

## Acetic acid recovery from a hybrid biological–hydrothermal treatment process of sewage sludge – a pilot plant study

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### ABSTRACT

A two-stage process consisting of anaerobic fermentation followed by sub-critical wet oxidation was used to generate acetic acid from sewage sludge at pilot scale. Volatile fatty acids, dominated by propionic acid, were produced over 4–6 days in the 2,000 L fermentation reactor, which also achieved 31% solids reduction. Approximately 96% of the carbon was retained in solution over the fermentation stage. Using a 200 L wet oxidation reactor operating in batch mode, the second stage achieved 98% volatile suspended solids (VSS) destruction and 67% total chemical oxygen demand (tCOD) destruction. Acetic acid produced in this stage was recalcitrant to further degradation and was retained in solution. The gross yield from VSS was 16% for acetic acid and 21% for volatile fatty acids across the process, higher than reported yields for wet oxidation alone. The pilot plant results showed that 72% of the incoming phosphorus was retained in the solids, 94% of the nitrogen became concentrated in solution and 41% of the carbon was converted to a soluble state, in a more degradable form. Acetic acid produced from the process has the potential to be used to offset ethanol requirements in biological nutrient removal plants.

**Key words** | acetic acid, anaerobic fermentation, wet oxidation

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### INTRODUCTION

Landfill disposal of sludge generated from municipal wastewater treatment is typical in New Zealand, but is subject to rising disposal costs, and fails to beneficially utilise the residue. The need for an alternative approach is desirable and can be achieved through the adoption of emerging technologies to derive greater value from sewage sludge. Volatile fatty acids (VFA), and specifically acetic acid, have further utility and production can be optimised during the acidogenic phase or anaerobic fermentation (Ghosh *et al.* 1987; Ponsá *et al.* 2008) of sewage sludge. Biological nutrient removal (BNR) plants, for example, require supplemental carbon substrate addition to work effectively. The acetic acid derived from anaerobic fermentation has been used as an appropriate carbon source in BNR processes (Banister & Pretorius 1998; Lee *et al.* 2014).

Wet oxidation is a technology to achieve sludge destruction carried out at sub-critical temperatures (180–374 °C)

and pressures in the presence of an oxidant. There has been a history of commercial plants using wet oxidation to treat sewage sludge including the Athos, VerTech and Zimpro processes. Acetic acid is a major product of sub-critical wet oxidation which, once formed, is recalcitrant to further oxidation during the hydrothermal stage (Shende & Levec 1999; Hii *et al.* 2014). Along with extensive solids destruction, a degradable chemical oxygen demand (COD)-rich liquor suitable for use in BNR processes is generated (Mantzavinos *et al.* 1996; Shanableh 2000).

The work reported on in this study describes a novel approach to both maximise waste solids destruction and VFA production. The application of a hybrid of anaerobic fermentation (acidogenesis) with an oxidative hydrothermal process (wet oxidation) takes advantage of the low cost of anaerobic digestion, the effective solids destruction of wet oxidation, and the combined VFA generation potential of both of these processes.

## METHODS

### Sample preparation and fermentation

Dewatered municipal biosolids from the beltpress of a local wastewater treatment plant (Rotorua, New Zealand) were collected and diluted with the beltpress underflow to give a concentration of 4–6% dry solids (DS). The biosolids were a mixture of primary sludge and secondary sludge from the Bardenpho BNR plant. The relative proportion of each sludge type was highly variable, but on average was approximately 32% primary and 68% activated sludge. Using a batch-fed system, whereby new material was fed twice daily, 1.0–1.2 m<sup>3</sup> of material was anaerobically fermented, feeding in at a rate of approximately 200 L/day. The loading rate was on average 4.9 ± 1.8 kg volatile solids (VS)/m<sup>3</sup> day. The temperature was maintained in the mesophilic range (36 °C) and controlled via a heated water jacket, and was operated with a 4.5–6 day retention time in a 2,000 L mechanically stirred reactor. The pH was maintained at pH 6.2 through the addition of sodium hydroxide (5 mol/L solution), with consumption on average 1.0 L/day. The fermented material was subsequently used in the wet oxidation stage.

