PRODUCTION OF BIOGAS WITH HIGH CALORIFIC VALUE FROM WASTEWATER VIA HYDROGEN ASSISTED ANAEROBIC DIGESTION

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ABSTRACT

Anaerobic digestion is a well-known technology for wastewater treatment and biogas production. This process has been used all over the world for treating a wide range of waste and wastewater streams with biogas being one of its most valuable products. However, there are still a few challenges with this technology such as low methane content of the biogas. In general, the biogas primarily contains about 60% of methane and 40% of CO_2. The CO_2 content of the biogas lowers the calorific value of this valuable and renewable gas and limits its industrial applications. Therefore, biogas upgrading mechanisms have been studied to remove CO_2 and other unwanted gases from the biogas. Biogas upgrading has gained attention particularly because many countries are moving towards renewable fuel production. Upgraded biogas can be an appealing substitute for natural gas.

Hydrogen-assisted biological biogas upgrading has been explored to convert CO_2 to methane gas with the help of CO_2-consuming hydrogenotrophic methanogens. These microorganisms use hydrogen and CO_2 and produce methane gas as the results of their biological activities. However, hydrogen gas can take other pathways in mixed culture systems such as anaerobic digesters where volatile fatty acids are produced as a result of biological reaction of CO_2 and H_2. In this context, the aim of this study was to identify the H_2 injection rate required to increase the methane content in the biogas.

The results demonstrated a positive effect of hydrogen addition on biogas upgrading. The methane content of the biogas in H_2-assisted anaerobic digestion (70%) was higher than that of conventional anaerobic digestion (45%). The results showed that after acclimation of anaerobic microorganisms to the added hydrogen, hydrogen gas uptake and sequestration of CO_2 occurred which resulted in the production of high quality biogas.

KEYWORDS

Anaerobic digestion, biogas upgrading, methane, hydrogen, CO_2 reduction

PRESENTER PROFILE

Afrooz is a PhD candidate at the University of Canterbury working on valorization of wastewater via anaerobic digestion. She is studying biogas production via anaerobic digestion and biogas upgrading (i.e. methane content). Afrooz is working as a Water Supply Engineer at the Christchurch City Council, focusing on Water Safety Plans, and specifically backflow prevention.

INTRODUCTION

Fossil fuels are the main source of energy generation world-wide; however, the resultant greenhouse gas emissions have provided an impetus for many countries to investigate and use renewable energy sources (EBA, 2017). For example, 82 % of New Zealand's electricity is currently produced from renewable energy sources, but the target is to go 100 % renewable by 2035 (New Zealand. Interim Climate Change, 2019). Renewable energy sources include hydro, geothermal heat, solar, marine (i.e. tidal, wave, or current), as well as biomass, with the latter referring to a wide range of energy carriers such as ethanol, wood or biogas.

Biogas is primarily produced in landfills or from the anaerobic digestion of a variety of organic waste streams such as crop/farm waste, food waste and sewage sludge. Biogas primarily consists of 50 – 60 % methane (CH_4) while carbon dioxide (CO_2) also constitutes a large proportion of the biogas mixture. This is unfortunate because a high CO_2 content means that, compared to its natural gas counterpart, biogas falls far short of meeting the calorific content required by many applications such as internal combustion engines (Persson, Jönsson et al. 2006). To illustrate, there are nationally-agreed specifications for the acceptable CO_2 content of biogas that is being injected in the grid or used as vehicle fuel in many parts of the world. For example, in Germany and Switzerland, the carbon dioxide content of biogas should not exceed 6 % while the specifications are stricter in France, where a qualified biogas must have CO_2 content of less than 2 % (Petersson and Wellinger 2009).

A high CO_2 content (40 - 50 %) reduces the calorific value of biogas to 23.4 MJ/Nm^3 which is much lower than the 35.8 MJ/Nm^3 of natural gas, which has near zero percent CO_2 content. This in time lowers the performance of biogas in combustion heat engines. To compound matters, biogas also contains other impurities such as H_2O, H_2S, and NH_3 which leads to corrosion and incomplete combustion in heat engines, not to mention poisonous emissions. Thus, for biogas to reach an appropriate quality, various techniques must be employed to purify or upgrade its characteristics.

