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Biogas Production on Demand Regulated by Butyric Acid Addition

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Abstract. Investigating effects of volatile fatty acids on the biogas process it was observed that butyric acid can be used for transient stimulation of the methane production in biogas plants operating with low energy substrates like cattle manure. Upon addition of butyrate the methane output of the reactors doubled within 24 h and reached almost 3-times higher methane yields within 3-4 days. Butyrate was quantitatively eliminated and the reactors returned to the original productivity state within 3 days when application of butyrate was stopped. The opportunity to use butyrate feeding for increased biogas production on demand is discussed.

1. Introduction

Limited availability of fossil fuels and global warming, which is associated with their use, represent major challenges for the future of modern societies. A sustainable energy supply requires the consistent use of wind, water and solar energy, but also the use of biomass for energy production. Only the latter is able to compensate for power shortfalls that may occur in adverse weather conditions.

Anoxic degradation of biomass yields carbon dioxide and methane as final products. Methane can be used as an energy source and could be provided by consistent use of waste streams from households, agriculture and food production industry. The formation of biogas requires a complex syntrophic interaction of biomass-degrading bacteria and methanogenic archaea [1-3]. The former group of organisms degrades biopolymers and thrives on fermentation of the monomers to yield complex mixtures of organic acids, alcohols, carbon dioxide and small amounts of hydrogen. The organic intermediates are further oxidized when methanogenic archaea are present and use hydrogen to form methane. This permits anoxic oxidation of organic intermediates to increase the yields of methanogenic substrates, e.g. acetate, hydrogen and carbon dioxide. In stable biogas processes the hydrolysis of biopolymers regulates the whole process, so that no more intermediates are formed, than the methanogens are capable to consume.

The production of methane is positively influenced by increasing biomass feeding only within narrow limits: the increased availability of fermentable substrates quickly leads to acidification and thus eliminates the methanogens from the system. Nevertheless it is well known that volatile fatty acids formed at the end of the fermentative process are readily converted into methane [4, 5]. These findings encouraged us to study the effect of large doses of butyrate on biogas quantity and quality. The data presented herein suggest that butyrate effectively increases the formation of biogas reversibly in short time and permits compensation of power shortfalls caused by adverse weather conditions.

2. Methods and Experimental Setup

Experiments were performed in continuously fed lab scale fermenters of 1 L volume with a content volume of approx. 0.8 L which was continuously stirred at 37 °C. The fermenters were fed multiple times per day to yield a total of 10 g organic matter/(L*d) with cattle manure (3.75 % organic dry matter). Neutralized sodium butyrate solution (pH 7) was added in 48 h intervals (80 mmol butyrate per injection). The fatty acid concentrations in samples were determined by HPLC as recently described [5]. Gas quantity and quality (CH_4- and CO_2-content) were monitored online with near infrared gas sensors (BlueSense).

3. Results

The laboratory fermenters constantly fed with cattle manure produced about 44 mL of gas per hour yielding approximately 2.1 L of biogas in 48 h. The methane concentration during these control periods was 67.5 % (Fig. 1). These values correspond to 63 mmol of methane formed per day.
Following the addition of 80 mmol butyrate, the rate of gas formation gradually rose from 44 mL/h to 86 mL/h. The biogas yield increased to 3.4 L over a time period of 48 h (162 % of control). Likewise, the gas quality improved yielding a methane concentration of up to 72 %. Repetition of butyrate additions in time intervals of 48 h further increased the maximum gas formation rate to about 100 mL/h for the second addition up to about 120 mL in continuation. The maximum methane concentration slightly increased to 74.7%. The average biogas yield per 2 days rose up to 4.9 L in 2 days and the methane yield reached up to 161 mmol in 48 h. The reactors readily returned to the original productivity state and latest three days after the last addition of butyrate gas formation rates, quality and methane yield returned to the original values.

