Renewable Energy 86 (2016) 497–506

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Quantification of methane losses from the acclimatisation of anaerobic digestion to marine salt concentrations

Keiron P. Roberts*, Sonia Heaven, Charles J. Banks

Faculty of Engineering and the Environment, University of Southampton, Southampton, SO17 1BJ, UK

ARTICLE INFO

Article history:
Received 9 June 2015
Accepted 21 August 2015
Available online xxx

Keywords:
Anaerobic digestion
High salinity
Adaptation
Inhibition
Hydrogen sulphide
Methane

ABSTRACT

The research assessed losses in methane production as a result of raising digester salt concentrations to marine values, and of increasing the feedstock sulphate concentration. Acclimatisation of inoculum from a municipal wastewater biosolids digester was begun by raising the concentration of chloride salts (Na, Mg, Ca and K) to 6–9 g L^{-1}, as initial experiments showed higher concentrations caused severe inhibition. After stable operation for four retention times salt content in the reactors and the feed was increased by 1 g L^{-1} every 14 days, up to 31.1 g L^{-1}. The digesters were fed daily in semi-continuous mode and monitored for performance and stability criteria including specific methane production (SMP). SMP was 6–7% less than in controls using the same feedstock without saline addition. After steady-state conditions were achieved at high chloride salinity, magnesium chloride was partially replaced by magnesium sulphate to give a range of sulphate concentrations. Higher sulphate concentrations caused initial instability, indicated by volatile fatty acid accumulation. This subsequently reduced and stable operation was achieved at marine sulphate concentrations, but with a ~5% loss in SMP due to interspecies substrate competition. High sulphate also affected pH, leading to gaseous H_2S production proportional to the applied sulphate load.

1. Introduction

If algal biofuels are to become part of the future portfolio of renewable fuel products then cultivation in seawater is probably the only realistic option for very large-scale production [16]. One promising approach is through the production of biomethane by anaerobic digestion (AD) of the whole biomass or of biomass residues after extraction of other products, including bio-oils [27,32] Although washing of seaweeds to remove salt before digestion has been normal practice [24], it is not realistic to consider this approach for micro-algae which are harvested at much lower biomass concentrations. Centrifugation and re-suspension in fresh water is technically possible, but is energy intensive and has a high water demand: both factors which are likely to make this approach economically unfeasible. Technologies are therefore needed that can deal with wet feedstocks with a high salt content [17] and in the case of AD this means developing a process that can operate at seawater concentrations of salt. The earliest study on the effect of the main cations in seawater (Na, K, Ca, and Mg) on AD was that of McCarty et al. [33] in which stimulatory, moderately inhibitory and strongly inhibitory concentrations were reported, all of which were substantially lower than the concentrations found in seawater. These findings have been reiterated in further work [5, 13, 28], and reported tolerances for sodium in non-acclimated mesophilic consortia are generally <12.0 g Na^+ L^{-1} for UASB reactors and lower for CSTR operation [8,13]. Higher thresholds have been reported, for example of 60 g Na L^{-1} [2]; this value, however, was interpolated from the results of batch tests at 20.8 and 120 g Na L^{-1}. Oh and Martin [34] adopted a fundamental thermodynamic approach and applied a stoichiometric model of methanogenesis to predict the inhibition thresholds of sodium. The results show clearly that in thermodynamic terms very high concentrations of sodium can be applied without potential inhibition. Achieving this, however, requires overcoming entropic limitations which can result in a loss of spontaneity. The work of Mottet et al. [35] showed successful methanogenesis using both a halophilic inoculum derived from a saline sediment and an inoculum taken from an industrial wastewater treatment plant with an influent Na concentration of 10 g L^{-1}. Both of these were tested to concentrations of 35 g L^{-1} in batch methanogenic tests, and showed methane conversion efficiencies

* Corresponding author.
E-mail addresses: K.P.Roberts@soton.ac.uk (K.P. Roberts), S.Heaven@soton.ac.uk (S. Heaven), C.J.Banks@soton.ac.uk (C.J. Banks).

http://dx.doi.org/10.1016/j.renene.2015.08.045
0960-1481/

close to those under non-saline conditions. Non-acclimated biosolids taken from a sewage sludge digester, however, could not acclimatise under the conditions of the batch testing.