### Wet oxidation

Prior to wet oxidation the fermented material was first diluted by approximately 50% to enable better pumping and to decrease the oxygen demand requirements during wet oxidation. The wet oxidation stage consisted of a 200 L pressure reactor which could be operated in both batch and continuous modes. The results described in this paper were for a batch wet oxidation whereby the reactor was filled with fermented sludge to a level of 30% under ambient conditions. A 20 barg over-pressure of Air (Industrial Grade, BOC, Rotorua, New Zealand) was applied and the reactor was heated to a temperature of 220 °C. To achieve the temperature rise from ambient to 220 °C took 2 h and the batch experiment was run for a further 3 h isothermally. The total operating pressure at 220 °C temperature was 43 barg. A continuous supply of pure O<sub>2</sub> (High Purity, BOC, New Zealand) was used to provide sufficient O<sub>2</sub> for substrate oxidation to occur throughout the experimental run. Liquid samples were taken periodically throughout the experiments and analysed for key analytical components.

### Heat recovery

A pilot plant experiment was carried out to ascertain the heat balance from the wet oxidation stage. The heat of reaction ( $Q_{\text{reaction}}$ ) was determined according to Equation (1)

$$Q_{\text{reaction}} = H_{\text{offgas}} + H_{\text{effluent}} - H_{(\text{in,sludge})} - H_{(\text{in,O}_2)} - Q_{\text{oil}} + Q_{\text{surr}} \quad (1)$$

where  $Q_{\text{reaction}}$  = heat of reaction (kW),  $Q_{\text{surr}}$  = energy loss to the surroundings (kW),  $H_{\text{offgas}}$  = enthalpy from offgas (kW),  $H_{\text{effluent}}$  = enthalpy from effluent (kW),  $H_{(\text{in,sludge})}$  = enthalpy from feed sludge (kW),  $H_{(\text{in,O}_2)}$  = enthalpy from oxygen (kW) and  $Q_{\text{oil}}$  = energy input from the thermal oil (kW).

The energy input supplied from the heating oil system ( $Q_{\text{oil}}$ ) was monitored at 5 s intervals throughout the experiment. A batch water phase was used to determine a value for  $Q_{\text{surr}}$ . The heat required to heat up water from ambient ( $Q_{\text{heatup}}$ ) was derived from the  $H_{\text{effluent}} - H_{(\text{in,sludge})}$  value. The introduction of continuously fed fermented sludge (3.5% d.s.) then allowed an estimate of the  $Q_{\text{reaction}}$  to be made from the reduction in energy input required.

### Sample analyses

Total suspended solids (TSS), volatile suspended solids (VSS), dissolved reactive phosphorus (DRP) and COD were determined using *Standard Methods for the Examination of Water and Wastewater* (APHA 1998). Dissolved organic carbon (DOC) was determined using a High TOC II analyser (Elementar, Hanau, Germany).

VFA concentrations were determined by an in-house method involving pH correction, with formic acid, followed by capillary gas chromatography (GC) with flame ionisation detection. The column used was a nitroterephthalic acid modified polyethylene glycol capillary column, DB-FFAP: 250 °C: 30 m × 530 μm × 0.5 μm ramped from 40 to 180 °C. Butan-1-ol solution as internal standard, and turbid samples were pre-filtered through a Nylon syringe filter (0.45 μm). Calibration curves of the VFA (acetic acid, propionic acid, iso-butyric acid, *n*-butyric acid, pentanoic acid and hexanoic) were prepared from 10, 20, 40 and 60 ppm standards. Test sample concentrations were then measured based on a comparison to the standards peak area.

Gas production from the fermentation pilot plant was measured using a Proline t-mass 65 F thermal mass flow meter (Endress & Hauser, Reinach, Switzerland). This was

calibrated using a drum-type Ritter gas meter. The gas composition was measured from discrete samples taken periodically and measured using a GC (Carle Instruments, Inc., GC, USA) with a thermal conductivity detector and helium as the carrier gas (22 ml/min, 54 °C).

Ammoniacal nitrogen (NH<sub>4</sub>-N) was analysed using a modified Dumas method (Rayment & Lyons 2011).

For metals analysis, the filtered solid samples were air dried at 35 °C and sieved. The <2 mm fraction was digested with a nitric/hydrochloric acid mix and analysis was completed using inductively coupled plasma-mass spectrometry (ICP-MS). Aqueous metals were determined with ICP-MS following filtration through a 0.45 µm membrane filter.

## RESULTS AND DISCUSSION

The pilot plant fermentation unit was operated over 1 year, and the wet oxidation pilot plant was used intermittently during this time. The process conditions in the fermentation pilot plant were periodically changed and so the results in this section represent a sub-set of the 1-year data, consisting of a distinct process condition, as described above.

