Evaluation of chemical, thermobaric and thermochemical pre-treatment on anaerobic digestion of high-fat cattle slaughterhouse waste

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ABSTRACT

This work aimed to enhance the anaerobic digestion of fat-rich dissolved air flotation (DAF) sludge through chemical, thermobaric, and thermochemical pre-treatment methods. Soluble chemical oxygen demand was enhanced from 16.3% in the control to 20.84% (thermobaric), 40.82% (chemical), and 50.7% (thermochemical). Pre-treatment altered volatile fatty acid concentration by ~64% (thermobaric), 127% (chemical) and 228% (thermochemical). Early inhibition was reduced by 20% in the thermochemical group, and 100% in the thermobaric group. Specific methane production was enhanced by 3.28% (chemical), 8.32% (thermobaric), and 8.49% (thermochemical) as a result of pre-treatment. Under batch digestion, thermobaric pre-treatment demonstrated the greatest improvement in methane yield with respect to degree of pre-treatment applied. Thermobaric pre-treatment was also the most viable for implementation at slaughterhouses, with potential for heat-exchange to reduce pre-treatment cost. Further investigation into long-term impact of pre-treatments in semi-continuous digestion experiments will provide additional evaluation of appropriate pre-treatment options for high-fat slaughterhouse wastewater.

1. Introduction

The Australian red meat processing industry consist of more than 150 slaughterhouses which for the financial year of 2013–14 produced 20.8 gigalitres of untreated wastewater (AMPC, 2015; Australian Bureau of Statistics, 2016). This wastewater contained high concentrations of pollutants, with average concentrations of 2657 and 1780 mg L⁻¹ for biochemical oxygen demand (BOD) and fat, oil and grease (FOG) respectively (AMPC, 2015). As a result, 37 kilotonnes of FOG entered waste streams. Subsequently, this waste requires several treatment interventions prior to discharge to sewage (Bustillo-lecompte & Mehrvar, 2015; McCabe et al., 2013).

A comprehensive list of primary, secondary and tertiary treatment technologies used by Australian red meat processors is published by Meat and Livestock Australia (MLA, 2002). Primary treatment options listed include static and rotary screens, screw presses, dissolved air flotation (DAF), and collection pits. These options can result in significant reductions in wastewater pollutant concentrations.

Secondary treatment involves biological treatment as either aerobic or anaerobic digestion, or a combination of both. Anaerobic digestion (AD) is a four-stage process which involves the action of microbes to digest organic waste to produce biogas — a combination of typically 20–50% carbon dioxide, and 50–80% methane gas. The capture of methane from Australian slaughterhouse wastewater via anaerobic digestion has gained momentum over the past two decades (IEA, 2015).

In order for AD systems to perform optimally, it is essential to focus on process stability. Control over influent stream is necessary to reduce the frequency and magnitude of shock loadings, and regulate FOG loading. In Australian slaughterhouses, recovery of FOG for sale as tallow is key for value adding. Following recovery of FOG as tallow, the remaining fat often collects in the anaerobic digesters. There are a number of potential drawbacks to FOG addition to AD feedstocks, including digester foaming, pipe blockages, clogging of gas collection and handling systems, crust formation, sludge flotation and washout, and digester inhibition (Long et al., 2012).

While these drawbacks have been acknowledged, FOG remains a potentially desirable substrate due to a relatively high theoretical methane potential of 1014 L per kg of volatile solids (VS) when compared with protein and carbohydrate at 480 L kg VS⁻¹ and 370 L kg VS⁻¹ respectively (Buswell & Neave, 1930; Verein Deutscher Ingenieure, 2006; Wan et al., 2011). Consequently, research has been focused on mechanisms to enhance FOG bioavailability, while avoiding digester inhibition (Chen et al., 2008). Many research projects have utilised codigestion to varying degrees of success, producing encouraging results. For example, Gelegenis et al. (2007) combined poultry manure with olive-oil mill wastewater at 3:1 v/v and yielded 21% more methane.
than the poultry manure control, while Davidson et al. (2008) observed a 9–27% increase in methane yield when adding 10–30% grease trap sludge on a VS basis respectively. While co-digestion in Australia has received little investigation, the country is actively pursuing research in this area (Astals et al., 2014).

