Fermentative volatile fatty acid production and recovery from grass using a novel combination of solids separation, pervaporation, and electrodialysis technologies

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Abstract

A novel combination of solids screening, centrifugation, microfiltration, pervaporation, and electrodialysis were used for the targeted and exclusive recovery of volatile fatty acids (VFAs) from an 80 L bioreactor. The bioreactor was continually-fed with grass waste, containing 40 g L^{-1} total solids, over three, seven-day, hydraulic retention times. A VFA solution with a concentration up to 4,500 mg L^{-1} was recovered. VFA yields were also increased from 707 to 875 mg of VFA per gram of volatile solids by alleviating end-product inhibition. Both these accomplishments are significant step-changes in adding value to waste, and increased substrate utilisation rates will be attractive from a waste remediation perspective.

Keywords

Anaerobic Digestion; Biorefining; VFAs; Electrodialysis; Platform Chemicals.

1. Introduction

In the United Kingdom, 4.6 Mt of green waste, including grass clippings, is composted every year (DEFRA, 2018; NIEA, 2018; SEPA, 2018; Welsh Government, 2014), requiring energy inputs of up to 12 MJ kg^{1} (Hermann et al., 2011; Lin et al., 2018) Composting also generates greenhouse gasses, yields a low value product and returns carbon, and organic physical and biological contaminants such as microplastics and heavy metals (Cattle et al., 2019) to the environment. Livestock numbers in the UK are also falling. The UK dairy herd population fell from 2.6 million in 1995 to 1.9 million in 2015, and there was an associated decline in dairy producers from 35,741 to 13,815 in the same period (Baker, 2015). The decrease in livestock population is predicted to continue (Chai et al., 2019), and so the demand for grass as an animal feedstock is also decreasing accordingly. Grass is one of the most easily-grown crops in the UK, with 5.2 million hectares of permanent pasture and 1.1 million hectares of temporary pasture (Agriculture and Horticulture Development Board, 2018), making up 26% of the landmass of the country.

Because of these factors, the anaerobic digestion of surplus grass to produce methane has emerged as an alternative use with considerable short term economic potential (Allen et al., 2016). According to Flesch et al., (2011). Fugitive emissions from methanogenic bioreactors account for up to 15% of the gas they produce however, and Scarlat et al., (2018) state that 18 billion cubic metres of methane from anaerobic digestion was produced globally in 2015. It is possible therefore that up to 2.7 billion cubic metres of fugitive methane emissions could have escaped to atmosphere in 2015. Given that methane is a greenhouse gas with a 20 year global warming potential 84 times greater than carbon dioxide, the continued and increasing production and storage of methane could begin to pose challenges to decarbonisation targets. To address this environmental concern, previous works (Hassan et al., 2019; Jones et al., 2015; Massanet-Nicolau et al., 2016) investigated hydrogen production from biowastes, as an

alternative to methane, by maintaining bioreactor conditions that arrested acidogenesis and alleviated end-product inhibition to increase hydrogen yields. Whilst hydrogen is not a greenhouse gas, there are more economically viable pathways to hydrogen production than the fermentation of waste streams, including the use of excess wind and solar energy for electrolysis, the cost of both of which are becoming increasingly competitive with conventional fuels (Tanoto et al., 2021). VFAs are another product of the fermentation of grass (Jones et al., 2021b), and include acetic acid, propionic acid, butyric acid, and valeric acid. These VFAs have considerable economic value due to their versatility, which makes them attractive across several industries (Table 1). Compared to the current market sizes of VFAs (Table 1), methane has less diverse uses and a relatively low economic value (Patterson et al., 2020). If VFA production from wastes can be achieved using established, industrially applicable processes then it could be a more attractive long-term prospect than the continued production of methane. Furthermore, platform chemicals utilised in the industries shown in Table 1 are currently derived from petrochemicals. If global dependence on fossil fuels is to be reduced however then alternative and sustainable sources for these chemicals must be found.

Arresting methanogenesis, and promoting acidogenesis by alleviating end product inhibition increases VFA yields (Jones et al., 2021a, 2021b). The engineering challenge however is that the membrane technologies required for VFA recovery are sensitive to the accumulation of solid and microbial matter, both of which are found in high concentrations in real-world waste streams. The second challenge is ensuring that any resultant VFA solution is free from bioreactor-derived impurities that would dimmish its value, such as phosphates, nitrates, and ammonium. These chemicals are also important substrates for fermentation and so removing them from the bioreactor will be detrimental to product yields.

Chalmers Brown, et al., (2020) show that combining pervaporation with electrodialysis can be used to prevent non-volatile compounds being removed from bioreactors, thereby yielding a more pure VFA solution than electrodialysis alone would allow, and a more concentrated VFA solution than pervaporation alone would achieve. This work however was carried out at bench scale on low-solids, synthetic wastewater. Combining the industrially applicable solids separation and non-targeted recovery of VFAs from Jones *et al*., (2021a, 2021b) with the pervaporation stage from Chalmers Brown *et al*., (2020) could represent a novel methodology with which to selectively recover and concentrate VFAs into a relatively pure solution, without having a detrimental affect on reactor performance in terms of total VFA yield.

The primary aim of this work is to demonstrate that the above novel combination of technologies can be used to recover VFAs from a continually fed grass waste bioreactor. The secondary aims are to investigate the hypothesis that the continuous recovery of VFAs will increase their overall yield by alleviating end-product inhibition, and to investigate whether the recovery of acetic acid will result in increased homoacetogenesis and therefore an increase in the proportion of acetic acid produced as a percentage of all VFAs.

2. Materials and methods

2.1. Experimental design and overview

This study was split into a PTFE-ED Phase and a Control Phase to test the hypotheses that VFAs could be recovered from a continuously fed grass bioreactor, and that their recovery would have a positive effect on total VFA yield by alleviating end-product inhibition. During the PTFE-ED Phase, VFAs were recovered from the bioreactor as described in Sections 2.5 and 2.6. During the Control Phase there was no recovery of VFAs.

