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Performance Evaluation of Oxygen and Air for the Microaerobic Removal of Hydrogen Sulphide in Biogas from Cow Manure Anaerobic Digestion

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The anaerobic digestion of cow manure produces a biogas containing hydrogen sulphide. We tested the removal of hydrogen sulphide from biogas by comparing the efficiency of oxygen and air as electron acceptors of oxidant actives. Research was performed in four 30L digester tanks under mesophilic conditions (37±0.2!) with a hydraulic retention time of 20 days. The concentration of hydrogen sulphide was successfully reduced from 8570 mg/Nm^3 to less than 500 mg/Nm^3 by both oxygen (flow rates of 0.5, 0.25 and 0.13 ml/min) and air (flow rates of 2.5, 1.25 and 0.63 ml/min). The removal efficiency of microaerobic supplied by oxygen and air is more than 96.0% and COD removal, VS reduction and methane productivity are not affected under microaerobic conditions. Biogas productivity increased by 27-30 mL/gVS fed and methane concentration decreased by 4-6 (v/v) % when air was added to the digester tank, as a result of nitrogen dilution. Sulphate, thiosulphate and elemental sulphur were found to be the main products of microaerobic digestive processes according O_2: Sin. By decreasing the supply ratio of O_2 to S we were able to decrease selectivity of sulphate, decrease thiosulphate formation, decrease the elemental sulphur in sludge and increase missing sulphur.

Key words: Biogas; Biological desulfurization; Hydrogen sulphur removal; Microaerobic; sulphur balance.

Cow manure has the potential to serve as a useful raw material for energy production due to its stable physicochemical properties[1] and abundance. Ten million tons of cow manure are estimated to be produced annually in China[2] and must be properly treated. When disposing of a manure substrate, anaerobic digestion (AD) is an important step in most treatment processes because of a large part of the organic matter, which can be transformed into BG(biogas)[3]. Biogas is a versatile renewable energy source used for the production of combined heat and power (CHP) and as fuel for vehicles or for the synthesis of chemicals and materials[4]. Nevertheless, biogas contains several pollutants formed during the AD of organic matter. The hydrogen sulphide is the main one.

Hydrogen sulphide is a toxic compound and bad-smelling gas, which reduces the lifetime of pipework and results in increased expense in the production and use of biogas [5]. For example, the normal operation of CHP requires a range of 100—500 mg/N m^3, depending on the specifications of the CHP manufacturer. The upper limit of 500 mg/N m^3 may not be exceeded[6]. In order for it to be efficiently used, hydrogen sulphide must be removed from the biogas to ensure use of its energetic potential.

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Different physical and chemical strategies have been employed to reduce the concentration of hydrogen sulphide in exhaust. These strategies have included chemical scrubbing[7], the addition of iron salts, pH control, activated carbon adsorption or incineration [8]. Despite the high hydrogen sulphide removal efficiencies of the above techniques, the physico-chemical processes inherent in these techniques require the use of additional chemicals and the disposal of waste products[9].

In the last few decades, biological treatment processes have emerged as cost-efficient and environmentally friendly alternatives to physico-chemical methods of removing hydrogen sulphide[10]. Biological desulfurization is based on the conversion of gaseous contaminants into CO_2, SO_4^{2-}/S^0, and H_2O under ambient pressures and temperatures. It is shown to have lower operational costs and use fewer harmful chemicals (sometimes even no harmful chemicals) compared to chemicals used in traditional physico-chemical processes[10]. Presently, biological technology to remove hydrogen sulphide is mainly limited to bioscrubbers[11] and biotrickling filters[12-13].

The removal of hydrogen sulphide from biogas by our proposed biological process is based on the utilization of sulphur-oxidising microorganisms. These microorganisms are both familiar and less well-known sulphur-oxidising bacteria such as *Thiomicrospira sp*. and *Thiobacillus sp*. [14]. The bacteria use oxygen as an electron acceptor in reactions that break down hydrogen sulphide through several intermediates shown in Eq. (1)[15]:

SH^{-}’!S^{0}’!$S_2O_3^{2-}$’!$S_4O_6^{2-}$’!SO_4^{2-} (1)

Depending on the conditions and the oxygen content available *Thiomicrospira* and *Thiobacillus* are often responsible for sulphide oxidation. The reactions were described in Eq. (2)-(4) [16]as:

$H_2S+1/2O_2 \rightarrow S^0+H_2O$ ΔG^o= -209.4 kJ/reaction ...(2)

$S^0+ 2H_2O +3/2O_2 \rightarrow SO_4^{2-}+2H^+$ ΔG^o= -587.1 kJ reaction ...(3)

$H_2S+2O_2 \rightarrow SO_4^{2-}+2H^+$ ΔG^o=-798. 2kJ/reaction ...(4)

The manipulation of oxygen and air to control hydrogen sulphide toxicity was recently used in wastewater AD treatment [17]. Additionally, methanogen was shown to have a higher tolerance to low oxygen concentrations than was previously thought in both granular [18] and suspended sludge [19]. Based on the recent success of wastewater treatment plants in removing hydrogen sulphide, we wanted to test the removal of hydrogen sulphide from biogas in an anaerobic digester. Our specific goal was to reduce the concentration of hydrogen sulphide to less than 500 mg/N m^3.