Alternatively, various pre-treatment methods have been identified and used to good effect in the degradation of waste activated sludge (WAS) prior to anaerobic digestion (Appels et al., 2008). Pre-treatments are aimed at augmenting hydrolysis, the rate limiting step, by improving the surface area to volume ratio of the substrates (Carrere et al., 2016). Methods such as thermobaric, chemical and bio-surfactant all achieve this increase in surface area to volume ratio of organics to varying degrees (Kim et al., 2003; Li & Noike, 1992; Mouneimne et al., 2003). Hydrolysis could also be enhanced by improving conditions for chemical reactions to occur, or introducing reagents that allow hydrolysis to occur more rapidly. For instance, thermobaric treatment will increase the rate at which hydrolysis occurs, while sodium hydroxide produces a saponification reaction to cleave long-chain fatty acids (LCFA) from glycerol (Mouneimne et al., 2003).

While much of the research on pre-treatments of high FOG substrates has centred on WAS, no studies have been performed on the effect they have on slaughterhouse wastewater to date (Harris & McCabe, 2015). This paper presents the results of three pre-treatment methods, namely chemical, thermobaric, and thermochemical, conducted on slaughterhouse DAF sludge as a first step in evaluating its effectiveness in enhancing anaerobic digestion.

2. Materials and methods

2.1. Inoculum and substrate

The inoculum was anaerobic sludge sourced from a covered anaerobic lagoon at a local slaughterhouse. Sludge was stored in an incubator at 37 ± 1 °C for 5 days prior to use. The DAF sludge used as substrate is the concentrated FOG residues collected by the dissolved air filtration unit. This material was used for its high FOG content and is representative of the fatty material entering the anaerobic digestion system of red meat processors. Substrate was collected as a 2 L grab sample from the DAF of a local red meat processing plant. Samples were immediately returned to the laboratory and stored at 4 °C. DAF sludge was stirred to achieve homogeneity prior to portioning waste into bottles for pre-treatment, or into reactors for digestion. The following DAF sludge characteristics were measured: pH, total solids (TS), VS, total chemical oxygen demand (TCOD), soluble chemical oxygen demand (SCOD), FOG, volatile fatty acids (VFA), measured as acetic acid equivalence per litre (HAcEq L⁻¹) (Table 1).

2.2. Pre-treatments for DAF sludge

Pre-treatment options were selected based on reported research which use WAS as a substrate (Li et al., 2015). For this current study, methods were selected that were expected to produce a positive impact on the degradation of FOG component of the wastewater (Harris & McCabe, 2015).

Chemical pre-treatment using 7 g NaOH/L was adapted from Kim et al. (2003) and allowed to react with the substrate for 24 h prior to digestion. Thermobaric pre-treatment was conducted using an autoclave at 121 °C for 30 min, and allowed to cool for 24 h before use (Kim et al., 2003). Thermochemical treatment was a combination of chemical and thermochemical treatment, with NaOH addition prior to autoclaving.

2.3. Biochemical methane potential testing

Tests were conducted using the Automated Methane Potential Test System II (AMPTS II; Bioprocess Control, Lund, Sweden). Inoculum and substrate were added at a ratio of 3:1 respectively on the basis of VS to avoid overloading the inoculum. Substrate was portioned based on weight, and rinsed into reactors with distilled water. Final reactor volume was approximately 400 mL of liquid with the remaining volume as head space in a 500 mL Schott bottle. Reactors were maintained at a site at a red meat processing facility. For the calculation of financial values, the waste parameters measured in this investigation will be utilised, a combined heat and power (CHP) unit with electrical conversion efficiency of 40% will be assumed, and an electricity cost of $0.15 AUD kWh⁻¹ and a natural gas cost of $8.15 AUD GJ⁻¹ will be used (AEMO, 2017). This does not take into account the use of heat from the CHP unit. Furthermore, this work does not consider the flow-on benefits to the AD system that may be established as a result of pre-treatment, as further work using semi-continuous digesters is needed to identify such benefits.