2.2. Bioreactor design

All fermentations took place inside a 105 L stainless steel bioreactor (Pharmatech, Birmingham, UK) with an 82.5 L liquid phase and 22.5 L gas phase. The gas phase of the bioreactor was continuously recirculated from the headspace and back into the liquid phase by a peristaltic pump (630U, Watson Marlow, Falmouth, UK).

Three gas sensors were installed inline on the gas recirculation loop to monitor the concentrations of hydrogen (Bluesens, Herten, Germany), carbon dioxide (MSHPS/HCO2/NC, Dynament, Mansfield, UK), and methane (MSHP/HCP/NC, Dynament, Mansfield, UK). When the gas phase pressure inside the bioreactor exceeded atmospheric pressure, pressure equalisation was achieved by allowing gas to exit the system via a positive displacement tip meter, which also recorded gas flow rate.

The pH and temperature of the bioreactor's liquid phase was continuously monitored by submerged probes (HI-1210B/5, Hana Instruments, Bedfordshire, UK; and LM35DZ, Texas Instruments, Dallas, USA, respectively). Gas concentrations, pH levels, and temperature were continuously monitored and logged using LabVIEW™ data acquisition software (National Instruments, Austin, Texas).

2.3. Feedstock

Feedstock was produced by suspending 5 kg of grass pellets in 95 kg of water, supplemented with 0.33% w/w macronutrients (Nutromex 123, OMEX, King's Lynn, UK), 0.02% w/w micronutrients (Nutromex TEA, OMEX, King's Lynn, UK), and 0.17 w/w silicon antifoaming agent (Dow Corning, Michigan, USA). The feedstock was stored in continuously stirred 200 L stainless steel drums (Pharmatech, Birmingham, UK) and its temperature was maintained at 4°C ± 0.5°C using external chilling jackets (Fluxwrap, Powerblanket, Salt Lake City, USA). The VFA concentration of the feedstock was monitored by headspace gas chromatography according to Cruwys et al., (2002) and replaced with fresh feedstock once VFAs were detected.

2.4. Bioreactor operation

At the beginning of each experimental phase, the bioreactor was filled with 4 L of inoculum and 79 L of feedstock, and no further feeding events took place for 24 hours to allow the microbial consortium to establish itself without being diluted out of the bioreactor. Digestate arising from the anaerobic digestion of sewage biosolids collected from a nearby municipal sewage treatment works (Eign, Herefordshire, UK) was used as inoculum. The inoculum was heated to 110°C for 20 minutes to inhibit methanogenic microorganisms, and introduced to the bioreactor once it had cooled to 21°C.

In both experimental phases, the bioreactor temperature was maintained at 35°C ± 0.5°C using a temperature probe in conjunction with a temperature controller (ESM3711H, RS Pro, Northamptonshire, UK) and heating jacket. If the pH level fell to less than 5.50 then 6 M sodium hydroxide was automatically added by a dosing pump (TPG500, SEKO Group, Rieti, Italy) until the pH level was raised back to 5.50.

In both experimental phases, continual feeding started 24 hours after filling the bioreactor. Once every six hours, 1.96 kg was automatically removed from the bioreactor's liquid phase via a peristaltic pump and a corresponding amount of feedstock was dosed into the reactor. This regime resulted in 11.79 kg of feedstock being fed each day, giving the 82.5 L liquid phase a seven-day hydraulic retention time. Each experimental phase ran for 28 days, equating to 4 hydraulic retention times, once continual feeding began.

2.5. Solids separation

The membrane technologies used to recover and concentrate VFAs in the PTFE-ED Phase are sensitive to the accumulation of suspended solids and microbial growth. Therefore, during the PTFE-ED Phase, a three-stage, batch, solids separation procedure was carried out once every

24 hours to produce a filtrate stream suitable for introduction to the pervaporation and electrodialysis apparatus, which will be described in more detail in Section 2.6.

At the start of each solids separation cycle, a diaphragm pump (CP-T50-PTT, Crest Pumps, Hampshire, UK) was used to abstract 20 kg from the liquid phase of the bioreactor into an external barrel on a weighing platform. The contents of this barrel were then screened to 250 µm in an ultrasonic vibrating sieve (Finex 22", Russell Finex, Middlesex, UK). The retentate was returned to the external barrel and the filtrate underwent further solids separation in a centrifuge (RPC-103, Oilybits, Dorset, UK). Similarly, the retained solids in the centrifuge were returned to the same external barrel as the retentate from the screening stage, and the centrate was then introduced to a bank of four hollow fibre filters prior to pervaporation and electrodialysis, which will be explained in more detail in Section 2.6. A schematic overview of this process is shown in Figure 1.

2.6. VFA recovery

A combination of pervaporation and electrodialysis (Figure 2) were used for the targeted recovery and concentration of VFAs following solids separation during the PTFE-ED Phase. This is the first time a combination of pervaporation and electrodialysis has been deployed at this scale and on a complex waste stream analogous to real world scenarios, containing high levels of suspended solids and microbial accumulation.

2.6.1. Pervaporation stage

Pervaporation during the PTFE-ED Phase was achieved using a stack of alternating PTFE membranes (Membrane Solutions LLC, USA) and spacers (PCCell GmbH, Heusweiler, Germany), supported by a metal enclosure. Each PTFE membrane had 0.45 µm pores, a polypropylene support layer, and a hydrophilic and hydrophobic face. The PTFE membranes and spacers were arranged in such a way that meant that one spacer would be in contact with

two hydrophilic faces, and the next spacer would be in contact with two hydrophobic faces (Figure 2). In this study, 10 pairs of spacers and membranes were used, with a total active surface area of 640 cm^2.

Volatile ionic compounds, in this instance VFAs, passed from the diluate stream, across the hydrophilic membrane faces, and into the neighbouring concentrate stream along a negative concentration gradient, maintained by downstream electrodialysis (Section 2.6.2). The concentrate stream is prevented from pervaporating back into the diluate stream by the hydrophobic membrane faces with which it is in contact.