There has been little research on the use of moderate aeration to lower biogas hydrogen sulphide levels during treatment of high concentration cow manure AD. Literature on MA (microaerobic) desulphurization has focused on the simulation of high S-containing wastewater AD, removal efficiencies (REs) of hydrogen sulphide and oxidation, and reduction potential (ORP) as a controlling parameter. In our experience, studies have neglected to measure the SO_4^{2-} and $S_2O_3^{2-}$ oxidized from hydrogen sulphide. Major disadvantages of SO_4^{2-} and $S_2O_3^{2-}$ formation are

- Useless elemental sulphur is formed;
- Formation of protons leads to acidification of the medium;
- SO_4^{2-} and $S_2O_3^{2-}$ ions have to be removed by the addition bleed water stream to prevent accumulation[20].

Conversely, it is a lack of information about the effect of MA supplied by oxygen and air conditions on biological desulfurization of BG from cow manure AD and the effect of oxygen dose on the formed of incomplete oxidation of sulphur particles and s–balance in MA desulphurization.

The present research employed MA conditions supplied by oxygen and air, with the goal of optimizing the practical applications of the AD process. The research evaluated the relationship between oxygen and sulphur consumption and how oxygen affects the sulphur species formed in MA desulphurization.

MATERIALS AND METHODS

Pilot-scale reactor and substrate

The treatment of cow manure AD and the removal of hydrogen sulphide were performed in four pilot-scale reactors (Continuous Stirred-Tank Reactor, CSTR (BIOTECH-30JS-4, China) with working volumes of 20L (30L total volume) shown in Fig. 1. Reactor temperature was controlled via heating threads bonded around the reactor and temperature sensors connected to a temperature controller (PT100, China). Oxygen was introduced by oxygen and air into the headspace of the reactor by a peristaltic pump. The reactors were stirred by an electric motor controlled by computer. The balance of sulphur and COD were monitored regularly by measuring the flows of influent, effluent and biogas and analyzing liquid and gas samples (sulphide, sulphate, thiosulphate, elemental sulphur, biogas productivity, biogas composition, COD, VS, pH and DO). The biogas composition (methane, hydrogen sulfide, carbon dioxide, O_2 and N_2) and their generation rates were corrected to the standard temperature and pressure (symbolized by the letter N).

Seed organisms for AD and MA desulphurization were obtained from anaerobic digesters of the North Wastewater Treatment Plant, Shenyang, China and have been maintained for inoculum purposes in the researchers' laboratory for several years. Cow manure was collected from a farm in the Daoyi development district, Shenyang, China.

Operational conditions

The pilot-scale study was developed in the cow manure AD from previous experiments. Initially, the cow manure was held in a pseudo-stationary anaerobic state. Digestion of cow manure was performed in the mesophilic range (37 ± 0.2°C) and the hydraulic retention time (HRT) was 20 days.

The four reactors were initially inoculated with 3L seed inocula and 2 kg cow manure. All substrate was flushed for 5 min with an oxygen-free flush gas (N_2). On the 10th and 15th day, 1 kg cow manure was added to each reactor. On each day, beginning on day 21, 1L of effluent was drained from the reactor and 0.4 kg of cow manure was diluted with water into 1L and then fed into each reactor. There was no supply of oxygen at this stage and the concentration of hydrogen sulfide was controlled at 8570.3± 430.5 mg/m^3.

After a start-up period of 20 days and 30 days AD without any oxygen supply, three distinct MA conditions were instituted in the four reactors. The reactors were separated into group 1 and group 2 as shown in Table 1 Sulphide, sulphate, thiosulphate, elemental sulphur, biogas composition and COD were measured at selected time intervals. All experiments were performed with paralleling vials.

Monitoring and experimental analysis

A pilot-scale AD of cow manure was monitored online by sensors for temperature (PT100, China) and pH (PHS-25C). DO was measured with a portable dissolved oxygen analyzer (HI9143, China).

Biogas production was measured by a wet type gas meter (LML-1, China). The amount of methane, nitrogen, carbon dioxide and hydrogen sulphide in the biogas were measured by a gas chromatograph (Shimadzu, GC14B, Japan) equipped with a thermal conductivity detector. Specifically, a GC column with TDX-01 (2m×3mm) and GDX-502 (2m×4mm) was used. The temperatures of the injector, column and detector were set at 40, 120 and 120°C, respectively. Helium was used as a carrier gas at a flow rate of 30 mL/min.