Upgraded biogas, as a promising alternative to natural gas, can play an important part in achieving a fully renewable electricity system by 2035 (New Zealand. Interim Climate Change, 2019). However, to be utilised either in the grid, in combustion gas engines, or turbines/micro-turbines; the quality of the biogas needs to meet a number of specifications associated with the concentration of its components. For instance, the goal is to obtain a biogas that contains no more than 1 – 3 % of CO_2. This upgraded and high-quality biogas is called biomethane

(Ryckebosch, Drouillon et al. 2011). To obtain biomethane (with a similar methane content of natural gas), various approaches have been explored. These methods fall into two main categories; namely, in-situ and ex-situ biogas upgrading processes.

Ex-situ biogas upgrading techniques aim at increasing methane content of the already produced biogas in a separate system than the digester. In these techniques, the generated biogas is carried to a following processing system for the impurities to be removed. Ex-situ biogas upgrading includes membrane technologies, absorption technologies, biological processes, water scrubbing, etc. However, the requirement for additional unit operation adds to the cost of the final biogas production system.

In-situ biogas enriching mechanisms include the modification of conventional anaerobic digestion processes to obtain a biogas with high content of methane. This happens through enhancing the operating conditions of the digester (i.e. retention time, temperature, pressure, etc.). In-situ biogas enriching can also be achieved via the addition of chemical substances in order to facilitate and/or accelerate methane producing reactions, while simultaneously impeding CO_2 production. Compared to other enhancement methods, in-situ biogas enriching is a more promising and sustainable way of obtaining biogas of a better quality (Sarker, Lamb et al. 2018). In addition, in-situ methods are able to remove excessive CO_2 content while at the same time are easily applied to existing anaerobic digesters, saving time, space, and capital costs (Alfaro, Fdz-Polanco et al. 2019). Therefore, this research aims at improving the methane content of the biogas produced during anaerobic digestion of wastewater.

MATERIALS AND METHODS

120-mL batch anaerobic digesters were set-up to study the effect of hydrogen addition on the methane content of the produced biogas. Digested sludge collected from the mesophilic digester of Christchurch Wastewater Treatment Plant was used as inoculum. The characteristic of the sludge is as follows: total solids (TS)= 30.35 g/L, volatile solids (VS)= 14.44 g/L, pH= 7.67.

A synthetic wastewater with an easily degradable carbon source (anhydrous glucose) was used as feed for the reactors. To find an adequate substrate to inoculum ratio, a preliminary set of experiments were run using various concentrations of glucose (0.25, 0.5, and 1 g sCOD/L). Anaerobic medium was prepared and added to the batch reactors to provide enough micro and macro nutrients for the microorganisms (Angelidaki et al, 2004). The batch reactors were filled with 30 mL of the digested sludge, different volumes of synthetic wastewater (to produce different initial concentrations of substrate) and different volumes of anaerobic medium to reach a working volume of 60 mL. The headspace of the reactors (60 mL) was flushed with N_2 to ensure anaerobic conditions. A blank with only digested sludge and de-ionised water (instead of synthetic wastewater) was also included in the experimental set up. The batch anaerobic digesters were incubated at 36^{o}C and methane production was monitored regularly. The

experiments were run until no biogas was produced which meant that all the easily degradable organic carbon had been converted to biogas.

A second set of experiments was run this time using greater concentrations of glucose, namely 1 g/L, 7 g/L, and 14 g/L. These concentrations were equivalent to 0.03, 0.5, and 1 g soluble chemical oxygen demand (sCOD)/g VS). At this stage, hydrogen was added to the reactors and a control with a mix of sludge and synthetic wastewater but no H_2 was also included. Table 1 shows the experimental conditions.

Table 1: Characteristics of the second-stage experiment: effect of substrate to inoculum ratio

	Substrate to inoculum ratio (g sCOD/g VS)	Hydrogen added
0.07, CTRL	0.07	No H_2
0.07, 4mL		4 mL
0.07, 8mL		8 mL
0.5, CTRL	0.5	No H_2
0.5, 4mL		4 mL
0.5, 8mL		8 mL
1, CTRL	1.0	No H_2
1, 4mL		4 mL
1, 8mL		8 mL

Once the best substrate to inoculum ratio was found, a third set of experiments was run to study the effect of the hydrogen addition approach on biogas production. For this set of experiments the substrate/inoculum (S/I) ratio was kept at the same level and only the headspace hydrogen level was changed. Table 2 shows the conditions of the third set of experiments.