2.6.2. Electrodialysis stage

During the PTFE-ED Phase, the concentrate arising from the pervaporation stage was continuously recirculated through the diluate chambers of an electrodialysis stack (ED 1000H, PCCell GmbH, Heusweiler, Germany) (Figure 2) with 25 cell pairs and an active area of 25,000 cm^2, across which 18 V of electrical potential was applied. The dissolved VFA molecules in this stream dissociated into their cations and anions and were attracted across oppositely charged membranes towards their oppositely charged electrodes. Their further migration towards the electrodes was then prevented by a similarly charged membrane resulting in an accumulation of VFAs in the concentrate stream consisting of 8 g L^1 sodium chloride. The diluate stream, now free from VFAs, was recirculated back to the PTFE stack's concentrate stream to maintain a negative concentration gradient between the PTFE diluate and concentrate streams, thereby allowing the continued recovery of VFAs from the PTFE diluate into the PTFE concentrate. To reduce electrical resistance, the electrodes were continuously rinsed with recirculating 0.25 M Na_2SO_4, and electrodialysis reversal was performed on a weekly basis to mitigate fouling on the membrane surfaces.

2.6.3. Retentate

During the PTFE-ED Phase, following solids separation (Section 2.5) the resultant solids were resuspended in the previous day's pervaporation stage diluate, which had been subjected to 24 hours of VFA recovery, and returned to the bioreactor. Returning the separated solids in this way had a diluting effect on the concentration of VFAs within the bioreactor's liquid phase and should therefore help to alleviate end-product inhibition, resulting in increased VFA yields. During the PTFE-ED Phase, each VFA recovery cycle would cause a mass of water, originally deriving from the liquid phase of the bioreactor, to be transferred across the electrodialysis stack from the diluate to the concentrate via osmotic drag. To ensure no water was lost from the liquid phase of the bioreactor, the mass balance of water was restored by the addition of water from an external reservoir before mixing and returning the bioreactor (Figure 1). Since no VFA recovery and no associated osmotic drag occurred during the Control Phase, no such addition of water from an external reservoir was undertaken.

2.7. Offline analyses

During both of the experimental phases, a 100 mL sample was taken from the bioreactor, and from the feedstock, three times each week. The samples were then analysed in triplicate for total solids and volatile solids concentration (Clesceri, L et al., 1999), soluble and insoluble carbohydrate concentration (Dubois et al., 1956), and soluble and insoluble chemical oxygen demand (Gaudy and Ramanathan, 1964). In the Control Phase, the feedstock and bioreactor samples were also analysed for acetic acid, propionic acid, butyric acid, and valeric acid three times per week in triplicate by headspace gas chromatography (HSGC) according to Cruwys et al., (2002) The same VFA analyses were performed during the PTFE-ED Phase however the concentrate reservoir was also analysed for VFA concentration according to the same regime.

2.8. VFA yield calculations

VFA yields were calculated according to the following equations to arrive at a yield expressed in milligrams of VFA per gram of volatile solids fed into the reactor (mg_{vfa} g_{vs}^{-1}). Firstly, the mass of individual VFA species, at a given time, were calculated by multiplying the VFA concentration, in mg L^{-1} at that time by the volume of the liquid phase of the bioreactor (Equation 1).

$$m_{vfa} = \frac{\rho_{vfa} \times V_{br}}{1000}$$

Equation 1. VFA mass calculation

Where: m_{vfa} is the mass of a VFA species in the bioreactor at a given time in grams, ρ_{vfa} is the concentration of a VFA species in the bioreactor at that time, and V_{br} is the working volume of the bioreactor in litres.

The feeding rate, *Qf*, expressed in terms of litres per day, was calculated by dividing the working volume of the bioreactor by the hydraulic retention time. From the feeding rate and the VFA mass calculations, the VFA production rate, in terms of milligrams of VFA per day (mg_{vfa} day^{-1}) can be calculated according to Equation 2, and accounts for the diluting effect the addition of VFA-free feedstock has.

$$Q_{vfa} = \frac{m_{vfa_{t1}} - \{[V_{br} - (t_1 - t_0) \times Q_f] \times \rho_{vfa_{t0}}\}}{t_1 - t_0}$$

Equation 2. VFA production rate calculation

Where Q_{vfa} is the production rate of a VFA species (mg_{vfa} day^{-1}), $m_{vfa_{t1}}$ is the mass of VFAs at "time one" (t_1), t_0 is "time zero", and Q_f is the feeding rate (L day^{-1}), $\rho_{vfa_{t0}}$ is the concentration of VFAs at time zero.

During the PTFE-ED Phase, this calculation was repeated to account for the diluting effect that the VFA recovery methodology had upon the bioreactor. In this calculation, Q_f was replaced

231 with $Q_{ptfe\text{-}ed}$, which is the rate at which VFA recovery happened. In this work, the rate of VFA
232 recovery was 20 L day^{-1}.

233 The mean production rate values for Q_f and $Q_{ptfe\text{-}ed}$ were then calculated and multiplied by the
234 number of days for which the experimental phase lasted to give the total mass of a given VFA
235 that was produced during that time period. Finally, the total mass of VFA was divided by the
236 total mass of volatile solids fed to arrive at the value for yield ($mg_{vfa}\ g_{vs}^{-1}$). These calculations
237 were repeated for each species of VFA, and then these yields were added to each other to arrive
238 at a total VFA yield.

