

# Acidogenic fermentation coupled with nitrogen recovery using a gas-permeable membrane to produce a VFA-rich liquor with a high C/N ratio

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**Abstract:** Mixed-culture anaerobic processes can handle a wide variety of organic wastes and convert them into value-added products within the biorefinery concept. Volatile Fatty Acids (VFAs) production from organic wastes is getting attention due to its increasing market demand to produce bio-based materials (bioplastics, biotextiles) or bioenergy (biogas, biodiesel, biohydrogen), among others. VFA-rich effluents usually have a high concentration of Total Ammonium Nitrogen (TAN) due to the ammonification of organic nitrogen during fermentation. However, the efficiency of certain downstream applications is improved when the VFA-rich stream has a high C/N ratio. Polyhydroxyalkanoates synthesis (Estevez-Alonso et al., 2021) and biogas production (Molinuevo-Salces et al., 2018; Rivera et al., 2022) are downstream bioprocesses that have shown an improved performance when a lower TAN content is present. Serra-Toro et al. (2022) successfully used a Gas-Permeable Membrane (GPM) contactor to recover TAN from fermentation effluents. This technology exhibits high potential for upcycling TAN from waste effluents as they are relatively simple to operate, consume little energy and produce a sealable fertilizer product (Darestani et al., 2017; Beckinghausen et al., 2020).

In the present study, the acidogenic fermentation of Organic Fraction of Municipal Solid Waste (OFMSW) combined with GPM technology for TAN recovery is studied to produce a VFA-rich stream with a high C/N ratio. Moreover, the impact of the lower TAN concentration on anaerobic digestion was studied as an example of the benefits that this combined treatment could bring to downstream bioprocesses.

Source-sorted OFMSW samples were collected from a mechanical-biological treatment plant of the Barcelona Metropolitan Area. Anaerobic digestion inoculum was obtained from an anaerobic digester treating sewage sludge at a municipal Wastewater Treatment Plant (WWTP).

A three-stage process was carried out including (i) OFMSW acidogenic fermentation, (ii) TAN recovery using a GPM contactor and (iii) anaerobic digestion. The acidogenic fermentation of OFMSW was carried out in a 30 L fermenter equipped with a pH probe, a mechanical stirrer, and a temperature control system (35 °C). The fermentation process was stopped when a slight increase of the media pH was detected. The fermentation liquid used in the GPM contactor was obtained after meshing and filtering (0.45 µm) the fermentation effluent.

The TAN of the liquid fraction was recovered as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> using a microporous hollow fibre polypropylene (PP) membrane contactor (0.5 m<sup>2</sup> active surface area). The GPM contactor experimental set-up consisted of two sealed and stirred tanks that contained 0.5 L of trapping solution (diluted H<sub>2</sub>SO<sub>4</sub> that never exceeded a pH value of 2.0) and a 1.8 L of feed solution (controlled at 35 °C and pH 9.0). These tanks were connected to a GPM module using closed loops for each stream (Serra-Toro et al., 2022). The process finished once >99% of TAN was removed from the fermentation liquid.

In the third stage of the process, the anaerobic biodegradability (rate and extent) of the nitrogen-spent fermentation liquid was tested at different TAN concentrations. Biomethane potential (BMP) tests were performed using serum bottles filled with anaerobic digestion inoculum and nitrogen-spent fermentation liquid at an inoculum-to-substrate ratio of 2 (on VS basis) and mesophilic conditions (35 °C). The evolution of biomethane production was followed using the gas density method (Justesen et al. 2019).

Figure 1 shows the results of one of the fermentation assays. During the fermentation batches, the VFA concentration increased from 20-22 g COD<sub>VFA</sub>/L to 37-40 g COD<sub>VFA</sub>/L within 6 days. Acetic, propionic, and butyric acids were the predominant VFA representing the 31-39, 21-27 and the 24-34% of the total VFAs (COD basis), respectively. The pH decreased from 6.7 down to 6.3 between days 0 and 6. TAN concentrations increased from 3.2-3.6 to 4.0-5.0 g N/L. The obtained VFA yield (0.6-0.7 g COD<sub>VFA</sub>/g VS) is in the upper range of those reported in literature (Fernandez-Domínguez et al., 2020; Strazzera et al., 2021), probably related to OFMSW composition and batch operation. The analysis of the microbial community of the fermentation assays is ongoing to elucidate the microorganisms responsible of this fermentation yield and product profile.