Sulphate and thiosulphate were measured by HPLC (Shimadzu, GC14B, Japan) according to the method described by van der Zee et al. [21].

The sulphide in the digesters was measured by spectrophotometer (UV-2000, China). The wavelength and narrow slit width were maintained at 665 and 2.0 nm, respectively.

Sulphur content in the sludge was estimated by an intelligent sulphur determination analyzer (KZDL-4, China). Samples were centrifuged at 5000 rpm for 10 min (LC-10ATVP, China) and the supernatant was filtered at 0.45 lm. Samples were combusted at 1200! for the final analyses and the sulphur was completely oxidized to sulphur dioxide in the detection cell (TCD).

The"missing sulphur"was estimated by subtracting the other analyzed sulphur species (sulphate, thiosulphate, sulphur and sulphide) from the total sulphur content of the sample.

Digestion performance was evaluated weekly by conventional parameters such as COD, VS, BG productivity and composition, pH, DO and total sulphide concentrations, according to standard methods [22].

RESULTS AND DISCUSSION

Operation of AD and MA supplied by pure oxygen

AD operations

Cow manure and inoculum sludge were mixed and anaerobically digested in the pilot-scale reactors. After 20 start-up stages, the average biogas productivity of cow manure without any oxygen supplied was 369.9± 14.6 mL/gVSfed and methane productivity was 237.4±48.0 mLCH$_4$/gSVfed, which means the concentration of methane was 64.2%. The concentration of hydrogen sulphur was 0.6±0.2% (8570.3±430.5 mg/N m^3). The removal efficiency (RE) of COD and VS were 55.9% and 45.6%, respectively. The results of the digestion performances of AD and MA are compared and summarized in Table 2.

As shown in Table 3, every day 400 g fresh cow manure with 644±12.8 mg/L sulphate was fed into the reactor after the initial 20 day start-up. The concentrations of sulphur species in digester effluent under AD without oxygen supply were 30.1±7.1 mg/L (sulphate), 212.0±15.6 mg/L (sulphide) and 71.0±13.2 mg/L (thiosulphate). The concentration of sulphur in biogas was 8.57±0.4mg/L (hydrogen sulphide) and in effluent sludge was 68.3±21.0 mg/L. The sulphur species present in effluent sludge were not analyzed because it is impossible to analyze.

MA supplied by oxygen operations

In the group 1 treatment?, oxygen was introduced to the reactor after the 51st day at the rate of 0.5 mL/min and at a flow rate of 0.04 m^3/m^3 d^{-1}. This corresponds to an O_2/COD ratio of 0.07 g O_2 per g influent-COD and an O_2/S ratio of 4 mol O_2 per mol influent-S, where all sulphide is oxidized sufficiently in theory. As shown in Table 2, the productivity of biogas and methane is not affected by the supplied oxygen and remained between 377.3±25.4 and 232.4±15.5 mLCH$_4$/g SVfed, respectively.

The hydrogen sulphide concentration of BG decreased from 8570.3±430.5 mg/Nm^3 in AD to an average of 146±55 mg/Nm^3 as a result of oxygen supplied at the rate of 0.5 mL/min and subsequent to hydrogen sulphide oxidation. The RE of hydrogen sulphide is 98.3%. Table 3 shows the composition of BG during this period. Oxygen was not completely utilized during hydrogen sulphide oxidation. Moderate amounts of excess oxygen escaped from the reactor on an average of 0.4±0.2 (v/v)% of biogas composition. Therefore, the oxygen flow to the bioreactor was reduced to 0.25 and 0.13 mL/min on the 81st and 111th day, representing 0.02 and 0.01 N m^3/m^3 reactor volume/d, respectively. The average hydrogen sulphide content of biogas during this period was 221±67 and 258±81 mg/Nm^3, respectively. The REs of hydrogen sulphide was 97.4 and 97.0%,

Table 1. Operational conditions of experiments

			Group1			Group2		
	Start-up	Anaerobic	MA supplied by oxygen			MA supplied by Air		
Operation time(d)	1-20	21-50	51-80	81-110	111-140	51-80	81-110	111-140
flow rate (ml/min)	0	0	0.5	0.25	0.13	2.5	1.25	0.63