Table 2: Characteristics of the third-stage experiment: effect of H_2 addition approach

	Substrate to inoculum ratio (g sCOD/g VS)	*Hydrogen added*
BLNK	No substrate	No hydrogen
CTRL	0.5	No hydrogen
10mL	0.5	10 mL
H_2- Flushed	0.5	Reactors flushed with H_2 instead of N_2

All experiments were run for 10 days or until no more biogas was produced. TS, VS, and pH were measured according to Standard Methods (APHA, 2005). The content of methane in the biogas was analysed by gas chromatography with a thermal conductivity detector (Agilent 7820A, China). A gas-tight syringe was used to collect 4-mL samples from the headspace of each reactor. For each analysis, 4 mL of gas sample at atmospheric pressure was injected to the GC. The setup of the GC-TCD method was as follows: Agilent 19095P-Q04 stainless steel column with 30 m× 530 µm× 40 µ; Helium carrier gas 10 mL/min with pressure 10.6 psi, oven temperature 30 °C; injector temperature 70°C; TCD temperature 155°C. All analyses was undertaken in duplicate/triplicate for quality assurance.

RESULTS AND DISCUSSION

The first stage of the experiments was run to identify the best concentration of substrate (i.e. S/I ratio) to ensure stable methane production. The results showed that higher amounts of glucose, hence greater levels of sCOD, resulted in higher methane content in the biogas (Fig 1). The initial concentration of sCOD increased from 0.25 to 1 g/L which resulted in the methane content (%) to increase from 15% to >30%.

Biogas production stopped after 7 days of the experiment which means that the microorganisms were able to degrade the sCOD very quickly. The fast degradation of sCOD suggested that the inoculum activity was likely high enough to deal with higher organic loadings. This led to the next stage of the experiment where greater concentrations of sCOD were used.