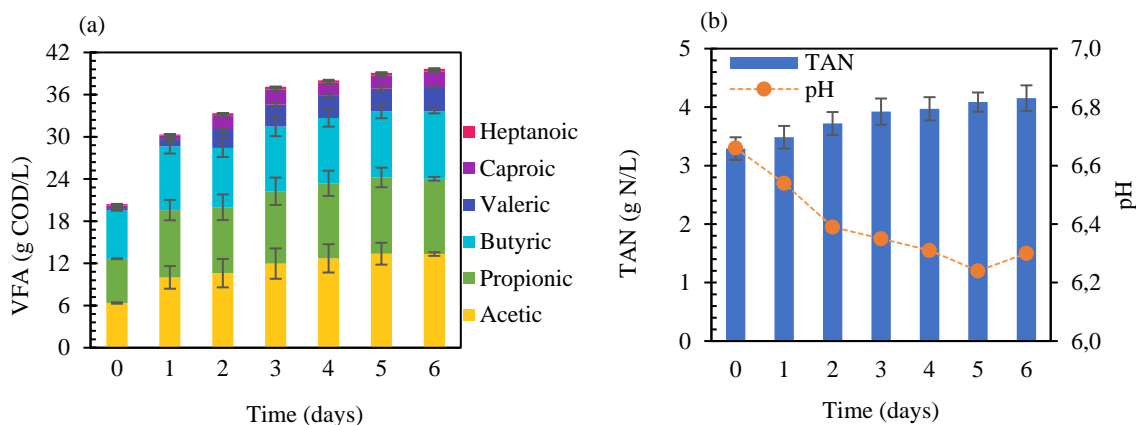


Figure 1 – VFA concentration (a), TAN and pH (b) evolution from OFMSW batch fermentation.

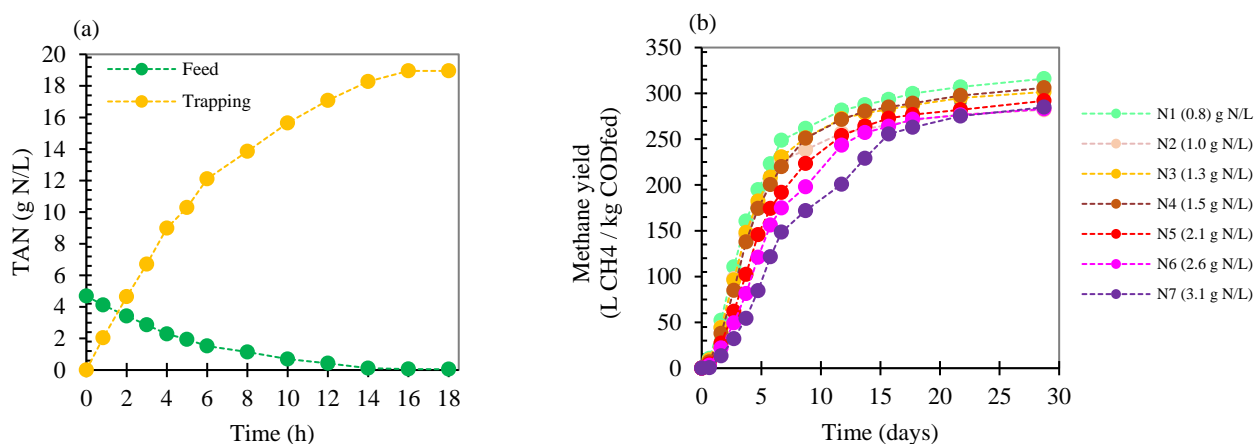


Figure 2 – TAN concentration evolution during the GPM nitrogen recovery (a) and methane curves at different TAN concentrations in BMP tests (b).

More than 99% of the TAN present in the fermentation liquid was recovered after 18 hours of operation by means of the GPM contactor (see Figure 2a). The TAN concentration in the trapping solution reached 16–19 g N/L since its volume was lower than that of the feed solution. VFAs were not detected in this (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution and its presence in the fermentation liquid did not highly affect the ammonia removal efficiency, which is consistent with other studies reported in the literature (Daguerre-Martini et al., 2018).

BMP tests showed that the highest methane yield was observed for the lowest TAN concentration condition (0.8 g N/L) reaching 316 L CH<sub>4</sub>/kg COD<sub>fed</sub> (see Figure 3). On the other hand, the lowest methane yield of 285 L CH<sub>4</sub>/kg COD<sub>fed</sub> was observed in the test with the highest TAN concentration (3.1 g N/L). The methane production kinetics were also affected by TAN concentration. These results show that mitigating the TAN concentration of the VFA-rich fermentation liquid could improve its anaerobic digestion yield and kinetics. These results can be related to the lower ammonia inhibition of methanogens at lower TAN concentrations (Jiang et al., 2019).

This study shows that the combination of acidogenic fermentation with ammonia recovery using GPM contactors could lead to the valorisation of TAN as a fertilizer product and the production of a VFA-rich stream with high C/N ratio that could enhance some downstream applications, such as biogas production.

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