ENHANCED METHANE YIELDS FROM MICROALGAL DIGESTION WITH VARIOUS PRE-TREATMENTS

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Abstract

Algae produced in High Rate Algal ponds are a potential source of energy via anaerobic digestion. Fresh algae and Algae Settling Pond (ASP) sludge were digested in semi-continuous anaerobic digesters at 20°C. The algae solids were given various pre-treatments prior to digestion to determine whether digestibility or final biogas quality could be enhanced. Fresh algae solids were either untreated or treated with ultrasound. ASP sludge was either untreated, or treated with acid, ultrasound, or heat. Anaerobically digested fresh algae produced high volumes of methane (0.21-0.23 m^3 CH_4 kg^{-1} VS removed) with methane contents of 60% (untreated) and 56% (ultrasound-treated). ASP sludge without pre-treatment produced much lower methane yield than fresh algae, at 0.014 m^3 CH_4 kg^{-1} VS removed. Ultrasound treatment increased the methane yield by only 14% (to 0.016 m^3 CH_4 kg^{-1} VS removed), but acid treatment increased the yield by 229% (0.046 m^3 CH_4 kg^{-1} VS removed) and heat-treated by 286% (to 0.054 m^3 CH_4 kg^{-1} VS removed). The biogas methane content was also much lower than that for fresh algae, at 26% (untreated), 23% (ultrasound-treated), 35% (acid-treated) and 46% (heat-treated).

Batch experiments showed an increasing proportion of methane in their biogas, up to 90%, although total gas production gradually decreased to low levels.

Keywords: microalgae digestion, anaerobic, biogas

Introduction

Wastewater treated in Advanced Pond Systems (APS) receives higher levels of treatment than in more widely used “conventional” wastewater stabilisation ponds. Incoming sewage may be initially treated in either an Advanced Facultative Pond, an Anaerobic Pond, or even an Anaerobic Digester, and the supernatant then enters a High-Rate Algal Pond, which is specifically designed to grow algae to produce oxygen for aerobic removal of dissolved organic matter, releasing nutrients, which are, in turn, assimilated by the algae. A paddlewheel circulates the wastewater around the ‘raceway’ style pond (20 cm s^{-1}) inducing turbulence which promotes the growth of colonial algae. These algae can be simply removed from the wastewater in Algae Settling Ponds (ASP), which are designed to settle and collect the algal solids for periodic removal every 3 to 6 months.

Micro-algal biomass has a variety of potential uses, including fertiliser, livestock feed, and extraction of vitamins and pharmaceuticals (Borowitzka, 1988). Algae are also a potential source of energy (Golueke et al., 1957). This study examines the anaerobic digestion potential of fresh micro-algae and algal sludge collected from the algal settling pond of an APS treating domestic sewage.

The ability of a variety of pre-treatments including heat-shock, acid treatment and ultrasound to enhance the degradability and methane production potential of fresh algae and ASP solids was tested. Each pretreatment was selected for its anticipated ability to disrupt algal cell walls in order to improve the digestibility of the algal biomass. Heat and acidic pretreatments were also selected for their potential practical application, as many industries have waste heat (particularly when combusting methane) or acid waste streams. Use of ultrasound was considered as it might also prove practical for short periods in a low volume waste stream.

Methods

Algal biomass was digested in un-mixed laboratory-scale anaerobic digesters (2 L glass culture vessels) that were kept in a constant temperature room at 20°C (psychrophillic temperature range). Digesters were initially inoculated with 500 mL of sludge from an experimental psychrophillic anaerobic digester maintained on site. Algal solids used in the digesters were obtained from the pilot-scale APS treating domestic sewage at the Ruakura Research Centre, Hamilton, New Zealand. A detailed description of this system has been presented previously (Tanner et al., 2005). Fresh algal solids were collected using plankton nets (45µm) either suspended within the High Rate Algal Pond, or on the discharge into the Algal Settling Pond (ASP). ASP settled algal solids (referred to hereafter as algal sludge) was harvested by decanting the surface water down to the algae sludge layer and pumping this layer out into a 200L drum which was stored in a cool room (2°C). Prior to digestion, the algal biomass was subjected to a variety of pre-treatments.