239 **3. Results and discussion**

240 **3.1. VFA recovery**

241 The primary aim for this body of work was to recover VFAs, via the PTFE-ED system, in a
242 solution that made them readily available for downstream use. Figure 3 shows that the
243 PTFE-ED methodology produced a solution of up to 4,500 mg L^{-1} total VFAs. Depending on
244 the degree of osmotic drag, this solution varied in volume from 20 to 30 litres and therefore a
245 mass of between 90 and 135 g of VFAs at any given time. Previous work (Chalmers Brown et
246 al., 2020) has shown that the PTFE-ED methodology can produce VFA solutions approaching
247 10,000 mg L^{-1} in model solutions and so further work would now be appropriate to determine
248 what level of VFA recovery can be achieved in real-world waste streams. Possible reasons for
249 the relatively low concentration in this study are that there was microbial consumption of the
250 VFAs as they accumulated in the concentrate reservoir, and that at room temperature the
251 volatility of the VFAs meant that they were lost to atmosphere. A decrease in the total
252 concentration of VFAs was first noticed on Day 10, and this decrease continued until Day 15
253 when it was decided to replenish the NaCl solution to prevent further microbial consumption.
254 The VFA concentration in the concentrate reservoir then increased immediately before

beginning to fall again after Day 22. In the work of Chalmers Brown et al., (2020) for example, much smaller volumes were used at bench scale, the model solutions did not contain microbial organisms, and the concentrate accumulated over a matter of hours rather than weeks. Further work would be useful to investigate why this system was unable to reach such high VFA concentrations for example by testing the addition of disinfectants or by keeping the concentrate reservoir at lower temperatures. This would be especially useful in maximising the overall efficiency of the system.

Figure 4 also shows that considerable concentrations of VFAs remain dissolved in the liquid phase of the bioreactor, despite the batch PTFE-ED recovery regime. This suggests that there is considerable scope to increase the duty cycle of VFA recovery. This would present an opportunity to increase the concentration of VFAs recovered into the concentrate reservoir, and could also have a positive effect on overall VFA yields and substrate utilisation, as will be addressed in the following sections. There is also good agreement between the proportions of VFA species in the concentrate reservoir and the bioreactor itself shown in Figures 3 and 4 respectively.

3.2. VFA yields

Figure 5 shows that overall VFA yields increased from 707 mg g_{vs}^{-1} during the Control Phase to 875 mg g_{vs}^{-1} when PTFE-ED was deployed. This is consistent with the hypothesis that the *in-situ*- recovery of end products, in this case VFAs, will alleviate end-product inhibition and result in greater VFA yields via prolonged acidogenesis.

Whilst the overall VFA yield was greater during the PTFE-ED Phase, the individual yields of propionic acid, butyric acid, and valeric acid were all higher during the Control Phase than the PTFE-ED Phase, decreasing by 13%, 34%, and 42% respectively. The overall VFA yield

increased by 24% in spite of these decreases, as a result of a 72% rise in the yield of acetic acid from the Control Phase to the PTFE-ED Phase (Figure 5).

The increased dominance of acetic acid in the PTFE-ED Phase is consistent with the hypothesis that recovering acetic acid, which is the end-product of homoacetogenesis, conditions would remain favourable for continued homoacetogenic activity, and therefore the preferential generation of acetic acid over other VFAs. Furthermore, as illustrated by Figure 6, no methane generation was detected during the PTFE-ED Phase whereas it was the dominant gas during the Control Phase. This data alone suggests that the recovery of VFAs makes conditions unfavourable for methanogenic activity, and when taken in conjunction with the increased proportion of acetic acid during the PTFE-ED phase, that the reason is likely to be a prolonging of homoacetogenic activity.

3.3. Substrate utilisation

By all metrics, substrate utilisation was greater during the PTFE-ED Phase than during the Control Phase as summarised in Table 2. This is consistent with the above data that higher substrate utilisation rates are required for greater yields. From a waste remediation point of view, increased substrate utilisation, especially in terms of chemical oxygen demand, is desirable. Furthermore, because the technology deployed herein is suitable for industrial processes, deployment to applications such as municipal wastewater treatment facilities is a realistic goal and increasing substrate utilisation rates, especially COD, is important for plant operations when it comes to discharging effluent to the environment. Because this methodology appears also to arrest methanogenesis by prolonging homoacetogenesis (Figure 6), it is possible that with a greater intensity of VFA recovery hydraulic retention times could be increased yet further, having the double benefit of yet further VFA yields and substrate utilisation without the bioreactor progressing to a methanogenic phase and continuing to produce VFAs.

This work has demonstrated that a combination of solids separation and membrane technologies is able to recover VFAs from real world wastes. The technologies used are scalable and industrially applicable, however in this study they were not optimised. The residual VFA in the bioreactor following recovery (Figure 4) means that there is scope to recover VFAs with greater intensity. It also stands to reason that doing so would mean that the acidogenic stage of fermentation can be prolonged further, increasing VFA yields and substrate utilisation accordingly. Alleviating the microbial consumption of recovered VFAs could also be achieved relatively easily via temperature control or disinfectants, allowing greater recovery concentrations to be achieved. A subsequent purification step using other technologies such as distillation or liquid-liquid extraction could also be used to produce a highly concentrated end-product. Therefore, further work is required to optimise the process to establish just how far the VFA yields and concentrations, and substrate utilisation rates, can be pushed.

4. Conclusions

A novel combination of solids separation and membrane technologies were used to recover VFAs, increase their yields, increase acetic acid proportions, arrest methanogenesis, and increase substrate utilisation rates. A VFA mixture of 4,500 mg L^{-1} was recovered with headroom to increase concentrations by arresting microbial VFA consumption. VFA yields were increased from 707 mg g_{vs}^{-1} to 875 mg g_{vs}^{-1} when PTFE-ED was deployed, and acetic acid proportions increased from 49% to 68%. No methanogenesis occurred during the 3 weeks whilst VFAs were being recovered, and VFA recovery increased substrate utilisation rates. Further work to maximise VFA recovery is called for.