Table 2. Digestion performance under AD and MA supplied by pure air or air

	AD	G1:MA supplied by oxygen (mL/min)			G2:MA supplied by air) (mL/min		
	-	0.5	0.25	0.13	2.5	1.25	0.63
COD in(g/L)	14.5±3.1	14.5±3.1	14.5±3.1	14.5±3.1	14.5±3.1	14.5±3.1	14.5±3.1
COD out(g/L)	6.4±1.4	6.0.±0.8	6.1±0.3	6.2±0.7	6.2±1.2	6.2±0.2	6.3±0.7
%COD removal	55.9	58.6	57.9	57.2	57.2	57.1	56.6
VS in(g/L)	68.6±5.4	68.6±5.4	68.6±5.4	68.6±5.4	68.6±5.4	68.6±5.4	68.6±5.4
VS out(g/L)	37.3±2.9	36.2±0.7	36.8±1.1	37.1±0.9	36.8±2.7	37.2±2.1	37.3±0.8
%VS removal	45.6	47.2	46.4	45.9	46.4	45.8	45.6
Biogas productivity (mL/gVSfed)	369.9 ±74.6	377.3 ± 25.4	371.5 ± 29.9	365.3 ± 28. 7	399.9 ± 35.1	389.2 ± 25.2	383.2 ± 44.9
Methane productivity (mL CH4/gVSfed)	237.8±48.0	232.4± 15.5	227.0± 18.3	225.2± 19.1	231.5± 19.9	225.5± 14.8	227.4± 26.6

respectively, slightly lower than that of previous period. The oxygen remaining in the biogas was reduced to 0.2±0.2% and 0.1±0.1% compared to the previous MA period, shown as fig.2

The MA by oxygen treatment results in a slight change to the COD balance. The REs of COD are 64.1%, 63.4% and 60.0% for MA supplied by differential oxygen flow, respectively. These values are a little higher than those of the AD treatment, VS removal efficient are corresponding to 47.2%, 46.4% and 45.9%, respectively. The concentration of methane and carbon dioxide is 61.6~62.8% and 38.1~37.9%. In general, the sulfate-reducing bacteria (SRB) has a much wider substrate range than that of methanogens[23]. Competition between methanogens and SRB for COD occurs under MA operations[24-25]. Although the load of oxygen was very low in comparison to that of COD, it is possible that hydrolytic facultative bacteria utilize the oxygen for the aerobic degradation of organic matter and methanogens are not inhibited by the presence of oxygen in the headspace. This fact is in agreement with the observations of Johansen and[26], who found an enhanced hydrolysis of primary sludge as a result of MA.

Oxygenation eventually decreases the level of hydrogen sulphide in biogas below 0.2% and shows how moderate oxygenation can be applied successfully as a strategy for the removal of hydrogen sulphide. The fate of sulphur species in the effluent digester under MA supplied by oxygen at the rate of 0.5 mL/min is changed obviously. The concentrations of sulphate and thiosulphate increased from 30.1±7.1 mg/L and 71.0±13.2 mg/L to 222.8±2.9 mg/L and 224.3±5.6 mg/L, respectively. The concentration of sulphide decreased from 212.0±15.6 mg/L to 35.4±16 mg/L. The amount of sulphide-S, thiosulphate-S, sulphate-S and sludge-S formed is mostly 88% of the amount of total sulfide-S. It was found that at least 11.9±1.8% sulphur leaves the reactor as either elemental sulphur, S-containing organic compounds and poly-sulfide. However, since elemental sulfur tends to attach to surfaces, it is extremely difficult to measure reliably. The S-containing organic compounds and poly-sulfide currently cannot be detected by any analytical methods.

Table 3. Average biogas composition (v/v)% during AD and MA

	CH_4	CO_2	H_2S	O_2	N_2
AD	64.3±2.1	35.1±2.3	0.6±0.2	0.0±0.0	0.0±0.0
N m^3 pure O^2/N M^3 feed					
2.5	61.5±1.7	38.1±1.6	0.0±0.1	0.4±0.2	0.0±0.0
1.25	60.2±0.8	38.4±0.9	0.1±0.2	0.3±0.2	0.0±0.0
0.63	62.8±0.5	37.8±0.4	0.2±0.2	0.2±0.1	0.0±0.0
N m^3 air/N M^3 feed					
2.5	56.8±1.2	37.4±0.9	0.0±0.0	1.0±0.1	4.8±1.2
1.25	57.7±1.5	38.4±1.6	0.1±0.1	0.7±0.2	3.1±0.9
0.63	58.2±0.9	39.1±1.4	0.2±0.1	0.4±0.2	2.1±0.5

Table 4. The relation of oxygen and sulphur supply ratio

	AD	MA supplied by oxygen		
Flow ratio	0	0.5	0.25	0.13
COD in (g/L)	14.5	14.5	14.5	14.5
COD out (g/L)	6.4	6	6.1	6.2
Total COD lost (g/D)	8.1	8.5	8.4	8.3
COD lost by oxygen (g/D)	—	0.4	0.3	0.2
Daily oxygen amount(g/D)	—	1.03	0.82	0.62
Oxygen used by sulpher(g/D)	—	0.63	0.52	0.42
Daily sulpher amount(g/D)	—	0.64	0.64	0.64
O2:S supply ratio	—	1.00	0.80	0.65