Pretreatments

Fresh algae solids were either (1) untreated or (2) treated with ultrasound (at 100% power in degas mode, Elma Sonicator 600 watts, Barnstead Lab-Line, Melrose Park, Ilinois) for 90 minutes prior to adding to the digesters. Algae Settling Pond (ASP) solids were either (3) untreated, or (4) ultrasound (for 90 minutes), or (5) treated with acid (HCl addition to obtain pH<2.0 left for 60 minutes then neutralised with NaOH addition), or (6) heat treatment (>80°C for 30 minutes on a laboratory hot plate, Barnstead Thermoline Cimarec2, Dubuque, Iowa (Ihrig, 2001))[1]. Pretreatment times were chosen for practical reasons of doing all pretreatments simultaneously, with longer times given to treatments which were anticipated to be less disruptive to algal cell walls e.g. ultrasound.

The digesters were operated in a semi-continuous mode with the algal solids or sludge added to the digesters on a twice weekly basis over 7 months. Supernatant (500 mL) was first removed from the digester and then replaced with an equal volume of the algae giving hydraulic retention times of 14 days.

The organic matter in the influent and effluent of the digesters was measured in terms of total and volatile solids by standard methods (APHA, 1998, methods 2540 B&E).

The volume of biogas produced within each digester was monitored using a plastic measuring cylinder inverted in a water filled glass jar of a similar depth to the cylinder. Biogas produced in the digesters was transferred through silicone tubing to the base of the cylinder, enabling both

[1] Similar pretreatments of heat and acid were not undertaken for fresh algae, as total collectable fresh algal biomass was not adequate for more than the two treatments tested.

collection and measurement of the gas volume. Biogas samples were withdrawn from the cylinder through a rubber septum in the base of the cylinder for gas composition analysis using a portable gas analyser (GA2000 plus, Geotechnical Instruments (UK) Ltd, Leamington Spa, England). The gas analyser was checked weekly against a certified Alpha Standard methane/CO_2 gas mix.

Batch Operation

After addition of the final dose of fresh algae or ASP solids to the digesters they were operated in batch mode with gas production and composition monitored daily for 2 months by which time production levels were reduced to an extent that continued analysis was impractical (around 20 mL per day).

Results and Discussion

Pretreatment of Fresh Algae and ASP Sludge

The organic loading rate and % volatile solids (VS) of the algae solids, the methane content of the biogas, and the methane production rate per kg of algal VS removed for each digester, are given in Table 1.

Table 1. Average organic loading rate and % volatile solids (VS) of the algae solids, the methane content of the biogas and the methane production rate per kg of algal VS removed for each digester. Values in brackets are standard deviations.

	Fresh Algae		Algal Settling Pond Solids			
Pretreatment	Untreated	Ultrasound	Untreated	Ultrasound	Acid	Heat
Organic loading per digester volume (kg VS m^{-3} d^{-1})	0.23 (0.29)	0.23 (0.29)	1.46 (0.44)	1.46 (0.44)	1.46 (0.44)	1.46 (0.44)
Average % VS of the algae	0.32% (0.40%)	0.32% (0.40%)	2.0% (0.6%)	2.0% (0.6%)	2.0% (0.6%)	2.0% (0.6%)
% Methane in biogas	60% (15%)	56% (13%)	26% (2.6%)	23% (7.8%)	35% (7.8%)	46% (10.6%)
Methane production (m^3 CH_4 kg^{-1} VS removed)	0.234	0.212	0.014	0.016	0.046	0.054
% Change in methane production of untreated		-9%		+14%	+229%	+286%

The higher organic loading rate of the ASP solids digesters compared to the fresh algae digesters was due to the higher %VS of the ASP solids compared to that of the fresh algae (Table 1). This difference in %VS highlights the difficulty of concentrating algal biomass by short-term passive harvesting. Development of an efficient and cost-effective algae harvesting technique would be a requirement for large-scale use of micro-algae for methane digestion.