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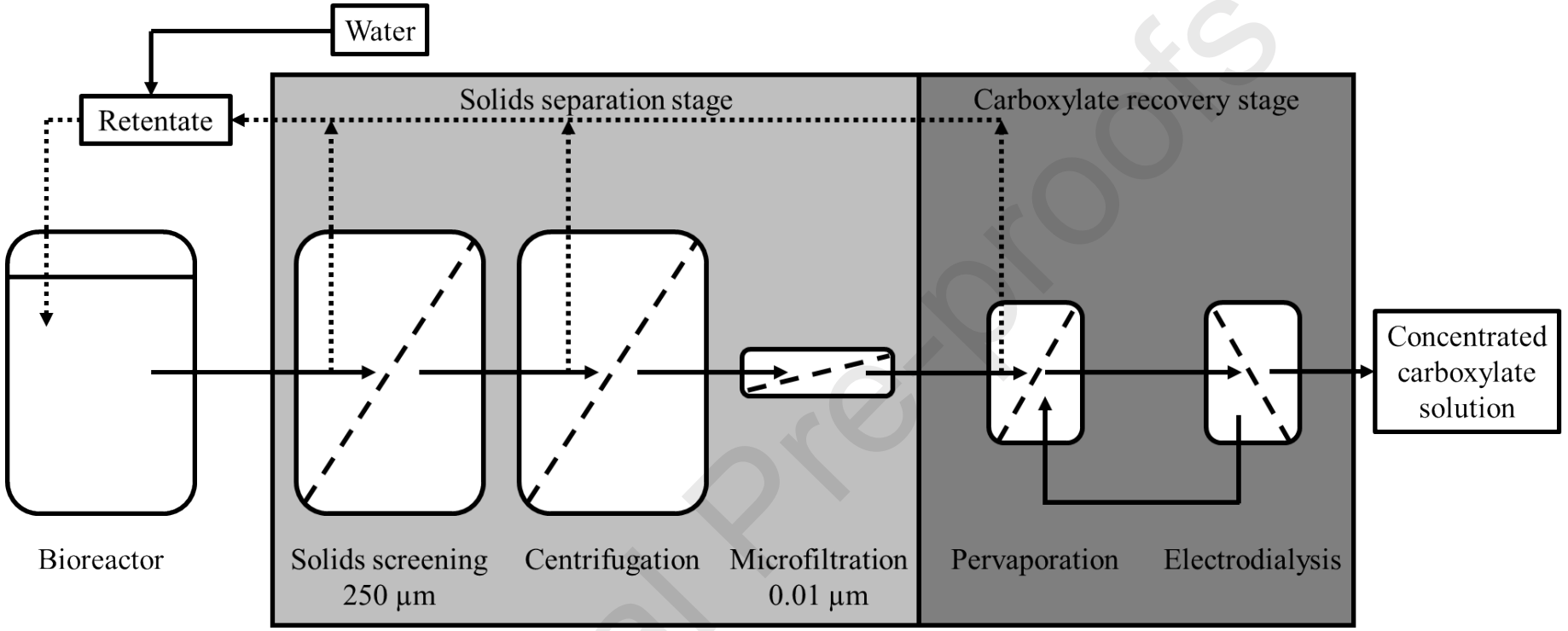
VFA	Uses	Annual market size		References
		Kilotons	USD	
Acetic acid	Disinfection* Herbicides* Platform chemicals* Food industry* Textiles*	16,300† in 2018	$16 bn by 2026‡	*(Jänisch et al., 2019) †(Dimian and Kiss, 2020) ‡(Acumen Research and Consulting, 2019)
Propionic acid	Food industry* Fungicides* Bactericide* Pharmaceuticals* Textiles* Plastics* Cosmetics*	350 – 470 in 2018†	$934 million in 2012‡	*(Jänisch et al., 2019) †(Atasoy et al., 2018) ‡(Markets and Markets, 2018)
Butyric acid	Food industry* Plastics*	50 in 2017†	$125 million in 2020‡	*(Jänisch et al., 2019) †(Baroi et al., 2017) ‡(Aghapour Aktij et al., 2020)
Valeric acid	Lubricants* Plastics* Food industry* Cosmetics* Pesticides*	No data	No data	*(Jänisch et al., 2019)

433 Table 1: Summary of the uses and market sizes of the volatile fatty acids in this study



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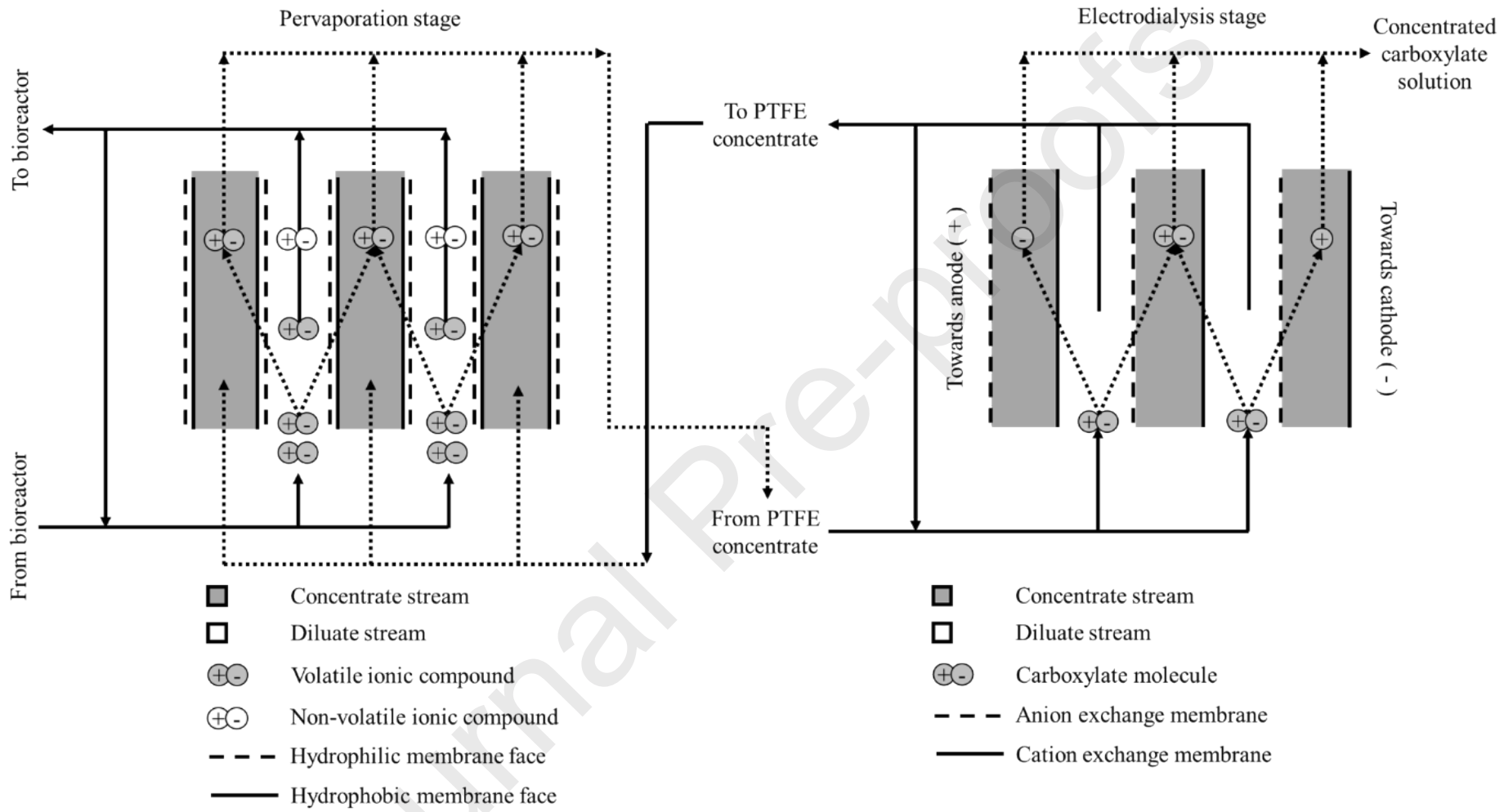
435 Figure 1. Schematic of the solids separation and carboxylate recovery process



