Volatile fatty acid production from apple pomace via anaerobic digestion

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The valorization of agro-industrial waste like those generated during fruit processing are attracting increasing attention in last decades in the context of the emerging circular economy. In the world, around 14 million tons of apple are processed per year and the solid waste produced (namely, apple pomace (AP)) accounts for 25% of the total processing biomass (Dhillon *et al*., 2013; Molinuevo-Salces *et al*., 2020). Around 20% of the AP produced is employed as animal or human feed (Dhillon *et al*., 2013). The rest is incinerated, composted or disposed into landfills, leading to negative environmental impacts. Therefore, looking for new ways to valorize AP aims to be both the solution to an environmental issue and an economic chance to exploit zero-cost organic waste.

In this perspective, anaerobic digestion (AD) has been commonly proposed as an alternative for solid organic waste management, producing methane as a form of renewable energy. Another alternative that is receiving increasing attention in last years, is the use of AD for the production of volatile fatty acids (VFAs), which are carboxylic acids consisting of short chains of carbon (usually six or fewer carbon atoms) such as acetic (ethanoic), propionic (propanoic), butyric (butanoic), valeric (pentanoic) and caproic (hexanoic) acids. Most of these compounds, which are of high industrial interest, are traditionally obtained via petrochemical routes. However, issues related to the availability and prices of petroleum resources together with environmental concerns are boosting the need of developing alternative production methods (Greses *et al*., 2020). Nevertheless, while AD of organic waste for methane production is a mature technology, the production of VFAs under anaerobic conditions is still under research. Thus, the purpose of this study was to evaluate the potential of VFA production through anaerobic digestion under different operational conditions as an alternative option for AP valorization.

The AP used in this study was provided by the Regional Research and Development Service of Asturias (SERIDA), Asturias (Spain). The AP was a fresh product obtained after apple pressing for cider production. The volatile solid (VS) content was 287.5 g kg^{-1} (99% of the total solid (TS) content). The anaerobic sludge used as inoculum was obtained from the municipal wastewater treatment plant of Valladolid (Spain).

The assays were performed to investigate the effect of initial pH adjustment and the addition of a methanogenic inhibitor without pH control on VFA production. Three batch assays were performed: 1) initial pH of 5.5, 2) initial pH of 10.0 and 3) addition of 2-bromoethanesulfonate (BES) without pH control. The ratio substrate (So) to inoculum (Xo) was 1, expressed as g VS g^{-1} VS, according to Esteban-Gutiérrez *et al*. (2018). The experiments were performed in 570 mL bottles with a working volume of 200 mL. A volume of 100 mL of inoculum (equivalent to 1 g VS) was added to each bottle. After that, the required quantity of waste corresponding with 1 g VS was added. Distilled water was added to each bottle up to a volume of 200 mL. Then, a solution of NaOH 1M or concentrated sulfuric acid was utilized to adjust initial pH to 10 or to 5.5, respectively. After initial pH adjustment, pH remained uncontrolled during an incubation period of 9 days. In addition, for the study of the influence of BES on VFA production, 2 g L^{-1} of BES was added to the bottles (Lukitawesa *et al*., 2020) without any pH adjustment. All the assays were run in triplicate. Three blanks for the determination of VFA production of inoculum at both evaluated pH values and with BES addition were run, containing only inoculum and water. After the set-up of each bottle, the headspace was flushed with N_2 in order to ensure anaerobic conditions. Then, the bottles were placed in an incubator at 38.8 ± 0.7 ºC. The volume of the gas produced was calculated by measuring the pressure of the bottle's headspace. Gas composition was analyzed periodically. VFA concentration and composition were determined in the liquid fraction using a gas chromatograph. For this purpose, 2 mL of liquid sample was removed from the bottles with a syringe ensuring the maintenance of anaerobic conditions.

The highest VFA production was similar for all tested conditions, around 5.0 g COD_{VFA} L^{-1} (Fig. 1). However, the VFA production profile suggests that the VFA production kinetic was favoured with an initial pH of 10. Specifically, the highest VFA concentration was reached on day 7 with an initial pH of 10 and on day 9 with an initial pH of 5.5. It is relevant when considering the production of VFA under semi-continuous or continuous mode. Thus, the adjustment at initial pHs higher than 5.5 would allow the operation at lower hydraulic retention times (HRT), which would increase the economic sustainability of the process. It is worth to mention that in that assay with an initial pH of 10, the VFA concentration decreased in the last days as a consequence of its consumption by methanogenic microorganisms (data not shown). The composition of the fermentation broth on the 9th day of incubation was greatly affected by the fermentation conditions (Fig. 2). When the pH was initially adjusted at pH 5.5, acetic and butyric acids were the main products. When the pH was initially adjusted to 10.0, the VFA profile changed. Acetic and butyric acid were the main products, with percentages of 46 and 29% of the total VFA, respectively. However, the proportion of propionic acid was also significant, comprising 11% of the total VFA. The less proportion of acetic acid in the fermentation broth could be due to the faster consumption by methanogens microorganisms. With the addition of BES, acetic acid represented 67% of the fermentation broth, while propionic and butyric acids accounted for 14% and 12%, respectively.

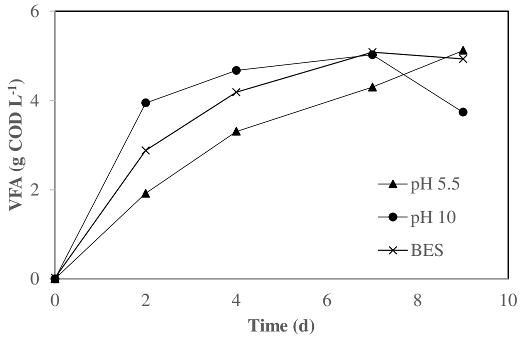

Fig. 1. Evolution of VFA production from AP under the three tested conditions.

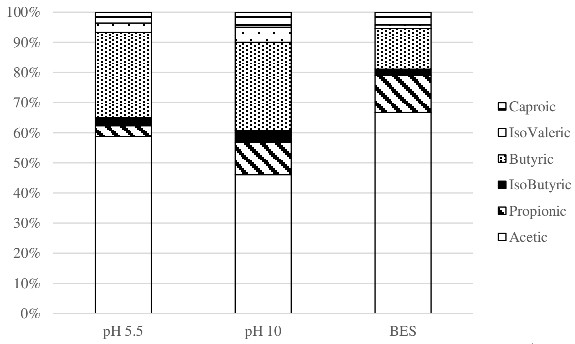

Fig. 2. VFA profile under the three tested conditions on day 9th of fermentation.

The VFA yields obtained in the present study were 0.87 g COD_{VFA} g VS_{fed}^{-1} for the assay at an initial pH of 5.5, 0.63 g COD_{VFA} g VS_{fed}^{-1} for the initial pH of 10.0 and 0.83 g COD_{VFA} g VS_{fed}^{-1} for the assay with BES. These values are higher than those reported in literature for AP fermentation, which varied between 0.12 and 0.34 g COD_{VFA} g VS_{fed}^{-1} (Cerdán *et al.*, 2021; Perimenis *et al.*, 2018). This value is also higher than the methanogenic potential for AP (0.39 g COD_{CH4} g VS_{fed}^{-1}) obtained by García-González et al. (2018). Therefore, AP is a substrate that merits further research due to the considerable valorization potential for VFA production.

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