When the oxygen flow dropped to 0.25 and 0.13 mL/min, the concentration of sulphur species in the effluent digester drastically changed. The "missing" sulphur (gap) percentage increased to 20.0±1.5% and 32.6±0.1%, respectively. Considering the molar ratio between oxygen and sulfide-S, it was changed to 2 and 1 mol O_2 per mol sulfide-S removed at oxygen flow of 0.25 and 0.13mL/min. Since some of the oxygen was used for COD oxidation, the initial oxidation of sulfide is caused by the transfer of two electrons from each sulfide molecule and the average oxidation state of the sulfur atoms is changed from -2 to 0. The elemental sulfur and polysulphides (S_n^{2-}) are the main initial oxidation products, rather than further oxidized sulfur compounds such as sulphite, dithionite and polythionates. According to the mechanism of sulfide oxidation described by[124], sulfide is primarily oxidized to polysulphides and elemental sulpher at pH values near or below 7. It is expected that at the pH level prevailing in AD reactors (7.0±0.2), the relative concentrations of polysulphides and elemental sulpher is equal. Therefore, it is reasonable to infer that polysulfide and elemental sulpher covers the gap between the removed sulfide-S and recovered elemental sulfur and thiosulphate-S.

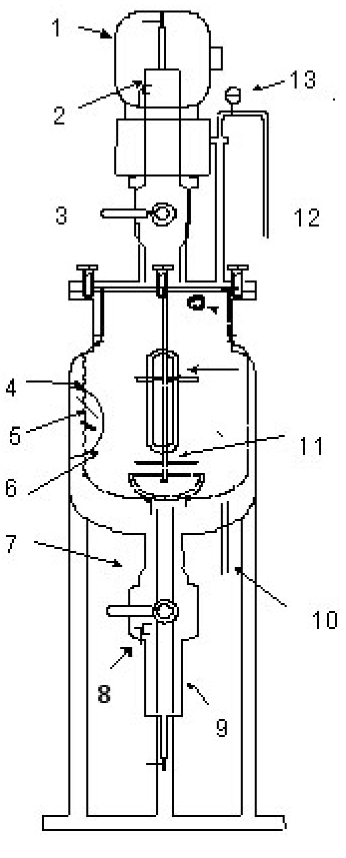

Fig. 1. Schematic diagram of experimental reactor (1. Mixing motor, 2. Inlet, 3.Inlet ball valve, 4. Thermocouple, 5.pH meter, 6. Water bath layer, 7.Outlet ball valve, 8.N_2 rectification, 9.Outlet, 10.Water inlet, 11.Mixing blade, 12. Nozzle, 13. Pressure instrument)

The experimental reactors maintained a stable pH between 7.0 and 7.2 during the study. The pH levels exhibited no differences between AD and MA conditions. DO concentration in the bioreactor was 0.21±0.06, 0.14±0.053 and 0.08±0.03ppm under conditions supplied by oxygen flows of 0.25, 0.13, 0.06 mL/min. The relationship between MA and DO was not significant. This is in contrast to the results of[27] that showed moderate oxygenation of bioreactors

In summary, when MA is supplied by oxygen, the RE of hydrogen sulphide is more than 97% for the three tested flow rates. It has no effects on the performance of methanogenic capacity and digestion.

MA supplied by Air

The results of the group 2 treatment were similar to the group 1 results. On the 51st day, a 2.5mL/min air flow was introduced from the headspace of the reactor. This is the same amount of oxygen as provided by the O_2 flow of 0.5ml/min. AD performance under supplied air is shown in

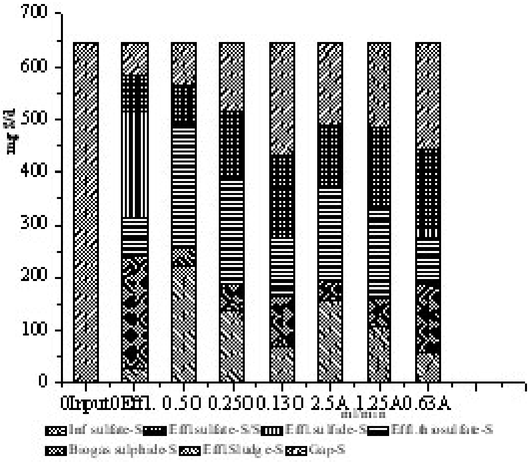

Fig. 2. Sulpher balance for the studied conditions with oxygen/air supply for every rate of reactive

Table 2. We showed that the productivity of biogas increased to 389.9±35.1mL biogas/VSfed and the concentration of methane and carbon dioxide decreased compared to concentrations seen in the AD period. We believe this to be a result of nitrogen dilution of the air supply. The productivity of methane remained stable at 221.5±19.9 mL/gVSfed. A similar yield was maintained under both MA supplied by air and AD conditions. During this stage, COD removal (59.3%) was slightly high relative to the anaerobic stage, while VS reduction was maintained at 46.4%. We observed no effects of MA supplied by air on methanogenic activity, except BG productivity and methane concentration.