2.4. Cost and energy calculations

Various parameters were investigated on anaerobic sludge and DAF sludge prior to digestion. VS and TS were analysed using a modification to standard method 2540G with a 20 h residence time at 105 °C (Standard methods for the examination of water & wastewater, 2005). Volatile fatty acids were analysed using photometric measurement of Merck volatile organic acid test kits (Cat. No. 101809) and FOG content was measured using a Wilks Infracal 2 analyser. Total COD was measured using Merck test kits following a dilution series. Soluble chemical oxygen demand was determined using centrifugation at 13,000g for 10 min and subsequent photometric measurement of the supernatant with Merck test kits both before and after biochemical methane potential (BMP) investigation.

Table 1 Characteristics of inoculum and untreated DAF sludge used in this work

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>TS (%)</th>
<th>VS (%)</th>
<th>VS/TS (%)</th>
<th>TCOD (g L⁻¹)</th>
<th>SCOD (g L⁻¹)</th>
<th>FOG (mg L⁻¹)</th>
<th>VFA (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inoculum</td>
<td>6.82</td>
<td>2.6 ± 0.00</td>
<td>1.99 ± 0.00</td>
<td>76.41 ± 0.02</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Substrate</td>
<td>4.16</td>
<td>14.56 ± 0.61</td>
<td>14.21 ± 0.59</td>
<td>97.57 ± 0.01</td>
<td>205</td>
<td>33.5</td>
<td>90000</td>
<td>6400</td>
</tr>
</tbody>
</table>

606
2.6. Statistical analyses

One factor analysis of variance (ANOVA) was used to detect a difference between trials. Due to small sample size, the non-parametric equivalent, the Kruskal-Wallis test was employed in an attempt to improve the resolution of the statistical investigation. In the event that both the ANOVA and Kruskal-Wallis tests were significant with $P < 0.05$, $T$-tests were used to further investigate between groups with the non-parametric Mann-Whitney test used to help account for low sample sizes. The $T$-test outcome has been reported where statistical significance was identified. Standard deviations are provided for values with $n$ greater than 1.

3. Results and discussion

3.1. Qualitative effects of pre-treatment on DAF sludge

Pre-treatment produced varying effects on substrate consistency, from creating a more gelatinous product in the thermochemical and chemical treatments, to a more liquid and particulate substrate in the thermobaric treatment. In particular, this had implications for the uniform portioning of thermobaric substrate into digesters.

3.2. Effect of pre-treatment on COD solubilisation

Thermobaric treatment slightly enhanced COD solubility from 16.3% to 20.84%. Kim et al. (2003) reported similar results with SCOD increased from 8.1% to 17.6% following thermobaric treatment. Thermochemo treatment produced the greatest change, increasing the soluble fraction of COD from 16.3% to 50.7% (Table 2). This was indicative of the hydrolysis and subsequent solubilisation of organic residues in the DAF sludge. Solubilisation of COD was also enhanced following chemical pre-treatment with 7 g L$^{-1}$ NaOH. Chemical pre-treatment increased SCOD content from 16.3% to 48.2%. Similar results were reported by Kim et al. (2003) in which WAS treated with sodium hydroxide exhibited an increase in SCOD from 8.1% to 39.8%. Karlsson (1990) further supports this outcome with an increase in% SCOD from approximately 13% to 38% when treated with NaOH at pH 11 at 90 °C. In contrast, when similar treatment was attempted by Massé et al. (2001) using sodium hydroxide at concentrations of 2–16 g L$^{-1}$ on pork slaughterhouse waste, the authors reported no decrease in SCOD after a reaction time of four hours. However, average size of fat particles was reduced to 73 ± 7% of the initial average. It is likely that, as the reactions were performed at room temperature, the surface area for reaction was poor. A modest increase in reaction temperature to melt apart the fat globules may have yielded a greater impact on SCOD. Massé et al. (2001) also discuss the results of Karlsson (1990), in which it was reported that NaOH was far more effective at hydrolysing proteins than lipids, and cite this as the mechanism by which SCOD is increased in similar pre-treatment investigations. Results by Kim et al. (2003) support the findings that NaOH is effective at solubilising protein, but do not elaborate on its effect specifically on lipids.