### Anaerobic fermentation

The feed and discharge from the pilot plant fermentation reactors were sampled regularly. Summary results for the sampled components are shown in Table 1. During this period of operation the VS destruction was on average 31%. The biogas yield was low relative to typical values seen in methanogenic reactors and was characterised by higher concentrations of carbon dioxide (60%) and lower concentrations of methane (31%). Nitrogen was present, partly from dissolved gases in the feed material, and partly from the process used to prevent a vacuum forming during feed and discharge.

The majority of the total COD (tCOD) was retained within the reactor through the fermentation process. Some COD was lost as the organic substrate was microbially converted to CO<sub>2</sub> and CH<sub>4</sub>. However, gas production was low and this only represented approximately a 5% COD loss, although the soluble COD did increase significantly. This is indicative of the hydrolysis of polymeric substances and solubilisation of particulate material, which is also demonstrated by the rise in DOC concentration which was observed.

The VFA concentration approximately doubled through fermentation to about 5 g/L. The levels of acetic acid and VFA were high, for a raw sludge, in the feed material,

**Table 1** | Pilot plant fermentation average data collected over 53 days of operation

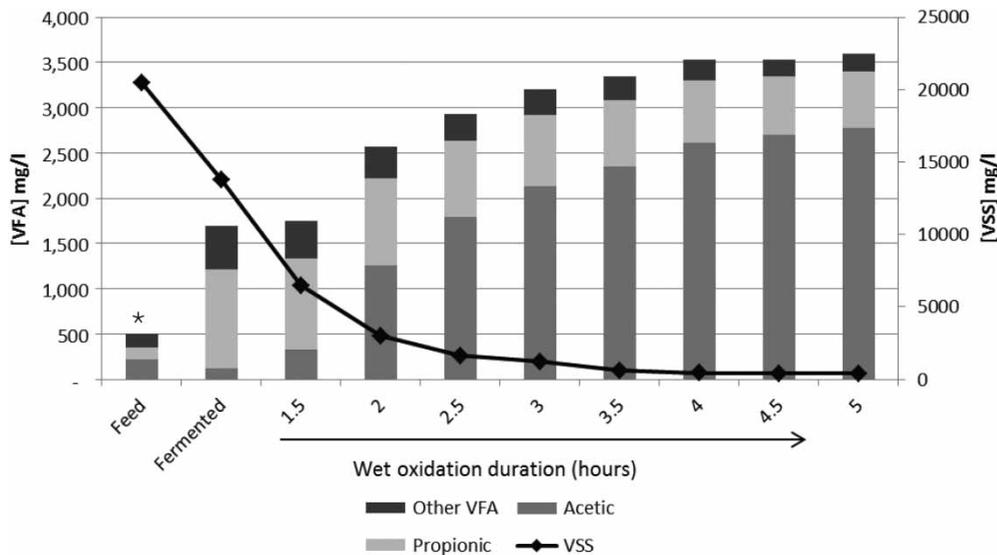
Component	Feed	Fermentation
TS (mg/L)	59,000 ± 4,000	42,600 ± 3,000
VS (mg/L)	50,000 ± 3,500	34,000 ± 2,600
TSS (mg/L)	48,600 ± 4,800	35,200 ± 3,500
VSS (mg/L)	41,800 ± 4,200	28,800 ± 3,000
% VS destruction		31% ± 20
% VSS destruction		28% ± 23
Biogas yield (m <sup>3</sup> /kg VS added)		0.110 ± 0.036
Gas production (m <sup>3</sup> /m <sup>3</sup> day)		1.34 ± 0.31
% CO <sub>2</sub>		60 ± 7
% CH <sub>4</sub>		31 ± 6
% N <sub>2</sub>		9 ± 14
VFA (mg/L)	2,629 ± 496	4,972 ± 644
Acetic acid (mg/L)	1,103 ± 194	313 ± 87
VFA yield (kg/t feed VS)		107 ± 56
Acetic acid yield (kg/t feed VS)		6 ± 11
Purity (tVFA-C/tDOC)	41	55
NH <sub>4</sub> -N	305 ± 54	870 ± 91
COD (total)	64,880 ± 6,184	62,718 ± 5,910
COD (soluble)	7,430 ± 1,060	14,868 ± 1,686
DOC	2,031 ± 326	4,652 ± 590
DRP	277 ± 31	386 ± 41

Error bars represent 95% confidence intervals for the mean.

which may indicate that some fermentative activity had occurred prior to it being fed to the anaerobic fermenter. The fermentation during this period of operation produced propionic acid as the predominant VFA with low concentrations of acetic acid. Propionic acid accumulation has been associated with anaerobic fermentations occurring at pH 5.5, with high loadings and micro-aerobic conditions (Wang *et al.* 2006). Production of propionic acid, at the expense of acetic acid, during fermentation can be potentially beneficial. For example, a high propionic acid concentration relative to acetic acid could improve any subsequent enhanced biological phosphorus removal which may occur (Chen *et al.* 2004).

