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Inline NH₃ removal from biogas digesters

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ABSTRACT

During biogas production from various types of substrates such as animal manure, fats and proteins, bacterial growth and biogas production can be inhibited by excessive ammonia (NH₃) concentrations. If NH₃ is removed from the biogas digester without damaging the digestion process, inhibition of the methane (CH₄) producing bacteria will diminish. This study shows that it is possible to remove a significant quantity of NH₃ from the biogas digester headspace and liquid phase by a simple gas circulation method where gas bubbles free of NH₃ is forced through the upper 30 cm of the liquid phase in the biogas digester, into the headspace and out of the digester. The suggested method improves conditions for anaerobic bacteria exposed to high concentrations of NH₃ by simply removing NH₃ from the digester.

In full-scale biogas production the system presented in this study can be improved by circulating headspace gas through an ammonia absorber and returning the NH₃ depleted biogas into the biogas digester. This method can also replace the need for mixing in biogas digesters.

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1. Introduction

In Denmark, most production of biogas takes place in continuously stirred tank digesters (CSTR) at either mesophilic or thermophilic temperatures. The main substrate is organic waste or pig- or cattle manure with fat, crops or proteins added as supplemental substrate/biomass [1,2].

The availability of organic wastes for anaerobic digestion is decreasing in Denmark and in order to produce cost-effective CH₄, focus is shifting towards using more animal manure for anaerobic digestion [3]. However, due to inhibition, CH₄ production from manure is often sub-optimal.

The inhibition is primarily caused by NH₃, and not its corresponding acid ammonium (NH₄⁺). Due to its small size and electric neutrality, NH₃ can penetrate bacterial cell membranes [4,5]. Inside the bacterial cell, NH₃ is protonated to NH₄⁺ effectively forcing anions, i.e. potassium, out of the bacterial cell

membrane distorting cell homeostasis. The exchange of NH₃ across the membrane dissipates the trans-membrane pH-gradient [6]. Although the sequence of cell events caused by NH₃ is not fully understood it is widely accepted that NH₃ has an inhibitory effect on CH₄ producing micro-organisms [7,8].

Studies on pig- and cattle manure have shown that NH₃ inhibition varies considerably from biomass to biomass.

Threshold values at which NH₃ inhibition begins ranges from 80 (mg L⁻¹) [9,10] to 150 (mg L⁻¹) [11,12].

This study focuses on a system for NH₃ removal from anaerobic digesters.

Existing methods for removing NH₃ from manure are based on degassing NH₃ by adjusting the temperature or pH of the biomass before it is fed to the digesters and recovering NH₃ in an absorber.

Another approach, the potential of which is investigated in this study, is to reduce the NH₃ levels inside the biogas

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digester during the digestion process. This will improve conditions for anaerobic bacteria exposed to high NH_3 concentration and will increase CH_4 production in any process inhibited by NH_3 .

The idea behind circulating headspace gas through an NH_3 absorber and returning it to the digester is to remove NH_3 from the digester and to promote additional mass transfer of NH_3 from the liquid into the circulated headspace gas.

Absorbers for NH_3 removal most often use H_2SO_4 to capture the NH_3 whereby ammonium-sulphate $(\text{NH}_4)_2\text{SO}_4$ is generated which can be used as a fertilizer. Also, as this system provides a great degree of mixing in the upper part of the digester, the need for mixing a CSTR with this system implemented is reduced.

The only specification to the absorber used for capturing the NH_3 , besides being able to absorb NH_3 , is that it should be airtight, and capable of circulating large quantities of gas and removing NH_3 at the same time. As such absorbers are well described in the literature and industrially readily available, they are not investigated in this study.

In order to evaluate the experiments and the performance of a biogas digester having an absorber connected, the anaerobic digestion model (ADM1) [13] was modified by including an NH_3 mass transfer coefficient (tc_{NH_3}) at different flows, temperatures and $[\text{NH}_3]$. Furthermore, the true mass transfer coefficient ($K_L a$) of NH_3 for the experimental setup was determined.

2. Methods

The experiments investigate a set-up without an absorber unit connected. To simulate a digester where an absorber had been connected and the NH_3 free headspace had been returned to the digester. In the laboratory ammonia free N_2 was pumped through a pilot-digester to see if by forcing ammonia out of the digester the partial pressure of ammonia (P_{NH_3}) in the headspace gas could be reduced sufficiently to reduce the liquid concentration of NH_3 .