Table 2

<table>
<thead>
<tr>
<th>Treatment</th>
<th>SCOD (mg L$^{-1}$)</th>
<th>(VFA) (mg L$^{-1}$)</th>
<th>SMP (mg CH$_4$ kg VS$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>35,000</td>
<td>6400</td>
<td>759 ± 4</td>
</tr>
<tr>
<td>Thermobaric</td>
<td>35,000</td>
<td>2300</td>
<td>823 ± 97</td>
</tr>
<tr>
<td>Chemical</td>
<td>147,500</td>
<td>14510</td>
<td>783 ± 6</td>
</tr>
<tr>
<td>Thermochemical</td>
<td>156,000</td>
<td>20976</td>
<td>822 ± 11</td>
</tr>
</tbody>
</table>

3.3. Volatile fatty acids production from pre-treatment

Thermochemical treatment increased VFA content by +228%, chemical treatment increased VFA content by +127%, while a loss of VFA content by -64% was measured in the thermobaric treatment (Table 2).

In contrast to Wilson et al. (2009), a large decrease in VFA content was measured after thermobaric treatment of the substrate. This can possibly be explained by loss of volatiles during the autoclaving process, as the vessel seal may have become compromised under the intensity of the autoclaving process. However, under the conditions of this experiment, similar losses should have been observed in the thermochemical treatment.

The increase in VFA content produced by the chemical and thermochemical groups was attributed to the addition of sodium hydroxide. Similar results were obtained by Mouneime et al. (2003) in which solid fatty residues from a wastewater treatment plant were degraded using sodium hydroxide and potassium hydroxide to yield VFA. This result demonstrated that treating with sodium hydroxide effectively enhanced hydrolysis of macromolecules to form organic acids. VFA liberation was greater in the thermochemical treatment possibly due to elevated temperature increasing the rate of both saponification and steam hydrolysis. This suggests that the majority of VFA production from sodium hydroxide addition occurred post-autoclaving.

3.4. Biochemical methane potential of treated DAF sludge

Anaerobic sludge was assessed for activity using a cellulose control, which achieved 80% of its theoretical specific methane production (SMP) by day 6. Thermobaric-treated DAF sludge produced an 8.49 ± 12.75% greater than the control ($P = 0.0821$); the chemical treatment group enhanced the SMP of DAF sludge by 3.28 ± 0.81% ($P < 0.05$); and the thermochemical treatment group 8.32 ± 1.40% ($P < 0.05$; Table 2).

The increase in SCOD and VFA concentration observed in the chemical (+31.9% SCOD, +127% VFA, +3.28% SMP) and thermochemical (+34.4% SCOD, +228% VFA, +8.32% SMP) treatments provided the basis that improvement in digestion parameters such as methane production or reaction kinetics should occur (Kim et al. 2003). Results obtained from the thermobaric treatment (+4.54% SCOD, -64% VFA, +8.49% SMP) appear to contradict this concept. Subsequently, positive relationships between SCOD or initial VFA concentration, and methane production or reaction kinetics were not demonstrated under the conditions of this experiment.

3.4.1. Thermobaric pre-treatment of DAF sludge

Although displaying the greatest variability, thermobaric treatment performed best in BMP testing (Fig. 1). While it is possible that thermobaric treatment of lipid-rich wastes to form inhibitory concentrations of LCFA could occur, such inhibition was not observed in this experiment. The lag period of 5 days in the control group was not observed, indicating that the thermobaric treatment produced effective hydrolysis that did not result in inhibition (Fig. 1). These results are supported by Wilson et al. (2009) who reported similar results in which thermobaric treatment of lipids did not produce LCFA at previously reported inhibitory levels.

