Role of gas accumulation in dry anaerobic digestion of wheat straws

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Abstract
In dry anaerobic digestion, biogas production is inhibited at high total solids contents. Such inhibition can likely be due to a slow diffusion of dissolved molecules into the digestate with subsequent local accumulation of inhibitory products.
In this study, we investigated the impact of H_2 and CO_2 partial pressure on dry AD. Specific batch tests operated were carried out with thin layer to limit gas diffusion. Results showed that initial H_2 partial pressure higher than 800 mbars had a strong inhibitory effect on methane production. The total substrate degradation yields were also impacted, indicating a direct inhibitory effect on hydrolysis. Interestingly, when H_2 and CO_2 were both added, they were consumed by homoacetogenesis/methanogenesis until CO_2 was completely exhausted. CO_2 was found to be the limiting element in case of H_2 inhibition. The reversibility of H_2 inhibition was also investigated by adding CO_2 at different reaction times. Results showed that hydrolysis and methanogenesis inhibitions were fully reversible after CO_2 addition even after 18 days of operation.
Our results give new insights on probable effect of local gas accumulation in dry AD processes.

Keywords
Biogas; Lignocellulosic residues; High solids; Dry anaerobic digestion; Gas transfer

INTRODUCTION

Over the past ten years, Dry Anaerobic Digestion (D-AD) has gained a wide interest in Europe especially when using agricultural waste or the organic fraction of municipal waste. In AD process, the organic matter contained in the waste is converted by anaerobic bacteria into a biogas composed of CH_4 (50-70%) and CO_2 (30-50%). The remaining organic matter is called "digestate" and can be further reused on land as fertilizer after considering sanitary and environmental impacts.
The key parameter that drives microbial processes in D-AD (>15% of total solids TS) is the low water content since microbial end-products could locally accumulate and inhibit methanogenesis (Abbassi-Guendouz et al., 2012).
Water availability depends on two forms: (1) the low available "bound water" where the water is chemically and physically bound to the substrate and (2) the high available "free water" where water can diffuse within the matrix to the microorganisms as well as organic substrates (Pommier and Chenu, 2007). When the total solids (TS) content increases, the quantity of free water decreases with a strong modification of the rheological behaviour of the substrate (García-Bernet et al., 2011). Thus, the transport of soluble compounds within the substrate can become a limiting factor (Bollon et al., 2013). Increasing the TS content usually leads to a reduction of hydrolysis and substrate degradation with a subsequent decrease in biogas production (Abbassi-Guendouz et al., 2012; García-Bernet et al., 2011; Motte et al., 2013). As an illustration, by increasing the TS content from 20 to 30%, Fernández et al. (2008) observed a decrease of organic waste degradation by 17%. At a TS higher than 30%, methane production was strongly inhibited by VFAs accumulation and decrease of pH (Abbassi-Guendouz et al., 2012).
Overall, the limitation of D-AD at high TS might be explained by the slow diffusion of dissolved molecules inside the organic matrix, generating a local accumulation of inhibitory products for methanogens at microbial scale (Martin, 2001; Staley et al., 2011). The inhibitory fermentative by-products could be not only Volatile Fatty Acids (VFAs) (Staley et al., 2011) but also dissolved

gases such as hydrogen (Abbassi-Guendouz et al., 2012). In a recent study, Abbassi-Guendouz et al. (2012) suggested that methanogenesis inhibition at solids content higher than 30% was likely caused by mass transfer limitation and more particularly by a local accumulation of fermentative gases, such as H_2 and CO_2, leading to further VFAs accumulation.

The aim of this study was to investigate the inhibitory effect of dissolved gases on D-AD and especially H_2 and CO_2, since they are both produced by acidogenesis. Batch experiments were designed and carried out to evaluate specifically the effect of H_2 and/or CO_2 partial pressure on methanogenesis in D-AD system.

MATERIAL AND METHODS

Batch experiments were carried out in four replicates during 13 days, with wheat straw as substrate at 25% TS, pH fixed at 8, and substrate/inoculum ratio of 3 (Volatile Solids basis).After inoculation and moisture content adjustment, a thin layer (< 1 cm) of 1 mm meshed wheat straw was first placed at the bottom of the flasks to avoid the effect of gas diffusion within the matrix. Different initial partial pressure of gas (H_2, CO_2 and H_2/CO_2 mixture) were applied: from 0 to 1 530 mbars of H_2, from 0 to 1 982 mbars of CO_2, and H_2/CO_2 mixture with H_2 and CO_2 ranging from 0 to 1 042 mbars and 0 to 433 mbars, respectively.
In a second part, another set of experiments was carried out by adding initially 1 000 mbars of H_2 and further addition of 400 mbars of CO_2 after different times of operation (11 and 18 days).
The medium was buffered and no pH variation was observed. The biogas was measured periodically throughout the experiments. The quantities of VFAs were measured at the start, before adding CO_2 and at the end of each experiment.

