as biobased solvents from urban biowaste. The nature of the final product could be modulated and chosen in function of specific operative conditions, resulting in a very powerful approach useful to produce specific final products.

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