### Wet oxidation of fermented biosolids

The wet oxidation stage, treating fermented biosolids, was characterised by a 97% VSS destruction. Owing to the heating lag, considerable solids destruction (78%) had occurred prior to the operating temperature being reached. The tCOD destruction was 67% across wet oxidation, which agrees



**Figure 1** | VSS destruction (mg/L) and VFA production (mg/L) over time through a hybrid pilot plant continuous fermentation and batch wet oxidation at 220 °C. \*Feed concentration was an average of the previous 6 days of feed samples and normalised based on the dilution used for wet oxidation.

closely with that seen by other researchers (Lendormi *et al.* 2001). The results of treatment through a long-term continuous fermentation and an exemplified batch wet oxidation are described in Figure 1.

A significant accumulation of VFA was observed over the experimental time course. VFA concentration increased during the fermentation stage and a further approximate doubling occurred through wet oxidation. Whereas propionic acid predominated through the fermentation stage acetic acid became the principal VFA produced following wet oxidation. The high acetic acid accumulation during wet oxidation was accompanied by a gradual degradation of propionic acid and other VFA components. This demonstrates the recalcitrance of acetic acid to hydrothermal degradation occurring due to kinetic limitations at the temperatures used in these experiments. The generation of propionic acid which was observed during fermentation, at the expense of acetic acid, may lead to higher oxygen demand requirements during wet oxidation given the recalcitrant nature of acetic acid.

The gross yield of VFA from VSS was 9% across the fermentation stage which had increased to 21% by the end of the wet oxidation (Table 2). Over the wet oxidation stage alone the gross yield was 27%, which was higher due to the VSS destruction that had already occurred during the fermentation stage. The gross yield of acetic acid was 16% across the whole process or 20% across the wet oxidation stage only (Table 2). This is favourable to acetic acid yields reported by other researchers of 10–11% (Shanableh 2000)

**Table 2** | Gross yield of acetic acid and volatile fatty acids across unit processes

Stage	Gross yield acetic acid	Gross yield VFA
Fermentation (kgVFA/tVSS <sub>feed</sub> )	–	95
Wet oxidation (kgVFA/tVSS <sub>fermented</sub> )	202	268
Fermentation + wet oxidation (kgVFA/tVSS <sub>feed</sub> )	155	206

and 12.9–14.9% (Hurwitz *et al.* in Shanableh (2000)) for wet oxidation alone.

Overall, the results demonstrate the combined benefit of fermentation and wet oxidation to boosting the VFA yield from the process.

### Heat balance

The wet oxidation of sewage sludge is an exothermic process (Hii *et al.* 2014). A heat balance derived from a pilot plant experiment confirmed that an exothermic process was occurring. Losses to the surroundings from the hydrothermal pilot plant were 23 – 25 kW and losses through the offgas ranged between 4 and 6.5 kW. For the pilot plant, the sludge wet oxidation provided 15–19 kW of additional heating to the system, representing the heat of reaction. Relative to the oxygen consumed, as determined by the tCOD destruction, the heat of reaction was 19.4 MJ/kg O<sub>2</sub> consumed. On a mass basis the  $Q_{\text{reaction}}$  was 14.5–16.1 MJ/kg. The heat of

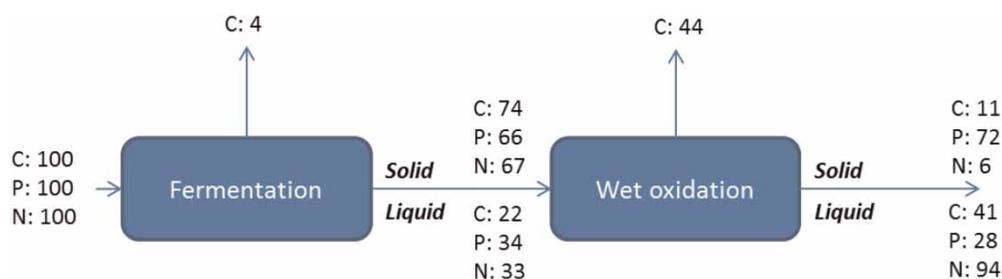


Figure 2 | Relative flow of carbon, phosphorus and nitrogen through treatment. Average of pilot plant data.

reaction provides sufficient heat to allow the temperature of the feed material to be raised to the wet oxidation operating temperature.