The methane content of the biogas from the untreated fresh algae was 60% (Table 1). The methane production rate (0.234 m^3 CH_4 kg^{-1} VS removed) was slightly less than that (0.280 m^3 CH_4 kg^{-1} VS removed) determined as feasible by Oswald (1988), and close to that (0.250 m^3 CH_4 kg^{-1} VS) recorded by Chen and Oswald (1998 , 0.25 L/g VS) for fresh algae pretreated at 100ºC, although their production rate is based on VS loading rather than removal. These were higher than from the untreated ASP algal sludge digester (26% and 0.014 m^3 CH_4 kg^{-1} VS removed), probably because the algal solids which had settled in the ASP had undergone some degree of anaerobic digestion within the pond, leaving a higher proportion of more recalcitrant solids.

Ultrasound pre-treatment of both fresh algae and ASP solids caused the biogas methane content to decline slightly (by 3-4%) compared to that from the untreated algae. The methane production rate of fresh algae was also reduced slightly (from 0.234 to 0.212 m^3 CH_4 kg^{-1} VS removed), however, further studies need to be conducted to determine whether these minor changes were a true treatment effect or simply variability in samples. It is clear, however, that this treatment had little benefit for methane production, and may even have reduced it. Perhaps the ultrasound caused cellular disruption of other microbes within the algae solids that were important for the digestion process.

Acid ($pH<2.0$) pre-treatment of the ASP sludge for one hour caused biogas methane content to increase to 35% methane and total production to increase three fold (to 0.046 m^3 CH_4 kg^{-1} VS) compared to untreated solids. The acid pretreatment probably altered algal cell wall components to enhance their availability for digestion. Increases in methane production with acid pretreatment have also been recorded by Irig (2001), however they used acetic acid for pH adjustment, which is also an organic precursor for methane production. In the present study pretreating with hydrochloric acid, and then neutralising with NaOH, unavoidably increased mean conductivity from 1604 to 8905 µs cm^{-1} but did not appear to inhibit methane production.

Heat pretreatment (>80°C for 30 minutes) caused a greater increase in biogas methane content to 46% methane and total production to increase by nearly a factor of four (to 0.054 m^3 CH_4 kg^{-1} VS) compared to untreated solids. As with acid treatment, the heat pretreatment probably also altered cell wall components to enhance their availability for digestion. Chen and Oswald (1998) achieved a 33% increase in methane production by heat (100°C, 8hr) pretreatment of fresh algae, whereas similar treatment of ASP algal sludge in the present study achieved 286% increase. However our untreated sludge is likely to have had low methane generation due to it having already undergone a significant degree of digestion in the ASP. Thus the remaining ASP sludge material probably comprised a high proportion of recalcitrant cell wall material which became more bio-available with heat treatment.

The relative proportions of methane and carbon dioxide for each treatment are shown in Figure 1, illustrating a roughly linear trend in this ratio for steady-state operation. Traces of hydrogen sulphide and ammonia were also present. The remaining fraction of the biogases probably contained hydrogen and nitrogen, neither of which could be measured by the gas analyser.