When air was supplied at a rate of 2.5mL/min, the hydrogen sulphide concentration of BG decreased to an average of 188 ±39 mg/N m^3 as a result of subsequent hydrogen sulphide oxidation. Since there is nitrogen dilution of air (Table 3) there is a slight decrease in solubility and oxygen is not completely utilized in hydrogen sulphide oxidation. Moderate excess oxygen leaves the reactor with an average of 1.0±0.2 (v/v)% of biogas composition. In order to optimize air flow and achieve a small decrease in methane concentration of BG, the air flow was reduced to 1.25 and 0.63 mL/min on the 81st and 111th days. The average hydrogen sulphide remaining in the biogas during this period was 281±36 and 345±56mL/N m^3, slightly higher than that of AD and MA supplied by oxygen. The REs of hydrogen sulphide of MA supplied by air at the flow rate of 2.5, 1.25 and 0.63ml/min is 97.8%, 96.7% and 96.0%, respectively. The oxygen remaining in the biogas is reduced to 1.0±0.1%ÿ0.7±0.2% and 0.4±0.2%.And nitrogen content is also reduced by 1~2 (v/v)% compared to that of previous period. The concentration of methane recovered is approximately 1(v/v)%(Table 3).

The effluent digester of MA supplied by air flow rates of 2.5mL/min recovered various concentrations of sulphur species, such as 158.0±15.2 mg/L of sulphate, 37.2±3.4mg/L of sulphide and 173.4±24.4 mg/L of thiosulphate. In the effluent sludge, the sulphur concentration was 120.5±11.0mg/L. The amount of sulphide-S, thiosulphate-S, sulphate-S and sludge-S formed was mostly 76% of the amount of total sulfide-S. Based on this calculation, at least 24% of the sulphur such as elemental sulphur, S-containing organic compounds and poly-sulfide, was left in the reactor.

When the air flow dropped to 1.25 and 0.63 mL/min, the concentration of sulphur species in the effluent digester changes. The "missing" sulphur (gap) percentage increases to 24.9±2.4% and 31.1±0.9%, respectively. The "missing" sulphur refers to MA supplied by oxygen.

In the second treatment group the pH was maintained between 7.2 and 7.4, while DO was stable at 0.20±0.05, 0.13±0.05 and 0.08±0.03ppm, similar to the first group.

In summary, MA supplied by air successfully removes more than 96% of hydrogen sulphide produced during AD when 2.5 to 0.63 mL/min air is employed. The hydrogen sulphide level of biogas is decreased below 500mg/ N m^3, which indicates that MA supplied by air at flow rate of 2.5~0.63mL/min can be applied successfully as a strategy for the removal of hydrogen sulphide from cow manure AD. Biogas productivity is increased by 27-30 mg/gVSfed during MA supplied by air as a result of nitrogen dilution in biogas. The methane concentration of biogas is lowered by 4–6 (v/v)%. Methane productivity is not affected by the introduction of air, as its value in MA conditions is similar or slightly lower than that in AD conditions.

Comparison of oxygen and air as oxidant reactives

In order to keep the amount of oxygen constant in the experiment, MA supplied in the oxygen and air treatment groups were provided at different flow rates. Neither of the gases used in the present research have shown an obvious effect on digestion performance under the conditions studied. Biogas productivity supplied by oxygen at 0.5 flow and air flow at 2.5mL/min is 377.3±25.4 and 389.9±35.1 mLbiogas/gVSfed, respectively. Biogas productivity supplied by air was a little higher than biogas productivity of pure oxygen because of the nitrogen dilution. The methane yields nearly the same (232.4±15.5 vs 231.5±19.9 $mLCH_4$/gSVfed). This result implies that methanogens are not inhibited by the presence of limited amounts of oxygen and oxygen is mainly used as an electron acceptor for sulphide oxidation. Similar results were found for the other two MA conditions. The dilution of biogas may also give rise to problems of combustibility. N_2 can be removed from gas streams by membranes or by low temperature pressure membranes (SPA).

Whether MA is supplied by oxygen or air does lead to a small change in the COD-balance. The COD REs of MA by differential oxygen supplied flows is 58.6%, 57.9% and 57.2%, respectively, which is slightly higher than that of the supplied air. These results were obtained when oxygen was introduced into the reactor from the headspace and some of the oxygen was used by hydrolytic facultative bacteria for the aerobic degradation of organic matter to increase the RE of COD. When air was introduced into the reactor from the headspace, the solution level of oxygen in the air was reduced by nitrogen dilution. Similar results were found in VS.