When dealing with digestion of marine-derived biomass another potential concern is sulphate, which is the second most abundant anion in seawater with a concentration of around 2.8 g SO_4 L^{-1}. Sulphur is required in concentrations between 1 and 25 mg L^{-1} for the healthy operation of an AD system, but at higher concentrations its reduction by sulphate-reducing bacteria (SRB) impacts on the digestion process. SRB have a higher growth rate and a lower half saturation value than methanogens [1], giving them a kinetic advantage in competition for acid intermediate products, and thus reducing the methane production potential of the system [14]. The activities of SRB lead to the formation of reduced sulphur compounds which are present as H_2S in the biogas and as both HS^- and dissolved H_2S in the liquid phase, in proportions depending on the equilibrium conditions. When metal ions are present, these will combine with sulphates to form insoluble metal precipitates. With the exception of these precipitated sulphur compounds, all forms of sulphur can be problematic in digestion and its ancillary processes. In the gaseous form H_2S is responsible for malodours and also for corrosion of combustion engines: this means it must be removed from biogas by scrubbing or absorption systems, and all exhaust gases must be treated for odour removal. In soluble form the toxicity of sulphides to methanogens depends on the equilibrium between HS^- and soluble H_2S, which is pH dependent. Variations in this parameter have a major effect on toxicity, as at pH > 8 the main component is the less toxic dissociated HS^-, whereas at pH < 7 soluble H_2S_{liq} is predominant. The latter is much more toxic, as the un-ionized molecule can pass through the cell membrane [28], producing sulphide/disulphide crosslinks between polypeptide chains within the proteins [12,30], which in extreme cases result in cell death. The equilibrium between HS^- and soluble H_2S is also influenced by temperature and salinity [3,7]. As most AD systems work in this pH range, it is not surprising that a wide range of sulphate concentrations have been reported as either inhibitory or toxic [12,21,22].

The reporting of sulphate toxicity/inhibition/competition values is particularly challenging because of the difficulties in accurate determination of the different forms of reduced sulphur; and for this reason limits are sometimes expressed simply in terms of input sulphate concentration. Threshold values must therefore be treated with caution, but at input sulphate concentrations above 1000 mg L^{-1} there will generally be a noticeable decrease in methane productivity through competition from SRB, especially if the COD:SO_4 is below 10:1 [9,19,25]. Concentrations of total soluble sulphide between 200 and 1500 mg L^{-1} have been reported as inhibitory and/or toxic both to the methanogenic consortium and to SRB, with 50–250 mg L^{-1} un-ionized H_2S_{liq} being inhibitory [12,21,22]. Methane productivity may also sometimes be compromised by the precipitation of essential trace metals as insoluble sulphides, thus potentially causing nutrient deficiency and further decreasing the efficiency of the system [6].

Although methanogenesis at seawater concentrations of salt has been demonstrated in batch culture using microalgae and a saline-tolerant inoculum [35], in practice, commercial operation will require supplies of inoculum that are readily available from large-scale sources [8]; can be successfully acclimated; and can be maintained under continuous feeding at an acceptable loading.

The aim of the current work was therefore firstly to quantify any loss in methane production as a result of the high salinity, and in particular to differentiate clearly between those associated with salinity and those due to sulphate. A secondary objective was to acclimate a methanogenic consortium taken from a municipal sewage sludge digester to high salt concentrations, in preparation for the digestion of a harvested but unwashed marine algal biomass in a subsequent experiment.

Table 1
Composition of BSM.

Component[a]	Unit	Quantity	
Trace element solution consisting of:	mL		1
HCl	mL L^{-1}	5.1	–
$FeCl_2 \cdot 4H_2O$	g L^{-1}	1.5	–
H_3BO_3	mg L^{-1}	60	–
$MnCl_2 \cdot 6H_2O$	mg L^{-1}	100	–
$CoCl_2 \cdot 6H_2O$	mg L^{-1}	120	–
$ZnCl_2$	mg L^{-1}	70	–
$NiCl_2 \cdot 6H_2O$	mg L^{-1}	25	–
$CuCl_2 \cdot 2H_2O$	mg L^{-1}	15	–
$Na_2MoO_4 \cdot 2H_2O$	mg L^{-1}	25	–
plus DI water to make up to 1 L volume			
Yeast (block bakers form)	g		23
Urea	g		2.14
Full cream milk (UHT sterilised)	mL		144
Sugar (granulated white)	g		11.5
Blood (freeze dried)	g		5.75
Ammonia phosphate	g		3.4
Tap water	L	to make up to 1 L	

[a] Formulation based on that used by Idrus et al. [10].

2. Materials and methods

The experimental work was divided into four phases. Phase 1 was a preliminary trial to assess salt dosing strategies and chloride salt mixes for a non-acclimated inoculum. Phase 2 used fresh inoculum that was spiked at different concentrations with a sulphate-free salt mix. Phase 3 used the acclimated inoculum from phase 2 and subjected it to increasing concentrations of chloride salts. Phase 4 assessed the effect of replacing a proportion of magnesium chloride with magnesium sulphate to give a range of sulphate concentrations.

Table 2
Experimental design.

Phase	Day	Added	R1&2	R3&4	R5&6	R7&8	R9&10
1	1–40	Salt g L^{-1}	8 (feed only)[a]	16 (feed only)[a]	10 (spike and feed)[a]	8 (feed only)[b]	0 (control)
2	1–64	Salt g L^{-1}	6	7	8	9	0 (control)
3	65–400	Salt g L^{-1}	Additional salt in salt-supplemented digesters and in feed increased by 1 g L^{-1} every 14 days up to day 350, then raised to 31.1 g L^{-1}				

Phase	Day	Added	F1	F2	F3	F4	F5	F6	F7	F8
4	400–580	Salt g L^{-1}	31.1	31.1	31.1	31.1	31.1	31.1	31.1	31.1
		SO_4 g L^{-1}	0.00	0.16	0.79	1.58	2.36	3.15	3.94	4.73

[a] Laboratory salt mixture.
[b] Commercial artificial sea salt.