

CONTINUOUS *IN SITU* EXTRACTION OF VOLATILE FATTY ACIDS IN AN ANAEROBIC DIGESTIVE SYSTEM

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KEY FINDINGS

Gas stripping was found to be inefficient and ineffective for the continuous removal and recovery of VFAs. An alternative *in situ* method, based on liquid-liquid extraction (LLE), was investigated. LLE was found to be more effective than gas stripping and the investigation showed that LLE was strongly dependent on pH, and the degree of extraction was higher in actual anaerobic digestion (AD) effluent than synthetic. Biocompatibility experiments were conducted with biochemical methane potential tests (BMPs) to test the toxicity of the solvents used in the LLE. Trioctylamine (TOA) in canola oil and Tributyl phosphate (TBP) in kerosene had the highest biogas production, $168.0 \text{ mL} \pm 26.15 \text{ mL}$ and $145.7 \pm 5.03 \text{ mL}$, respectively. These two solvents (extractant and diluent) had slightly higher methane percentages compared to the control (9.73 ± 1.33), with $12.62\% \pm 2.82\%$ for TOA in canola oil and $14.68\% \pm 6.73\%$ for TBP in kerosene. Based on the BMPs, LLE studies have shown that there is opportunity to co-produce VFAs and biogas. An experimental 17 L scale-up run demonstrated the potential for producing both biogas and VFAs continuously.

INTRODUCTION

VFAs are linear short-chained carboxylic acids with a low molecular weight and contain six or less carbon atoms. These acids are high value commodity chemicals and have a wide range of applications in industry, ranging from bioplastics to bioenergy. VFAs are currently produced commercially by petrochemical-based processes. The global demand to lessen the environmental impact of fossil fuels has attracted the use of alternative energy and resources that are renewable and sustainable. The production of VFAs through AD has increased significantly over the past few decades as AD can be used as a waste disposal method which can produce potential energy through the production of biogas. VFAs are present in this system as intermediates and are used as substrates for the production of biogas.

There are studies that have reported recovery of VFAs from the AD broth using adsorption, esterification, distillation, membrane separation, precipitation, electrodialysis and liquid-liquid extraction. Many of the studies use these recovery methods for downstream processing (*ex situ*). Recently, studies have used these methods *in situ*, whereby the recovery method is used 'on site' but in an external configuration. An *in situ* configuration is preferred as it improves productivity and increases yield, more importantly, it can be used to prevent product inhibition. Alternatively, an *in situ*-internal configuration is possible whereby the extraction method is placed inside the reactor/digester. Although, an *in situ* configuration internally could complicate the process, it can significantly reduce capital costs through the removal of additional equipment required for external *in situ*.

Each extraction technique has its own advantages and disadvantages that are associated when placed in an *in situ* manner. From these techniques, gas stripping and LLE were selected as it is economic and environmental friendly (solvent dependent).

METHODOLOGY

The main goal of this study was to determine an *in situ* extraction method for the continuous recovery of VFAs in an AD system, while co-producing biogas. To achieve this, laboratory-scaled experiments were conducted using a synthetic solution of VFAs. Gas-equilibrium and liquid-liquid equilibrium experiments were conducted for gas stripping and LLE, respectively. The preferred method of choice was then selected for further testing using actual AD effluent and to test the toxic effects of the extraction process on the digestive organisms. A batch scale-up AD process is currently being analysed with the continuous *in situ* extraction of VFAs.

MAIN RESULTS

The Table 1 below shows the results obtained for the gas-equilibrium experiments using pure carbon dioxide. From the table, it can be seen that very small amounts of VFAs were extracted, if any. This implies that it would take a tremendous amount of gas to strip the VFAs from the broth. Similar results were achieved using equimolar amounts of carbon dioxide and methane gas. The negative values seen in the table is attributed to HPLC error. Therefore, gas stripping was concluded to be ineffective and inefficient for the purpose of this study.

Table 1: Percentage of total VFAs extracted from the gas equilibrium experiments using pure carbon dioxide at 40°C

Sample	pH	% Extracted
1	2.0	0.18 ± 0.95
2	3.5	-0.12 ± 0.70
3	4.5	0.30 ± 0.13
4	5.0	-0.03 ± 0.55
5	6.0	0.91 ± 1.42
6	7.0	-0.08 ± 0.29

The preliminary results for the LLE using two extractants and three diluents showed promising results. Further experiments were investigated using actual AD effluent. The results for the

AD effluent were compared to the synthetic solution and can be seen below in Figure 1.

From the figures, higher degrees of extraction were observed using actual AD effluent than the synthetic VFA solution. The analysis of the individual VFAs showed that caproic acid was present in the AD effluent, whereas the synthetic solution only contained acetic, propionic, butyric and valeric acid. It is known from literature that the more carbon atoms the acid has, the easier the VFA is extracted into the organic phase. This is due to lower solubility limits of the larger VFAs.