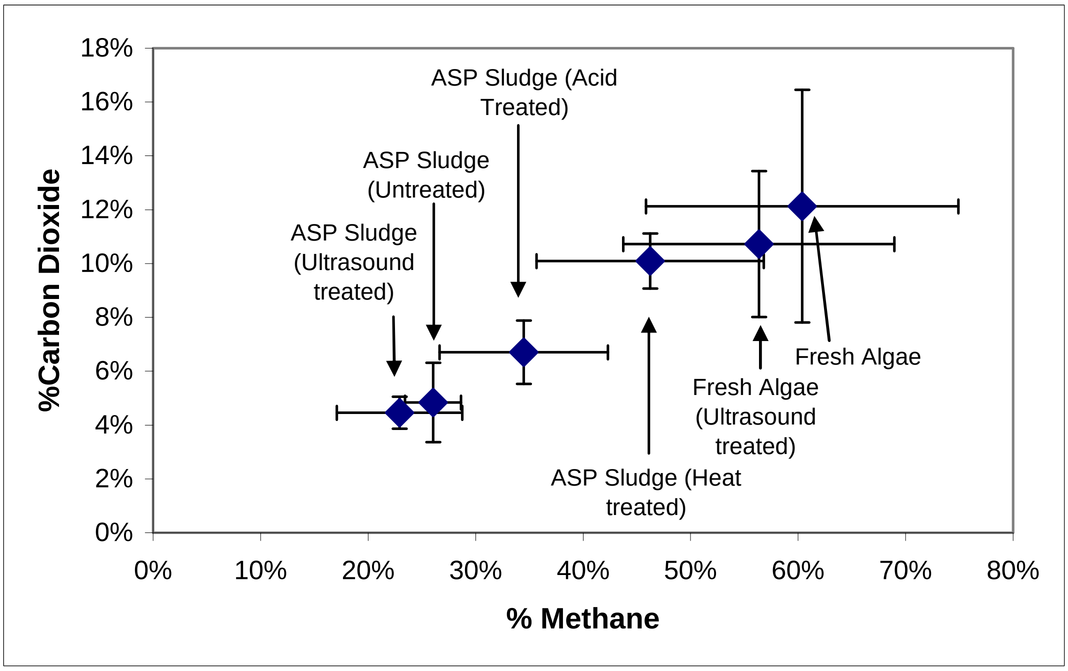

Figure 1. Relative production of Methane and carbon dioxide for each treatment under steady-state operation. Error bars are 1 standard deviation (1 S. D.).

Batch Operation

The final digester batch operation study confirmed the results of the previous semi-continuous digester experiments. Daily gas production increased to a maximum in all digesters by day 2, after which it declined over the two month monitoring period (Figure 2). Both maximum daily gas production (225 mL d^{-1}) and total gas production (4.2 L) were higher for the fresh algae compared to those of the ASP solids (150 mL d^{-1} and 1.7 L respectively) (Figures 2 & 3). Moreover the daily gas production declined to below 50 mL d^{-1} by day 6 (Figure 2). Ultrasound pretreatment did not significantly affect maximum daily gas production of the fresh algae (230 mL d^{-1}) but total gas production was reduced (3.4 L). Ultrasound reduced peak gas production of ASP sludge to about a third (60 mL d^{-1}), but total gas production was not influenced (1.7L). Acid pretreatment reduced both maximum daily gas production (~90 mL d^{-1}) and the total gas production of the ASP sludge (to 1.4 L). Heat pretreatment did not affect maximum daily gas production for the ASP sludge but it did increase total gas production (to 2.2L) compared with the untreated sludge.