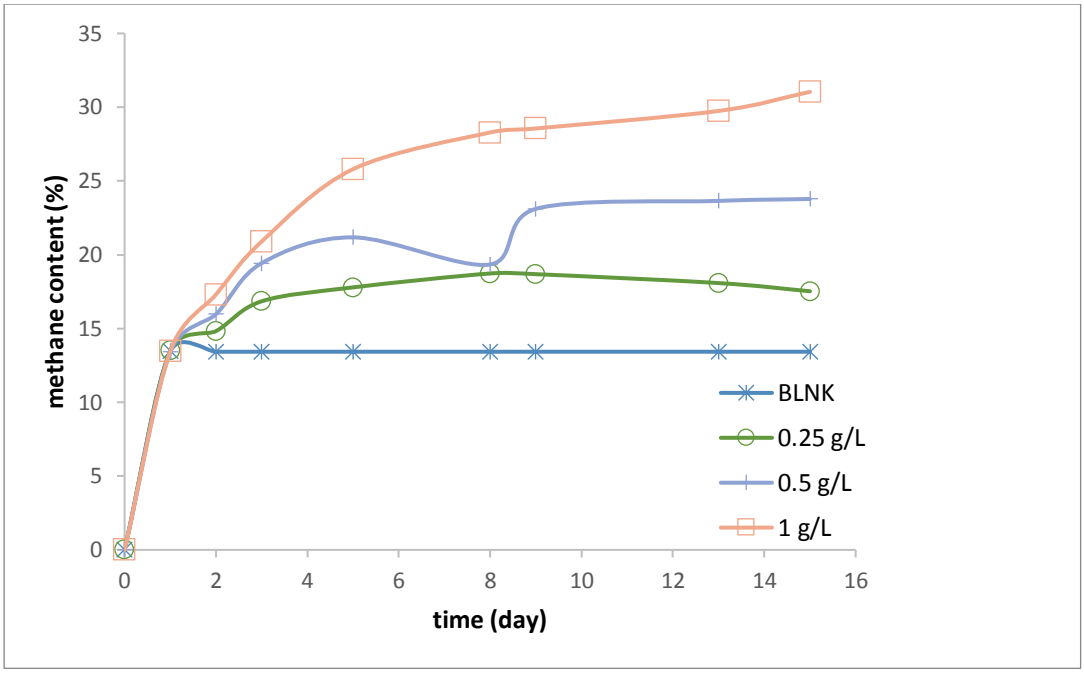

Figure 1: 1st stage- methane content of the biogas produced

For the second experimental stage, the inoculum used was the same as in the first stage. This sludge was incubated at 37.5°C for 3 weeks for degassing; that is to say, to eliminate endogenous methane production. In this stage, higher amounts of glucose (i.e. sCOD) were used. The initial substrate concentrations used in the batch tests were 1, 7 and 14 g sCOD/L. This was equivalent to S/I ratios of 0.07, 0.5 and 1 g sCOD/g VS, respectively. At this stage, different volumes of hydrogen (at atmospheric pressure) were also added to the reactors to study the effect of hydrogen addition on the methanation of the synthetic wastewater. Figure 2 shows the results of the second-stage of experiment.

It is noted that the results of the second-stage experiment, as well as those in the first stage, indicated lower methane content of the biogas than expected from a WWTP sludge. This can be due to the wide window of time between the time that the sludge was collected from Christchurch wastewater treatment plant and the time that the experiments stared (i.e. degassing period) which led the microorganism to be dormant.

The results also showed that the highest substrate to inoculum ratio of 1 g sCOD/g VS resulted in poor methane production (less than 15%). These reactors stopped producing methane after 4 days of the experiments and hydrogen addition did not improve its biogas production. This was probably caused by an overloading of the reactors with a high dose of substrate.

The greatest final methane content was observed in the reactors fed with 0.5 g sCOD/g VS inoculum (Fig 2). Hence, this value was taken as the best S/I ratio for the current experiment. Furthermore, higher amounts of hydrogen added to the reactors resulted in greater methane percentages in the biogas. Therefore, the next stage of the experiment was run by keeping the organic loading rate at the

same level (i.e. 7 g sCOD/L or 0.5 g sCOD/ g VS inoculum) and only hydrogen content of the reactors were changed.

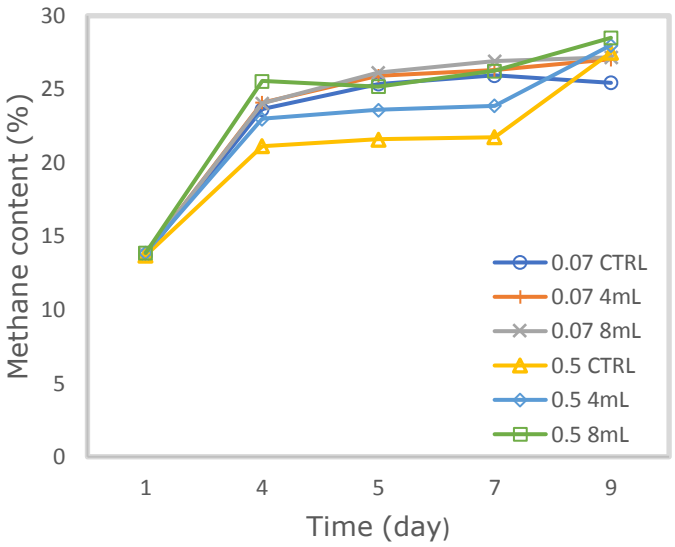

Figure 2 second stage- methane content

For the third stage of the experiment, fresh sludge from the same digester (Christchurch Wastewater Treatment Plant, Bromley) was used. Furthermore, the duration of sludge degassing was shortened to 5 days to avoid the inactivation of the microorganisms. In this stage the effect of the mode of hydrogen addition on methane production was studied. For this purpose, blank and control reactors were compared with reactors that contained varied levels of hydrogen. A set of reactors contained 10mL hydrogen; and the last set of reactors were purged with H_2 as opposed to the other reactors which purged with N_2 to investigate the effect of excess hydrogen content on the reactors.

All the reactors produced higher methane contents than the previous stages which proved that fresh sludge, hence more active microorganisms, results in a better methane content of the biogas. The methane content of the control reactor was in line with the methane content that is produced in a digester (approximately 50% methane) (Fig. 3).