MAIN RESULTS

Specific H_2 inhibition of methanogenesis and hydrolysis in D-AD

From 0 to 600 mbars of initial H_2, a slight increase of CH_4 production was observed from 25.2 ± 3.5 mL CH_4/g_{VS} in the controls to 39.6 ± 4.9 mL CH_4/g_{VS}. Such increase was due to the consumption of H_2 added initially. At higher initial p_{H_2}, the cumulative production of CH_4 decreased from 39.6 ± 4.9 mL mL CH_4/g_{VS} for an initial p_{H_2} of 600 mbars down to 8.45 ± 1.46 mL CH_4/g_{VS} for an initial p_{H_2} of 1 555 mbars., with a transition phase between 650 and 800 mbars. Therefore, an initial p_{H_2} higher than 800 mbars induced a strong and stable inhibition of methanogenesis at TS content of 25%.
No accumulation or significant change in VFAs was observed whatever the initial p_{H_2}, and inhibition of the methanogenesis step was also not related to a pH decrease. In addition, the acetogenesis was not inhibited and no other metabolic pathways were found for a high p_{H_2} like for example a production of butyrate or caproate (Arslan et al., 2012). Therefore, VFA accumulation or changes in pattern cannot explain the observed methanogenesis inhibition, as previously shown in wet AD (Ahring and Westermann, 1988; Amani et al., 2010; Siegert and Banks, 2005).
When considering the total amount of metabolic products (VFAs, H_2), the total substrate degradation rate (Figure 1) decreased according to the initial p_{H_2}. Since no sugars were accumulated in the bulk phase, these results suggest a strong inhibition of hydrolysis at initial partial pressure of H_2 higher than 800 mbars. It is well known that hydrolysis is the limiting step in D-AD (Pavlostathis and Giraldo-Gomez, 1991) and the composition of the substrate (morphological and chemical) can have a strong effect on this step, especially the quantity of lignin for lignocellulosic wastes(Monlau et al., 2012). The present study clearly shows for the first time a strong inhibition of hydrolysis by H_2 partial pressure in D-AD.