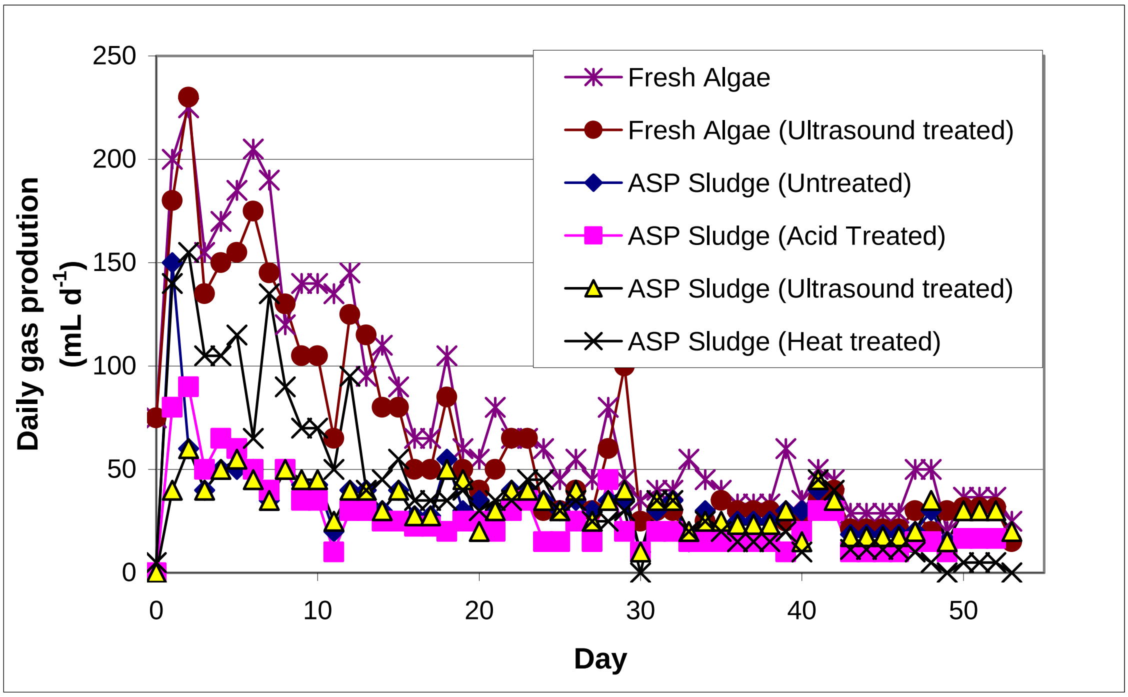

Figure 2. Changes in biogas (CH_4, CO_2 and other gases) production from batch digesters with fresh algae or ASP solids operated over two months.

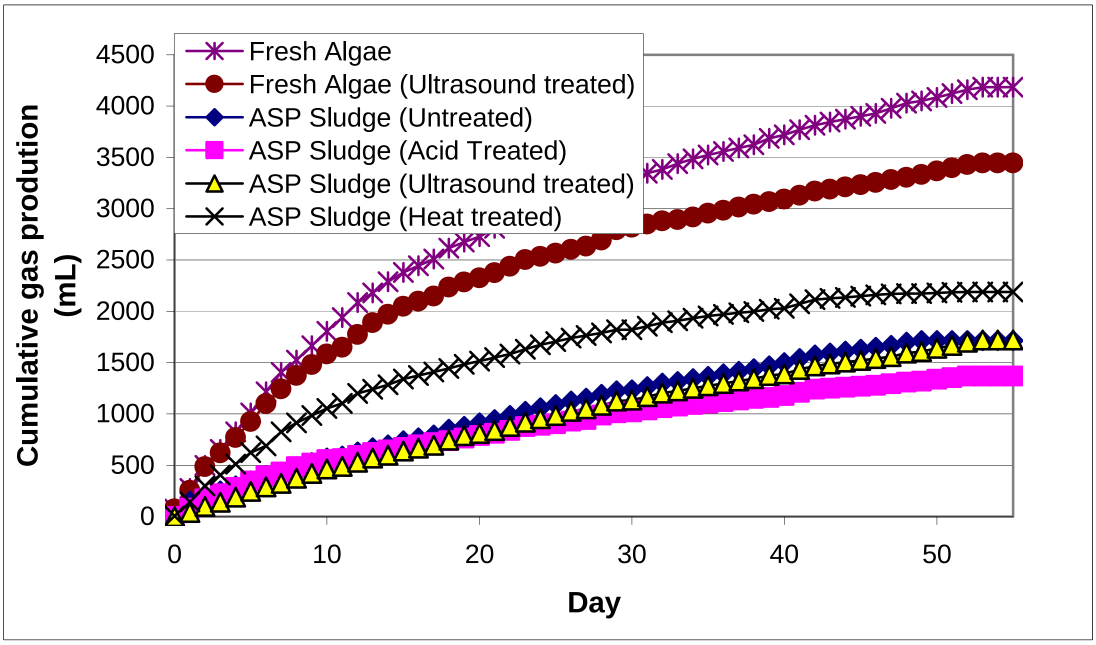

Figure 3. Cumulative biogas production (Terminal dose).