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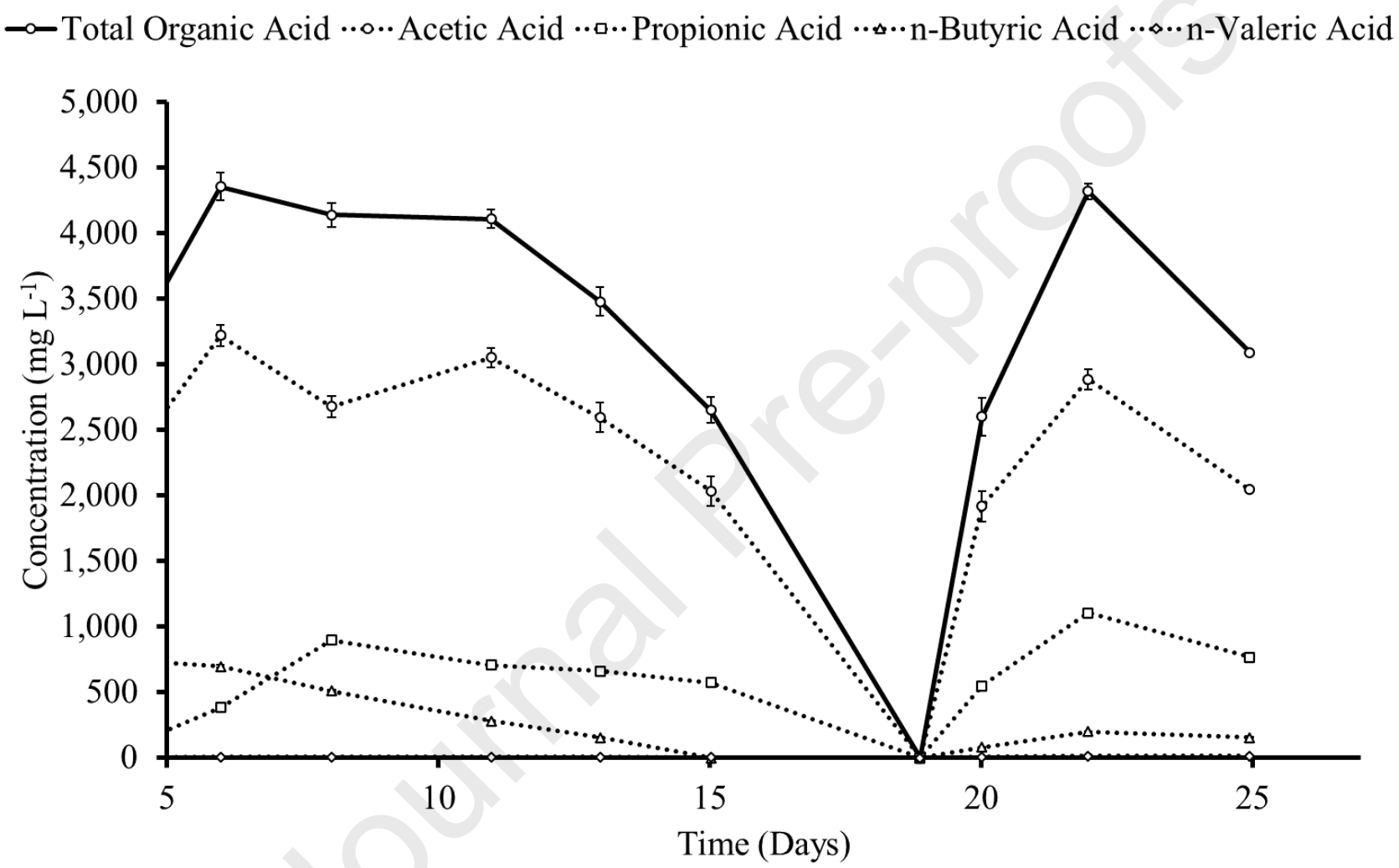
437 Figure 2. Process flow diagram of the pervaporation and electrodialysis systems operating in series