These results demonstrated that additional external heat inputs would not be necessary for the process given that it is an exothermic reaction. Under hydrothermal processing, oxidation of organic material takes place in the aqueous phase. This negates the need to dry or dewater the material first, prior to wet oxidation, leading to potential cost savings.

### Nutrient mass balance

A balance of carbon, nitrogen and phosphorus through the hybrid process is graphically presented in Figure 2. This is based on averaged data from multiple results obtained from pilot plant fermentation and wet oxidation experiments. Gaseous carbon losses were small during the fermentation stage and overall 41% of the input carbon was retained in aqueous effluent phase. Phosphorus was associated largely with the solids fraction and nitrogen had predominantly solubilised. Gas samples showed no evidence of volatilised nitrogenous compounds. Through the fermentation stage the anaerobic conditions had resulted in some solubilisation of the phosphorus fraction. However, this phenomenon was reversed under the wet oxidation conditions in the second stage, and phosphorus was precipitated in the solid phase. This has the potential to be optimised further by precipitating out more of the phosphorus and could be used as a source of phosphorus in fertiliser production (Blöcher et al. 2012).

The presence of nitrogen, mainly as ammoniacal nitrogen, in the effluent of the wet oxidation stage affects the potential for the effluent liquor to be used as an aid to denitrification in a BNR plant. A further processing stage to strip the ammonia may therefore need to be added to reduce the nitrogen content and enable a high-carbon containing effluent to be reused beneficially. The high concentrations of ammonia (850 mg/L) in the liquor may drive favourable

economics of such a process step, given that recovery as an ammonium sulfate solution is feasible.

### Solids analysis

A portion of the wet oxidised liquor was filtered and the retained solids composition was analysed (Table 3). Vacuum filtration produced a solid fraction of 30% DS. Some carbon (252,000 mg/kg DS) and nitrogen (22,400 mg/kg DS) were not solubilised and remained associated with the solids phase. The presence of high residual carbon, as shown in Table 3, is evidence that for this data set, less VSS degradation had occurred. The solid contained approximately 8% phosphorus, or 25% as phosphate. These are similar concentrations to commercially available fertilisers. Aluminium, calcium, magnesium and iron were also present with each making up 1–5% of the total dry mass. The key heavy metals Cd, Hg, As and Pb were below New Zealand voluntary limits for fertilisers applied to land (NZFMRA 2009), with the Cd:P ratio significantly below the limit. If the solid residue were to be

Table 3 | Elemental composition of wet oxidised filtered solids (average of sampled solids from five runs)

Component	% as dry weight	% present in solid phase	Component	% as dry weight	% present in solid phase	
S	0.1	–	As	} sum < 0.4	54	
N	2	24	Cd		99	
C	25	47	Cr		100	
SiO <sub>2</sub>	13	–	Cu		99	
PO <sub>4</sub>	25	94	Pb		100	
Al	3	100	Hg		100	
Ca	3	98	Ni		98	
Fe	3	99	Zn		99	
Mg	2	97	Other		24	–

classified as biosolids then Cu, Hg, Ni and Zn would exceed Class A guideline concentrations for application to land (NZWWA 2003).

Using X-ray diffraction on the dewatered treated solids allowed for identification of the minerals struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ), quartz ( $\text{SiO}_2$ ), tridymite ( $\text{SiO}_2$ ), cristobalite ( $\text{SiO}_2$ ), plagioclase ( $\text{NaAlSi}_3\text{O}_8$ ) and mascagnite ( $(\text{NH}_4)_2\text{SO}_4$ ).

A mass balance based on 30% DS concentration and known dissolved element concentrations was used to determine the percentage of each element present in the solid phase (Table 3). As already mentioned, a large degree of solubilisation of carbon and nitrogen had occurred. Arsenic was the most soluble of the metals. Other heavy metals were not soluble and accumulated mainly in the solid phase.

## CONCLUSION

The hybrid biological-fermentation process to treat sewage sludge was evaluated at pilot plant scale. Overall, this process achieved:

- a significant reduction in volume with a 97% VSS destruction occurring in an exothermic process;
- hydrolysis through anaerobic fermentation to achieve initial conversion to VFA components;
- accumulation of acetic acid through the wet oxidation stage and the gradual degradation of other VFA components, such as propionic acid generated during the fermentation stage;
- an effluent liquor enriched in acetic acid;
- a solid fraction containing phosphorus with potential suitability for use as a fertiliser.

The pilot plant results showed that the process is a viable technology which can return high concentrations of VFA-containing liquors. Future work will be undertaken to scale up the technology to treat at a larger demonstration-plant level.

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