In terms of the removal of hydrogen sulphide, both reactives were effective at a similar level of performance. REs of hydrogen sulphide are higher than 96% and the concentration of hydrogen sulphide is below 500 mg/N m^3 in all cases. This means an adequate CHP operation condition is guaranteed when biogas is used.

Regarding the energetic use of biogas, methane production and methane concentration of biogas are maintained when oxygen is supplied; however, a reduction in engine efficiency might be expected when burning biogas produced under MA conditions supplied by air due to nitrogen dilution despite similar methane production observed in AD conditions.

As a first approach to examining the economic savings and expenses involved in the utilization of air or pure oxygen for hydrogen sulphide removal, Porpatham et al. (2007) found that a decrease in methane concentration from 70% to 59% only reduces the energetic performance of a spark-ignition engine by 0.9% for the same mass flow of methane. Therefore, the utilization of costless air seems to be more profitable when the engine design takes into account the expected lowered methane concentration and small decreases in methane concentration shows no significant variation in energetic efficiencies. In contrast, the advantages of oxygen supply are the following:

- Methane content is not lowered under MA operation;
- Biogas productivity is not affected by limited oxygen introduction;
- There is no need for additional equipment to treat hydrogen sulphide when biogas is employed for CHP.

The concentration of sulphur species in an effluent digester under MA supplied by an oxygen flow rate of 0.5mL/min and an air flow rate of 2.5mL/min are 222.8±2.9 mg/L and 158.0±15.2 of sulphate, 35.4±16.7 and 37.2±3.4mg/L of sulphide, 224.3±5.6 and 173.4±24.4mg/L of thiosulphate. The concentrations of sulphate and thiosulphate are higher than that of sulphide because sulphur oxidation favorably responds to the introduced oxygen. When we compare air and oxygen the oxygen solubility is reduced because of nitrogen dilution and results in less oxygen that can be used in sulphur oxidation and formation of sulphate and thiosulphate. Similar results were also found under two other MA conditions.

Sulphur and oxygen balance during MA operations

In MA conditions supplied by oxygen and air the hydrogen sulphur level of biogas decreases below 500mg/N M^3, indicating that moderate oxygenation can be successfully applied as a strategy for the removal of sulfide from biogas. S-containing compounds resulting from the biological oxidation of hydrogen sulphide under MA supplied by oxygen or air conditions can be generally described by a sulphur balance (Table 3). The reactors were fed with 644±12.8mg/d sulphur, mainly in the form of sulphate and organic sulphur-containing compounds.

In contrast, sulphur species and their concentrations are changed during both AD and MA reactor operations.

In the AD phase where no oxygen was supplied, 64.4±5.8% of the sulfate-S removed could be recovered as sulfide-S in effluent and biogas (32.9±2.4% in effluent digester and 31.5±3.4% in BG). Sulphate and thiosulphate (15.7±3.1%) and sulphur (10.6±3.3) were conserved in the effluent digester and effluent sludge. The gap of 9.3±5.8% in the S-balance was “missing”, which may be retained in the process as elemental sulphur, S-containing organic compounds or poly-sulfide. S-containing organic compounds and poly-sulfides were not detected by any of the analytical methods applied. The top of the reactor was not completely air-tight and we observed sulfur formation on the top of the reactor. It was suggested that sulphate was easily accessible for sulphate-reducing microorganisms, while organic sulphur in the form of proteins, or cell constituents, was only a small part of the sulphur reduced. A large portion of the sulphur left the bioreactor as sulphide in AD operations. A higher amount of total sulphide was found in the outputs of the reactor when oxygen was used instead of air, probably as a result of a slightly lower pH during that digestion period (7.0–7.2) compared to the experiment with air (7.2–7.4). A small part of the sulphur appears as thiosulphate in the effluent.

The ratio (effluent + biogas)-sulphide-S:influent -S((HS$^-$-S$_{effl.}$+S$_{gas}$):S$_{in}$) decreased from 0.64 in AD to 0.06, 0.08 and 0.16 in MA supplied by an oxygen flow rate of 0.5, 0.25 and 0.13ml/min operations and to 0.06, 0.09 and 0.22 in MA supplied by an air flow rate of 2.5, 1.25 and 0.63ml/min operations. This indicates that introduction of limited oxygen promoted sulphide oxidation in all reactors. The levels of hydrogen sulphide in BG decreased considerably, corresponding to a maximum of 2.2 %(v/v volume) of the influents (Table 3). The distribution of sulphide throughout biogas and effluent will depend on the operation conditions, especially the pH, the volume of biogas produced and the oxygenation dosing.