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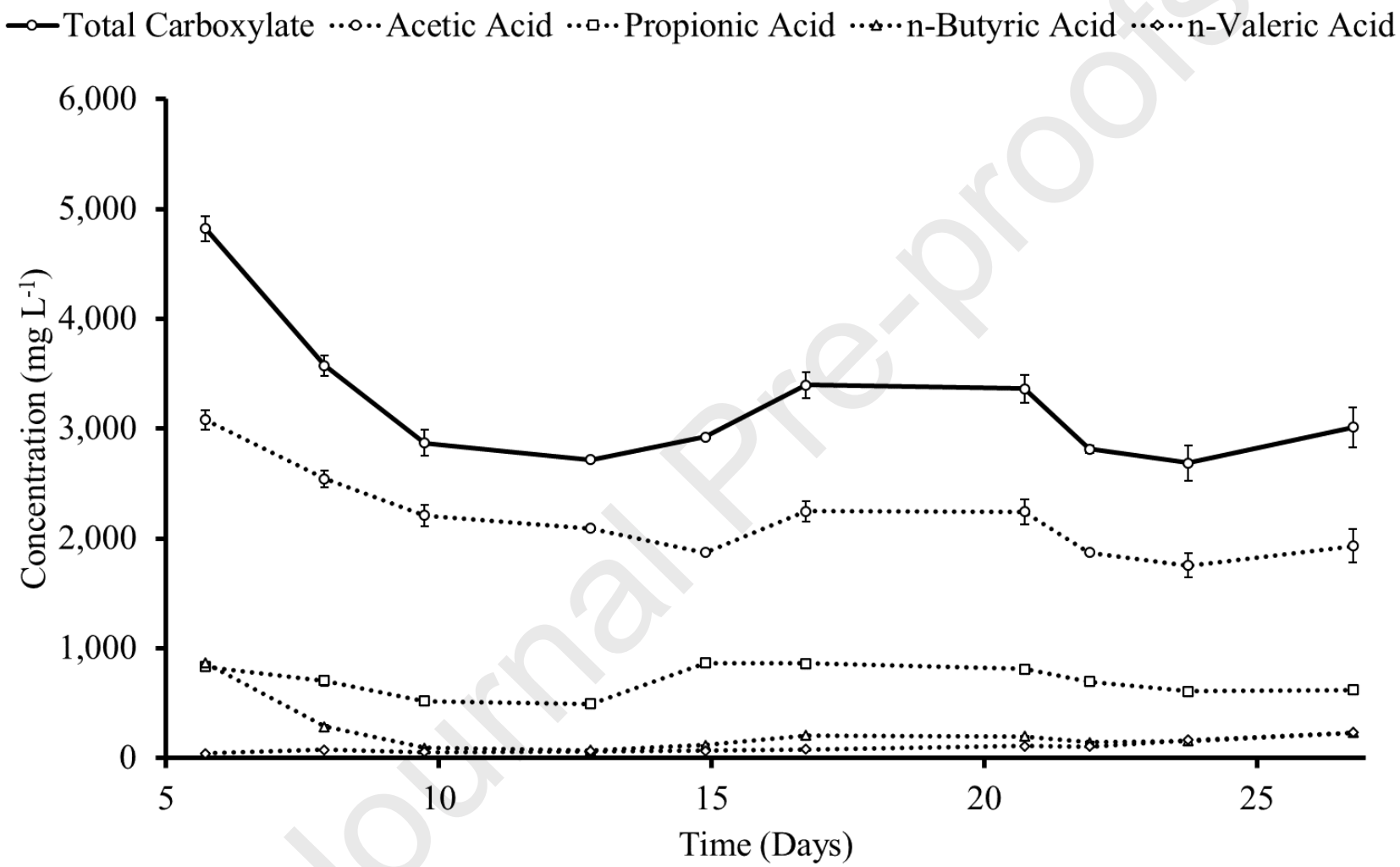
439 Figure 3. The concentration of the recovered VFAs in the concentrate reservoir throughout the experimental phase



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441 Figure 4. The concentration of VFAs remaining within the bioreactor during the experimental phase