The control reactors which did not contain any hydrogen and the reactors in which 10 mL of hydrogen was injected showed the same methane content of the biogas. This suggests that 10 mL of hydrogen was not enough to foster hydrogenotrophic methane production. In contrast, the reactors with hydrogen-filled headspace produced a very high content of biogas.

The methane content of hydrogen-purged reactors reached above 50% after 4 days and remained at above 70-75% for the rest of the experiment until the reactors stopped producing anymore biogas. This showed that hydrogen addition to digester can upgrade the methane content of the biogas by 40% compared with a reactor that is not fed with hydrogen.

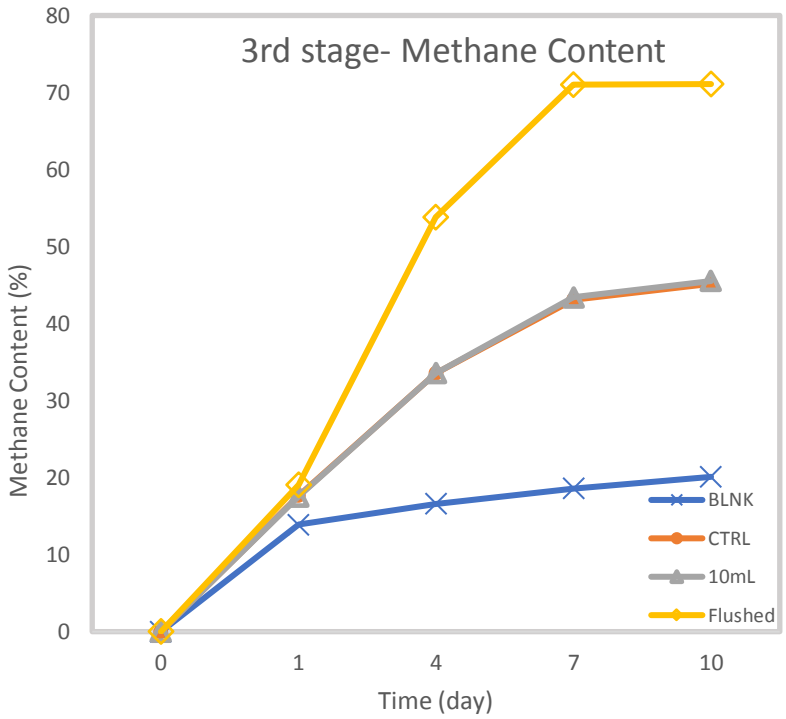

Figure 3: Third Stage- effect of hydrogen addition on methane content of the biogas

A biogas with high content of methane has more calorific value and therefore improves the performance of CHP engines at wastewater treatment plants. This enhances CHP engines and produces more heat and power to cover the required energy for running a wastewater treatment plant. The benefit of hydrogen assisted biogas upgrading system is that it can be applied to the existing digesters with the same engines without a need for changing the configuration of the infrastructure.

The findings of this experiment showed that hydrogen assisted biogas upgrading systems have a few challenges that need to be addressed in the next stages of this on-going research.

Comparing the systems with and without hydrogen addition showed that, when hydrogen was added to the system, biogas and methane production rate decreased. Although a very high methane content of biogas was produced, the biogas production rate was lower than the expected level in these systems. This can be explained by the fact that reaction of CO_2 and H_2 might take two different pathways. One leads to methane production and the other results in acetate production (and other VFAs) (Vechi et al 2021). High VFA concentration has a negative effect on biogas production of microorganisms (Siegert et al 2005). In this case, adding hydrogen gas to the reactors (purging the headspace with hydrogen) resulted in high availability of hydrogen for homoacetogens that lead to production of more VFAs consequently lower rates of biogas production.

The next step for this ongoing research will be looking at addressing the observed low biogas production rate in hydrogen assisted biogas upgrading system. It is

hypothesized that adding optimum level of hydrogen (compared to overloading the reactor with hydrogen gas) and recycling the headspace biogas to increase the availability of hydrogen will balance the competition between microorganisms and improve methane production rate along with the great methane content that was found in the current research. This on-going research also aims studying biogas upgrading system via bioelectrochemical systems.

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