It can be seen that LLE is strongly dependent on the pH. Higher degree of extraction was observed at low pHs, where the undissociated form is dominant, and low degree of extractions at high pHs. However, AD systems are susceptible to acidification which can cause digester failure due to VFA accumulation. Therefore, a more desirable approach would be to insert the LLE inside the reactor (*in situ*) as a controlling mechanism.

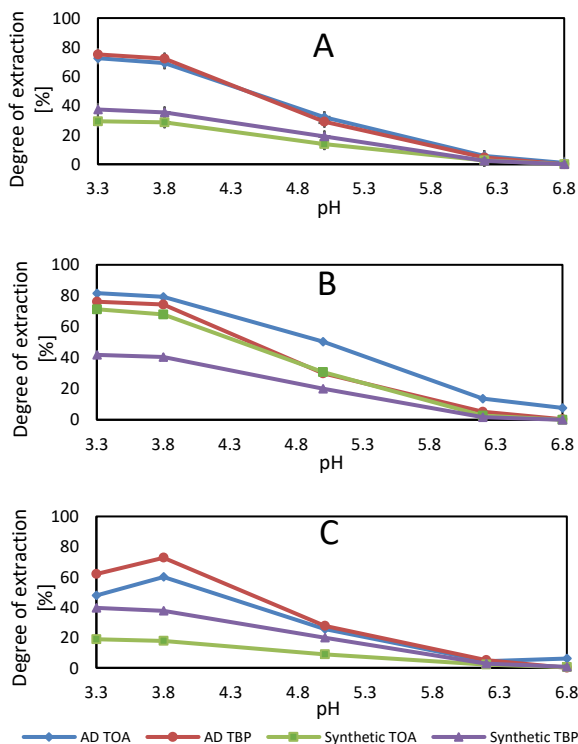


Figure 1: Degree of extraction (% E) of total VFAs from 20 vol% TOA or 20 vol% TBP in canola oil (A), oleyl alcohol (B) and lamp oil (C). LLE extraction was performed using AD effluent and a synthetic solution of VFAs in a range of pHs at 37°C.

For an *in situ* extraction method, it is important for the solvent to have low toxicity effects on the microbial consortia. Biocompatibility tests were conducted by testing the effects of the solvent on the consortia through biochemical methane potential (BMPs). The samples containing the solvents were compared to a control sample. The results of the BMPs can be seen in Figure 2.

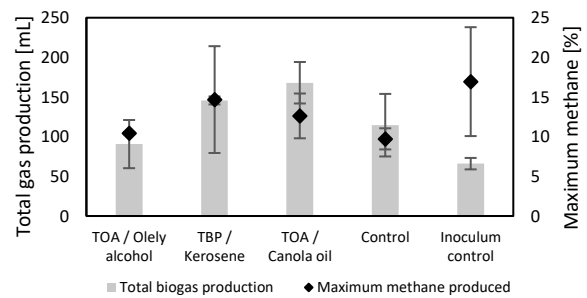


Figure 2: Biocompatibility test of solvents in BMPs by measuring the total biogas production and maximum methane percentage observed in a 28 day digestion period. Solvents consisted of 20 vol% extractant and diluent.

From the figure, it is evident that the solvents used in the experiment have a low toxicity towards the anaerobic bacteria. TOA in canola oil and TBP in lamp oil were biocompatible with the microbial consortia as methane production still occurred. Higher methane percentages were observed for these solvents, 12.62% ± 2.82% and 14.68% ± 6.73% respectively, as well as higher amounts of biogas produced (168.0 mL ± 26.15 mL and 145.7 ± 5.03 mL). TOA in oleyl alcohol performed slightly worse compared to the control, with low gas production 90.7 mL ± 30.37 mL but still maintaining a slightly higher methane percentage of 10.44% ± 0.13%

A scale-up experiment in a modified 17 L bioreactor was conducted with TOA in oleyl alcohol. The modified bioreactor can be seen in Figure 3. TOA in oleyl alcohol was chosen as the solvent had the highest final VFA concentration of 5.84 ± 0.36 g/L from the BMPs. The scale-up experiment resulted in 0.087 g of VFAs, with a concentration of 0.186 g/L. The digester produced 6.71 L of biogas with a methane percentage of 43%.

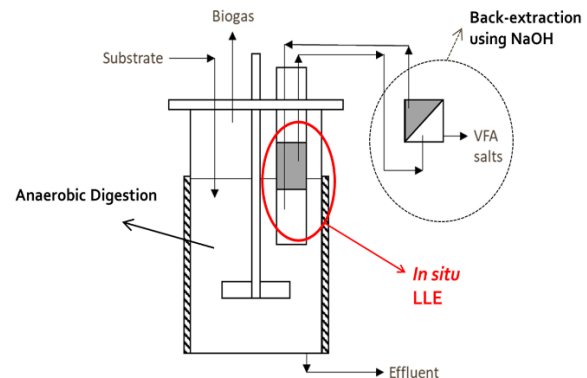


Figure 3: Modified 17L digester that incorporates LLE with solvent regeneration using a pH swing back-extraction.

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