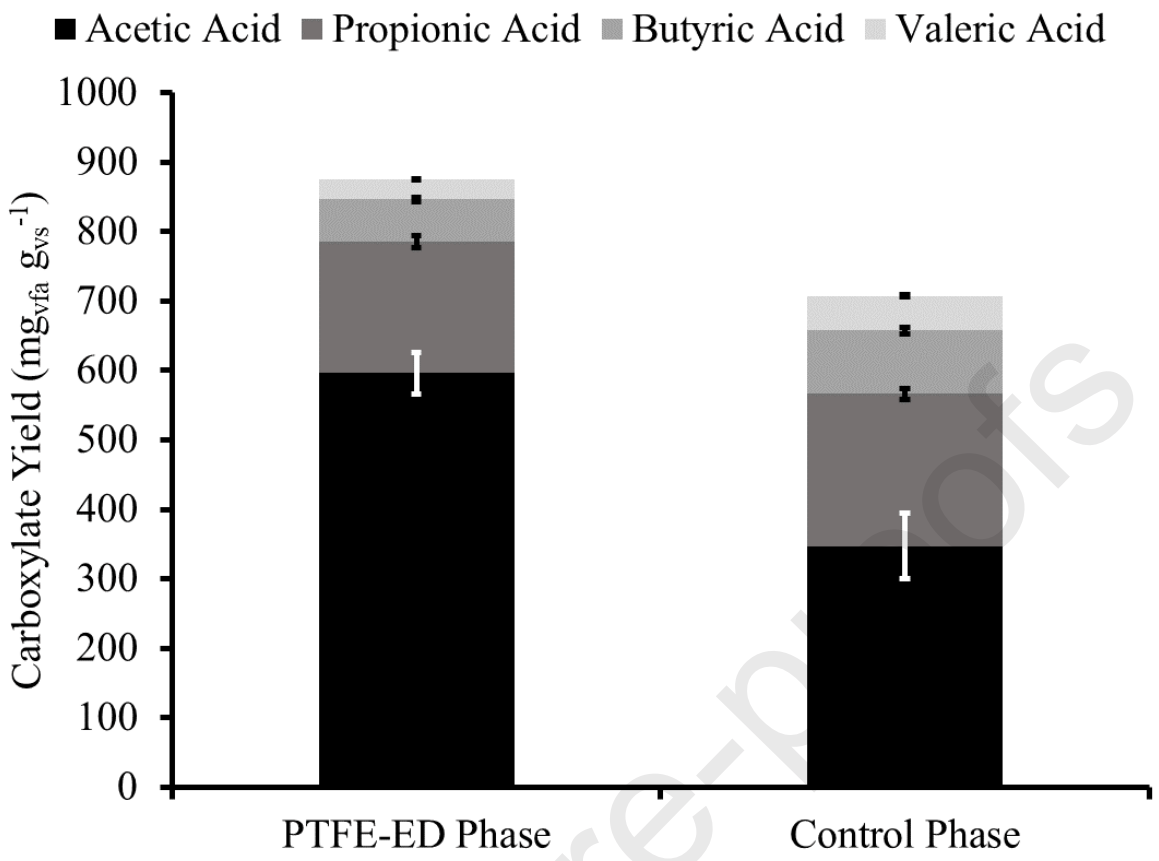
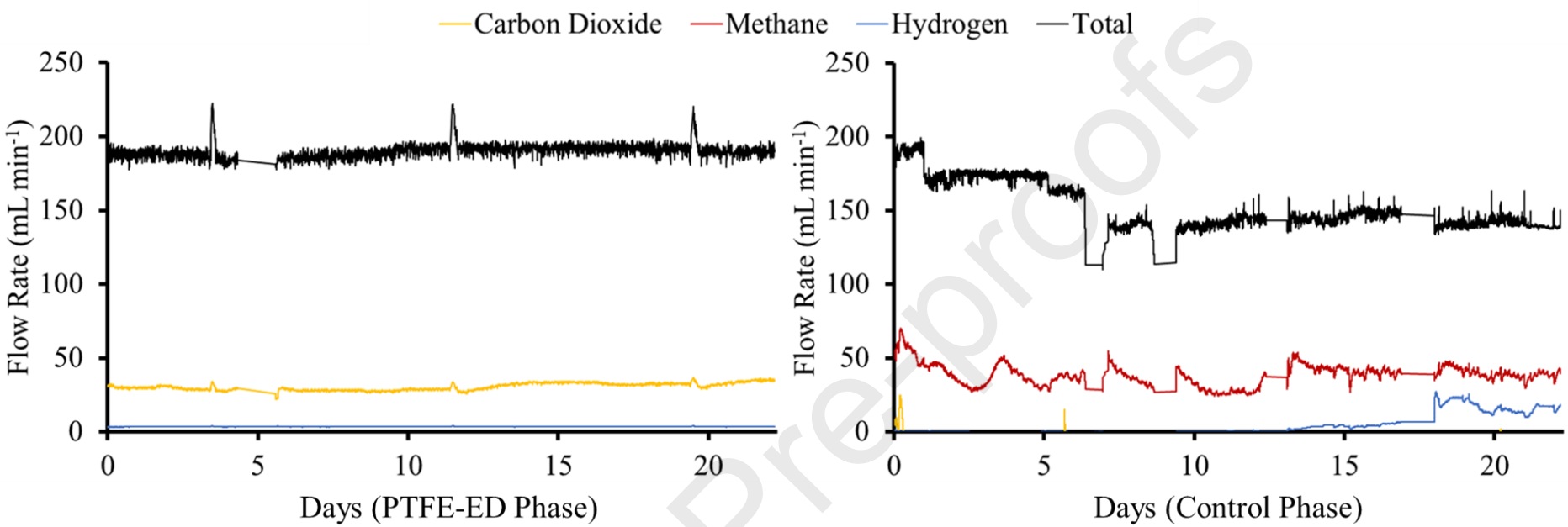


Figure 5. The overall yields of carboxylates in the experimental phase and the Control Phase



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445 Figure 6. Gas composition and flow rate during the PTFE-ED Phase and during the Control Phase

Metric	Feedstock (g L^{-1})		Reactor (g L^{-1})		Utilisation	
	Control	PTFE-ED	Control	PTFE-ED	Control	PTFE-ED
Total solids	41.18 (±3.41)	42.13 (±3.06)	37.02 (±1.65)	32.70 (±2.46)	10%	22%
Volatile solids	36.98 (±3.38)	37.59 (±3.04)	29.00 (±1.60)	28.18 (±2.23)	22%	25%
Soluble COD	10.44 (±0.81)	17.40 (±1.83)	6.23 (±0.53)	4.52 (±0.43)	40%	74%
Suspended COD	24.48 (±1.39)	24.32 (±2.03)	17.78 (±1.64)	12.64 (±1.19)	27%	48%
Total COD	34.92 (±1.20)	41.72 (±4.10)	24.01 (±1.77)	17.15 (±1.63)	31%	59%
Soluble carbohydrates	1.78 (±0.18)	2.69 (±0.27)	1.69 (±0.17)	1.38 (±0.13)	4.6%	49%
Suspended carbohydrates	24.01 (±2.02)	20.29 (±1.67)	14.13 (±1.17)	9.77 (±0.89)	41%	52%
Total carbohydrates	25.78 (±2.27)	22.99 (±2.20)	15.83 (±1.48)	11.16 (±1.18)	39%	51%

Table 2. Substrate utilisation rates in the Control Phase and the experimental phase

CRediT author statement

Alan Guwy: Conceptualization, **Rhys Jones** curation, Writing- Original draft preparation. ***Rodrigo Fernandex Feito:*** curation
Jaime Massanet-Nicolau, Richard Dinsdale, Alan Guwy*:* Supervision, reviewing

• System recovered VFAs from continually fed 83 L grass bioreactor over 3, 7-day HRTs

452 • 4,500 mg L^{-1} solution of VFAs produced, suitable for platform chemical use

453 • VFA recovery increased mean VFA yield from 707 to 875 mg_{vfa} g_{vs}^{-1}

454 • COD, carbohydrates, TS and VS utilisation increased during VFA recovery

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