This system of one-way transport of N_2 through the digester is effectively the same as recycling NH_3 depleted headspace gas. By bubbling the recirculating gas through the digester liquid phase, the transport of NH_3 is increased by the increased gas–liquid interphase caused by the gas bubbles. The turbulence in the liquid further promotes NH_3 mass transfer into the digester headspace.

As the gas bubbles of N_2 rise through the liquid the partial pressure of NH_3 (P_{NH_3}) increases. The P_{NH_3} limit in the bubbles and thus in the digester headspace is reached when vapour–liquid equilibrium is reached. This equilibrium value can be predicted using the Henry's law constant for NH_3 (H_{NH_3}) that relates the liquid $[\text{NH}_3]$ to the headspace P_{NH_3} .

2.1. Theory for the simulation model

In this study manure is considered a non-ideal aqueous solution. Thus, the concentration of NH_3 is a function of temperature (T), total ammoniacal nitrogen (TAN), or $[\text{NH}_3]$ plus the concentration of ammonium ($[\text{NH}_4^+]$), pH based on measured hydrogen ion activity $\{H^+\}$, the dissociation

constant of NH_4^+ ($K_a^{\text{NH}_4^+}$), the specific activity coefficient of hydrogen ions (f_{H^+}) and the ionic strength (I), which again depend on the concentration of all ions in the solution, including H^+ , and how those ions are affected by ionic strength (Eq. (1)).

$$[\text{NH}_3] = f(T, \text{TAN}, K_a^{\text{NH}_4^+}, f_{H^+}, I, \{H^+\}) \quad (1)$$

In a near ideal aqueous solution, the concentration of NH_3 can be approximately calculated from [TAN] and pH assuming that $\text{pH} \approx -\log_{10}[\text{H}^+]$ and $f_{H^+} \approx 1$ (Eq. (2)).

$$\text{NH}_3 = \frac{\text{TAN}}{1 + \frac{[\text{H}^+]}{K_a^{\text{NH}_4^+}}} \quad (2)$$

$K_a^{\text{NH}_4^+}$ at temperature T can be calculated using the van't Hoff equation (Eq. (3)) and the dissociation constant at the reference temperature (T^r) by considering the difference in heat of formation (ΔH^0) between NH_4^+ and NH_3 and R , the universal gas constant.

$$K_{a,T}^{\text{NH}_4^+} = K_{a,T^r}^{\text{NH}_4^+} \cdot \exp\left(\frac{\Delta H^0}{R} \cdot \left(\frac{1}{T^r} - \frac{1}{T}\right)\right) \quad (3)$$

In non-ideal solutions such as pig manure, the hydrogen ion concentration $[\text{H}^+]$ has to be determined from the pH value as measured by a pH-meter corrected for the specific activity coefficients of H^+ (f_{H^+}). Thus, the specific activity coefficient of H^+ has to be known to determine $[\text{H}^+]$ as pH-meters measures hydrogen ion activity $\{H^+\}$ and not $[\text{H}^+]$ (Eq. (4)).

$$\text{pH} = -\log_{10}\{H^+\} \quad (4)$$

Thus, $[\text{H}^+]$ can be determined from the measured pH as shown in (5).

$$[\text{H}^+] = \frac{1}{f_{H^+}} \cdot \{H^+\} = \frac{1}{f_{H^+}} \cdot 10^{-\text{pH}} \quad (5)$$

Several correlations for calculating f_{H^+} exist. Which to choose to get the most precise prediction of f_{H^+} depend on the ionic strength I as defined in (6) where z_i^2 is the squared charge of ion 'i' and $[i]$ the concentration of ion i:

$$I = 1/2 \cdot \sum_i [i] \cdot z_i^2 \quad (6)$$

For $I < 0.5$ in simple non-buffered 1:1 electrolyte solutions [14] showed that the specific ion activity coefficients could be predicted using Eq. (7) with a b -value of 0.3.

$$\log_{10} f_i = -0.51 \cdot z_i^2 \cdot \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - b \cdot I \right) \quad (7)$$

As pig manure contains several buffers and multiple ions it is markedly different from a non-buffered 1:1 electrolyte solution, the Davies equation cannot be expected to predict activity coefficient well in manure.

However, it has been shown [15,16] that for pig manure a b -value of 0.078 provides accurate activity coefficient predictions for $I < 0.5$.

As most dissociation constants change with ionic strength, the calculation of ionic concentrations must include the effect of ionic strength.

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