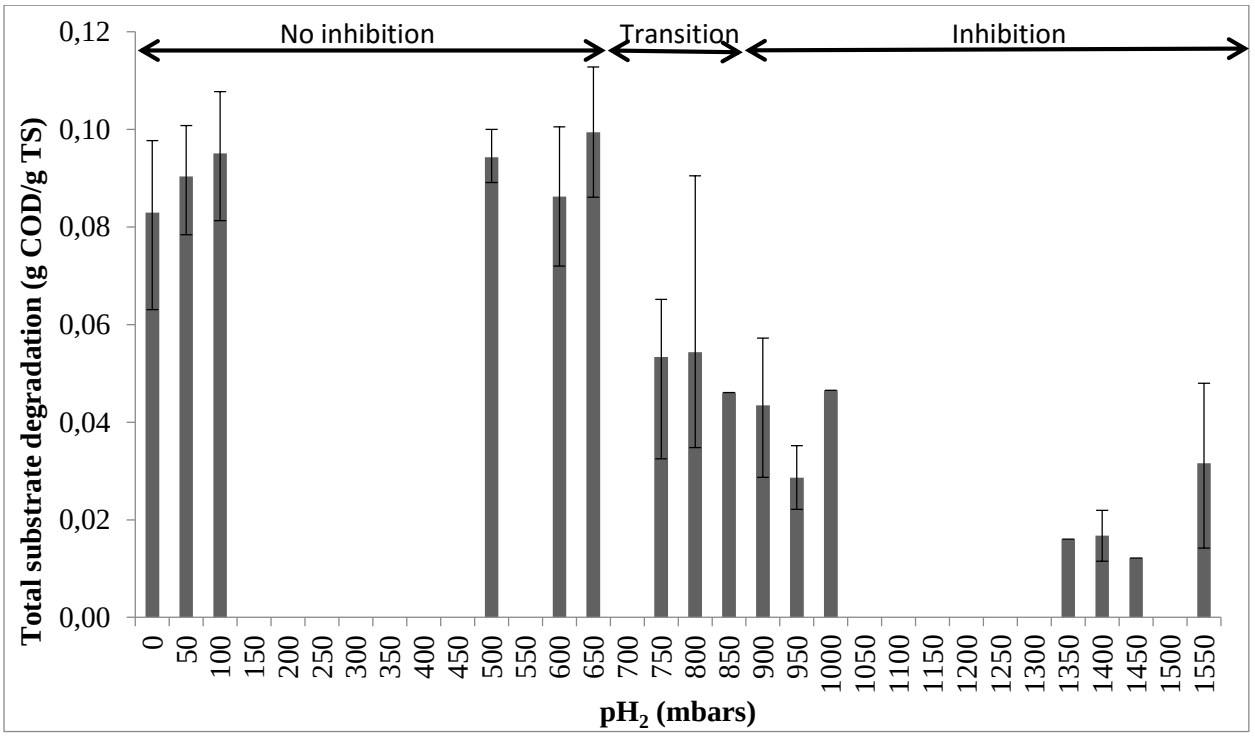

Figure 1: Substrate degradation (g COD at the end/g TS –g COD at the beginning/g TS) according to the initial partial pressure of H_2 in mbars at 25% of TS, 35°C and pH 8. TS: Total Solids; COD: Chemical oxygen demand.

Interestingly, at low initial p_{H_2}, H_2 was totally converted to acetate and methane. At an initial p_{H_2} higher than 750 mbars, H_2 was not fully consumed and H_2 remained in headspace at the end of the experiments. From 750 to 1 000 mbars, a part of initial H_2 was used to produce acetate by homoacetogenesis (Montero et al., 2009) but H_2 was not totally consumed since some H_2 remained at the end of the experiment. CO_2 accumulation was also monitored and at a p_{H_2} ranging from 0 to 750 mbars, CO_2 was produced due to the microbial activity and a decrease of the released CO_2 was observed from 38.98 ± 10.45 to 15.33 ± 2.3 ml CO_2 /g_{VS} in the controls and at 750 mbars of p_{H_2} respectively. Over 750 mbars, no CO_2 was accumulated in the headspace. Since the increase of the remaining amount of H_2 in headspace was correlated to a decrease of remaining CO_2, it was concluded that CO_2 production was the limiting factor for further H_2 consumption (Florin and Harris, 2008). This hypothesis was tested by adding both CO_2 (400 mbars) and H_2 (1 000 mbars) at the start of the experiment. After correcting methane production by the methane produced using the added gases, methane production was similar in the mixture of H_2/CO_2 and in the control. Therefore, in that case, no methanogenesis inhibition occurred. These results confirm that CO_2 production can be considered as the limiting factor when p_{H_2} is high.

Reversibility of the H_2 inhibition in D-AD

Since adding CO_2 can prevent the H_2 inhibition of hydrolysis and methanogenesis, we investigated the reversibility of the H_2 inhibition by introducing CO_2. An inhibitory p_{H_2} of 1 000 mbars was added at the start of the experiment and CO_2 (400 mbars) was further added at different times (11 and 18 days) to test the reversibility of the inhibition.

For both experiments, H_2 inhibition stopped after CO_2 addition. The profiles of cumulated production of CH_4 after adding the CO_2 shows: (1) a rapid increase of CH_4 production mainly due to H_2 and CO_2 consumption, (2) a short lag phase with a slower production of CH_4 and (3) a constant and stable CH_4 production and substrate degradation as observed in the control. These last

experiments clearly showed the reversibility of hydrolysis inhibition by H_2.

CONCLUSION

This study provides new insight about the effect of fermentative gases and more particularly H_2, on D-AD when using wheat straw as substrate. By adding CO_2, hydrolysis inhibition by H_2 was not only suppressed but was also fully reversible. This indicates that CO_2 could be a limiting factor in D-AD when inhibition by H_2 occurs. Our results were however obtained with a thin layer substrate to avoid the effect of the gas diffusion. In real D-AD digesters, combined effects of inhibition as well as gas diffusion can occur. Nevertheless, hydrolysis inhibitory effect of H_2 can take place at a local scale, and may be one of the main reasons of the decrease in overall digester performances in D-AD.

ACKNOWLEDGEMENTS

This work was supported by the French Environment and Energy Management Agency (ADEME) and the French Institute for Agricultural and Food Research (INRA).

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