Time required to degrade the pre-treated substrate was similar to the control. However, the thermobaric treatment had produced equivalent gas volume as the controls by approximately day 9, effectively improving digestion time by 3 days (Fig. 1). Furthermore, Gianico et al. (2013) suggested that the increased organic solubilisation resulting from thermobaric pre-treatment had likely converted a fraction of recalcitrant material to a more degradable form. This explanation supports the greater production of methane in the thermobaric and thermochemical groups.
3.4.2. Chemical pre-treatment of DAF sludge

Chemical treatment was expected to saponify the lipid component of the DAF sludge, and subsequently induce LCFA inhibition (Wilson et al., 2009). However, treatment did not extend the lag period exhibited in the control group, and even appeared to reduce any inhibitory impact (Fig. 2). While treated reactors completed digestion after 12.67 ± 0.58 days, methane production equivalent to the control was achieved by day 10, effectively reducing digestion time by 2 days.

3.4.3. Thermochemical pre-treatment of DAF sludge

Thermochemical-treated DAF sludge performed similar to thermobaric and chemical treatments. While the SMP was comparable to thermobaric-treated DAF sludge, the digesters still experienced a 4 day lag period (Fig. 3). The profile of rate of gas production retains the inhibitory phase in the first 4 days of digestion, after which the profile appears to follow more comparable to the thermobaric treatment (Fig. 3). Methane production in the treatment group was equivalent to the control group end point by day 11, producing an effective improvement in digestion time by 1 day.

3.5. Implications for use of pre-treatments in slaughterhouse industrial applications

3.5.1. Chemical pre-treatment

While pre-treatment with 7 g NaOH L\(^{-1}\) demonstrated a high degree of COD solubilisation, the economic outcome of increasing methane production was minimal at 3.28%. Sodium hydroxide pellets could be purchased for approximately $467 AUD per 1000 kg. Assuming infrastructure were in place to remove residual FOG from waste streams to be made available for pre-treatment, this would allow for the treatment of 143 m\(^3\) of FOG-rich waste. With an improvement of 3.28%, this would be worth $185 AUD as electricity, or could offset natural gas worth $229.60 AUD. This is insufficient to cover the cost of sodium hydroxide pre-treatment and is likely not a viable option. Furthermore, following pre-treatment, this material would likely require neutralisation with acid prior to dosing to the anaerobic digester. However, this does not take into account the flow-on effects of greater treatment efficiency, and the effects on anaerobic digester operation.

3.5.2. Thermobaric pre-treatment

Given the 8.32% increase observed from thermochemical pre-treatment, and a load of 143 m\(^3\) of FOG-rich waste would generate an extra 28172 MJ. Converting to electricity with a 40% conversion efficiency provides 3130 kWh. The value of this as electricity is $470 AUD, and used to offset natural gas would be worth $230 AUD.

The cost of performing this treatment is heavily dependent on the water content. With a specific heat capacity of 4.18 J g\(^{-1}\) °C\(^{-1}\), water is energetically expensive to heat, and the economics of the treatment could be improved through dewatering (Table 3). With a TS content of 14.56, and a water content of 85.44%, 117.2 MWh of electricity would be required to heat 143 m\(^3\) of material from 40 to 100 °C. At an estimated cost of $0.15 AUD kWh\(^{-1}\), this would cost $17580. In contrast, if
3.5.3. Implication summary

Thermobaric pre-treatment is the most viable option for the pre-treatment of DAF sludge under the conditions of this investigation. Pre-treatment efficacy can be greatly enhanced through reasonable dewatering to limit the amount of heat wasted heating water, and utilisation of heat exchange to reduce active heating costs. Utilisation of CHP technology will further improve the economics of thermobaric pre-treatment.

4. Conclusions

This work identifies that methane yields can be enhanced by 3.28%, and 8.49% by chemical and thermochemical treatments respectively. SCOD and VFA concentrations can also be greatly increased. Early inhibition was reduced by thermochemical (-20%) and thermobaric (-100%) pre-treatments. Preliminary assessment of economic viability identified thermobaric as the most viable pre-treatment technology for industrial application under the conditions of this investigation.

Thermobaric pre-treatment efficacy can be greatly enhanced through utilisation of heat exchange, and substrate dewatering. CHP technology could further improve the economics of thermobaric pre-treatment. Semi-continuous investigations are necessary to assess on-going benefits of thermobaric pre-treated DAF sludge.

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References


Beddow, A., Neave, S., 1930. Laboratory studies of anaerobic digestion. Department of Agriculture, Washington DC.


Berlin, Heidelberg.