Sulphate, thiosulphate and elemental sulphur have been suggested as the main products of MA operations according to the following equation: (O_2: S_{in}). The general tendency of the introduction of MA conditions to the reactors resulted in an increase in the ratio effluent (sulphate-S + thiosulphate-S): influent-S with more oxygen loads (O_2: S_{in}). The oxygen was introduced into the reactor from the headspace and the hydrogen sulphide produced by sulphate reducing bacteria was iodized under limited oxygen concentrations. The reason that the concentrations of sulfate and thiosulfate were lower in MA supplied by air than in oxygen was that nitrogen diluted the oxygen. This allowed the oxygen to permeate into the digester and cause sulphide oxidation to occur in lower air flows. Strongly oxidized sulphur species, such as thiosulphate and sulphate, slightly increased as a result of energetically more favorable reactions in the MA operation with an increased flow. When lower oxygen/air ratios were applied, S-thiosulphate decreased in comparison to the previous rates, and S-sulphate was negligible for the lower oxygen/air ratio. This suggests a mechanism of hydrogen sulphide removal as the chemical equilibrium is not displaced because only the sludge surface in the digester is in direct contact with the gas in the headspace. We found similar results in two other sets of conditions.

Furthermore, it is clear that at least a fraction of the sulphur left the reactor as elemental sulphur. This“lost”sulphur corresponds to the elemental sulphur not analysed in this research but observed in the conductions, effluent and headspace of the biodigester. Since sulphur tends to attach to surfaces, it was not possible to assess this fraction reliably, but was detected visually as elemental sulphur concentrations in the effluent samples.

Product selectivity in relation to molar O_2:H_2S supply ratio

We estimated the amount of oxygen utilized in the reactors from the sulphur and COD balance, performed according to stoichiometric reactions. We only considered MA supplied by oxygen conditions because the dilution of nitrogen affects the oxygen utilization under MA supplied by air. Oxygen was employed as the electron acceptor for sulphide and parts COD oxidation.

The oxygen fraction used for COD degradation and oxidation and the formation of carbon dioxide is fairly constant in all cases and about 38.89–32.41% of the total oxygen supplied (Table 4). This is the reason the REs of COD under MA supplied by oxygen were slightly higher than AD operations. The rest of the oxygen (60~70%) left the reactor mixed with the produced biogas and was employed for hydrogen sulphide oxidation.

When the supply ratio of O_2: S is 1.0, the selectivity for sulphate formation is 34.6±0.4%. When the supply ratio of O_2: S is between 0.8 and 0.65, the selectivity for sulphate formation decreases to 21.4±0.2% and 10.8±0.4%, respectively.

Selectivity for thiosulphate formation is 34.8±0.9%, 31.4±0.4% and 16.9±1.7% as the supply ratio of O_2: S is 1.0, 0.8 and 0.65, respectively. We found that selectivity for sulphate and thiosulphate formation decreases with decrease of the supply ratio of O_2: S. It is probably a result of lowered oxidation of sulphide, which is energetically more favorable for sulphide-oxidising bacteria (see Eqs.

(2)–(4)) and selectivity for elemental sulphur in sludge. Missing sulphur increased when the O_2: S supply ratio decreased. In all experiments, the H_2S concentration in the gas flow leaving the reactor was below 500mg/Nm^3. In order to avoid sulphate and thiosulphate production in effluent digesters we recommend selecting an O_2: S supply ratio of 0.65 as MA supplied by oxygen for biological desulphursation technology. In our experience the O_2: S supply ratio was affected by the operation conditions and substrate and even the microbial activity levels.

CONCLUSIONS

Biological desulphursation of BG from AD of cow manure by MA supplied by oxygen and air provides a relatively simple strategy for reducing emissions hydrogen sulphide levels below 500mg/Nm^3 without obvious effects on methane productivity and digestion performance. The REs of all reactors was more than 96.0%. When comparing oxygen and ambient air as oxidants, the utilization of available air seems to be more profitable when it is applied to a new plant where the engine design takes into account the expected lowered methane concentration.

The ratio (effluent+biogas)-sulphide-S:influent-S decreases from 0.64 in AD to 0.06, 0.08 and 0.16 in MA supplied by oxygen flow rates of 0.5, 0.25 and 0.13ml/min and to 0.06, 0.09 and 0.22 in MA supplied by air flow rates of 2.5, 1.25 and 0.63ml/min. The introduction of limited oxygen promoted sulphide oxidation in our study.

Sulphate, thiosulphate and elemental sulphur have been descibed as the main products of MA processes according to the formula: (O_2: S_{in}). The general tendency towards MA conditions in the reactors led to an increase in the ratio effluent (sulphate-S + thiosulphate-S): influent-S with more oxygen loads (O_2: S_{in}).

Selectivity for sulphate and thiosulphate formation decreased and elemental sulphur in sludge and “missing” sulphur increased in conjunction with a decrease in the O_2: S supply ratio. We suggest using an O_2: S supply ratio of 0.65 for MA supplied by oxygen for biological desulphursation technology.

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