The initial methane content of the biogas from the digesters in the batch digester study were a little lower than the "steady-state" concentrations following the previous 7 months of semi-continuous operation (Figure 4). The biogas from the ASP sludge digesters had considerably lower initial methane content (11 - 43%) compared with the biogas from the fresh algae digesters (64 & 71%). Maximum biogas methane content in the fresh algal digesters (85 – 90%) was achieved by day 7 and remained at this level for the duration of the experiment. However, the maximum biogas methane content in the ASP sludge digesters (80 – 86%) was achieved between days 20-27, with the exception of the heat pretreated digester which achieved approx. 80% (by day 11). Digester biogas content remained at these levels for the remainder of the experiment.

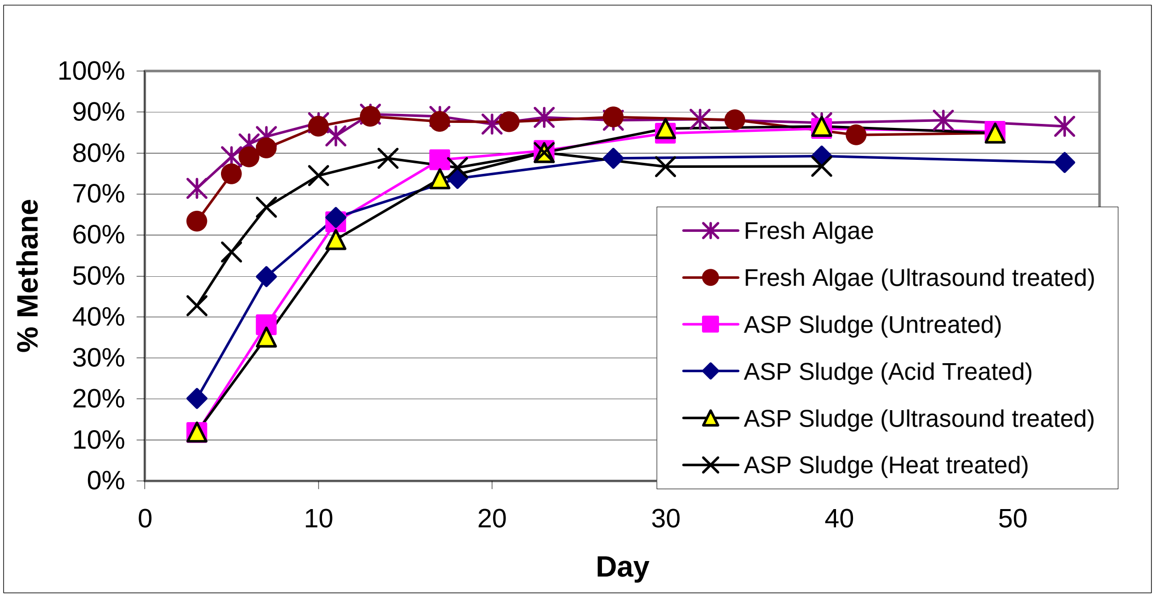

Figure 4. Biogas methane content from batch digesters with fresh algae or ASP sludge operated over two months.

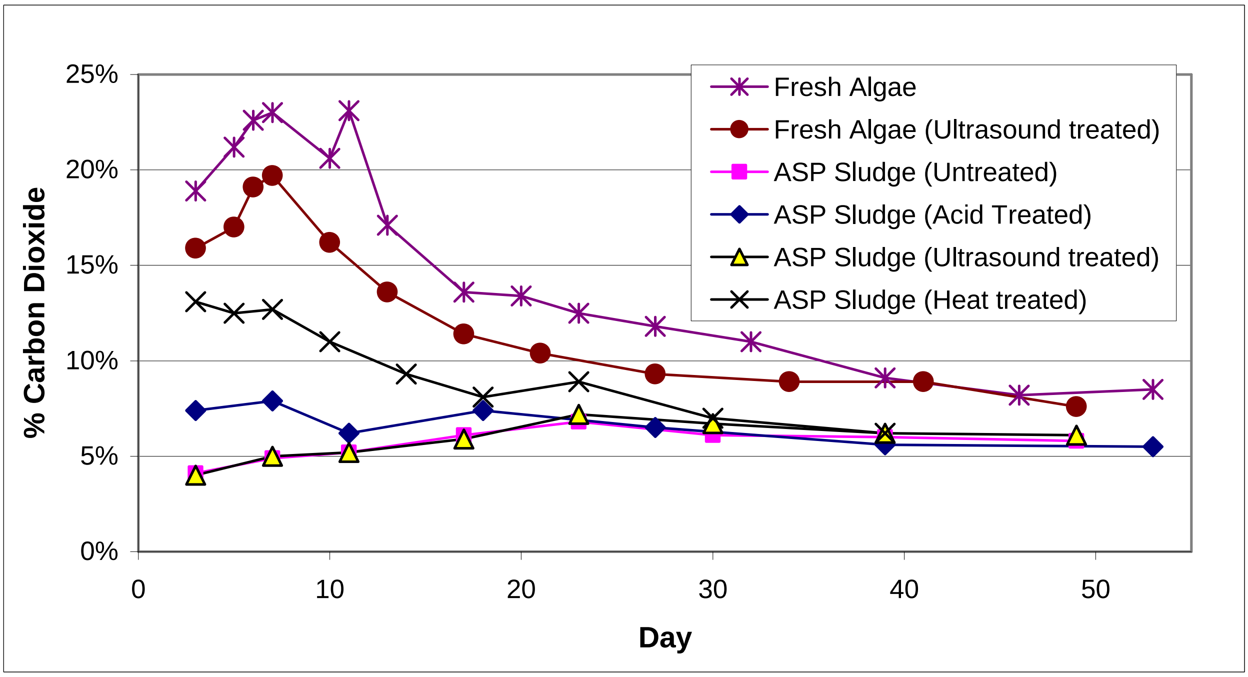

Figure 5. Percent carbon dioxide content of biogas from batch digesters with fresh algae or ASP sludge operated over two months.

Carbon dioxide, the other major gaseous product of anaerobic digestion besides methane, was low in the biogas from the ASP solids digesters (5–7%) and remained fairly constant over the experimental duration, with the exception of the heat pretreated ASP solids digester, which had a CO_2 content above 10% initially, but this reduced to 5–7% after the first month of digestion (Figure 5). The carbon dioxide content of the biogas from the fresh algae digesters initially increased, but then rapidly decreased to 5–7% after the first month of digestion (Figure 5). As carbon dioxide decreases and methane increases in relation to each other, the "quality" of the gas improves in potential combustibility.

Conclusions

Fresh algae were rapidly digested to produce high amounts of methane and carbon dioxide, presumably as labile cell contents are digested. Digestion of ASP solids produced less methane which probably reflects partial digestion of the settled algae within the ASP. Of the three pretreatments tested, both heat and acid treatments appeared to improve the digestibility of algae solids. Further research is desirable on heat treatment of fresh algae, and also the minimum heat inputs (temperature and time) required to provide maximum methane production from ASP sludge.

Acknowledgements

We wish to acknowledge Jason Park for assistance during the research. This research was funded by the NZ Foundation for Research Science and Technology (FRST).

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