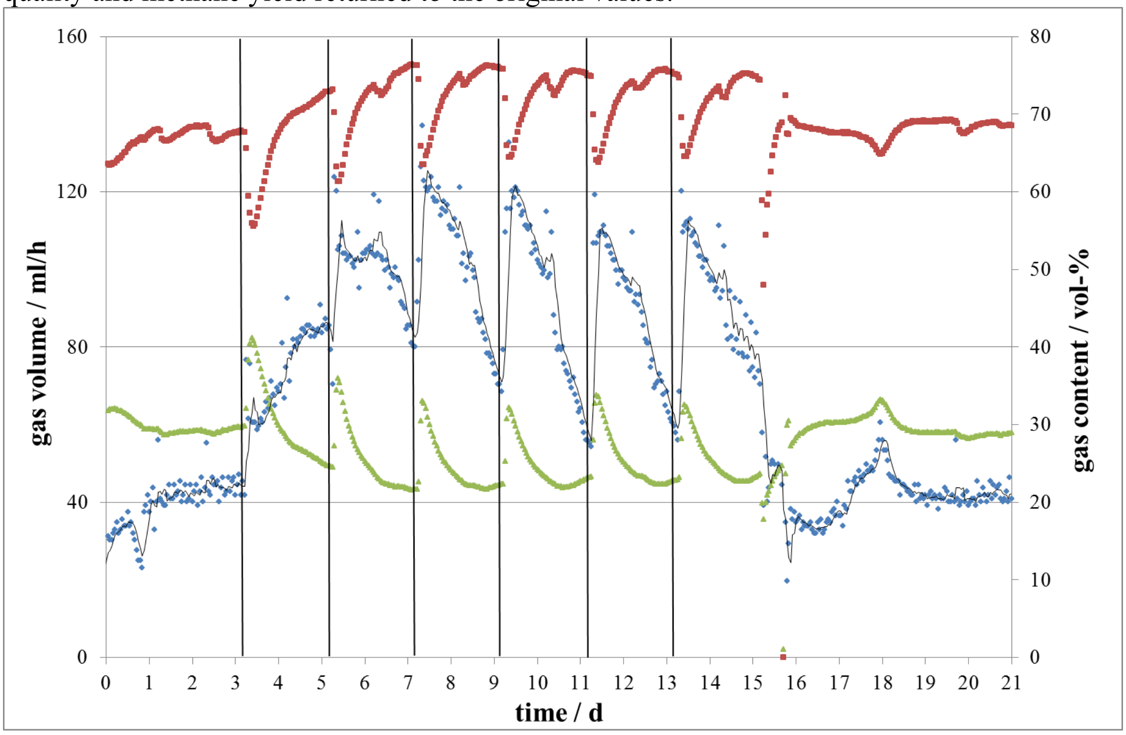

Figure 1. Continuous records of biogas formation rate and gas quality. The gas volume formed per h (blue diamonds) and the concentrations of methane (red squares, upper curve) and carbon dioxide (green triangles, lower curve) are shown. The points of butyrate addition (vertical lines) are indicated.

The stepwise increase in gas formation rates and methane yield in the beginning suggest a period of adaptation. This adaption was also evident when the fatty acids concentrations in the reactor were monitored (Fig. 2). When solely fed with cattle manure, the only fatty acid detectable in significant equilibrium concentrations (8 mM) was acetate. The concentrations of propionate (1.2 mM), butyrate (not detectable) and *iso*-butyrate (not detectable) were significantly lower. As expected, the addition of butyrate (100 mmol/L digestate, 80 mmol in total) caused an immediate increase of its concentration to about 60 mM. The addition of the next portion of butyrate caused further increase to 74 mM. The degradation of butyrate was evident in the intermediately formed acetate; its concentration increased up to 67 mM within 3 days. Beyond this point, however, the acetate concentration showed regular periodic ups and downs one day each displaced from the butyrate additions. It is clearly evident from the course of butyrate concentrations that the fermenter biocoenosis readily consumed butyrate once "trained". 24 hours after the first addition, 87 % of the originally measured butyrate could be detected. After the third addition, only 15 % of butyrate was left after 24 hours, compared to the initial concentration. Another interesting finding was the observation of increasing concentrations of the other fatty acids, which rose significantly to concentrations substantially above the initial levels.

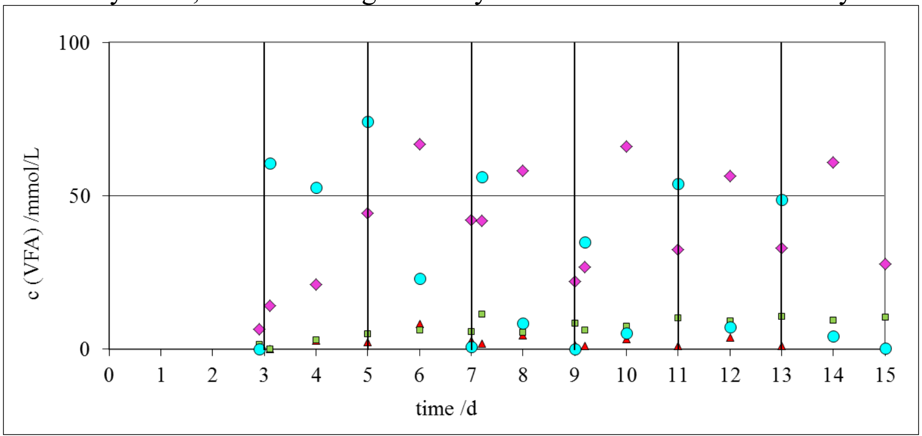

Figure 2. Concentrations of volatile fatty acids in the fermenter. The concentrations of acetate (magenta diamonds), propionate (green squares), butyrate (cyan dots) and iso-butyrate (red triangles) are shown.

4. Discussion

Previous studies suggested that about 1/3 of the methane produced from cattle manure is formed from short-chain fatty acids [5]. In particular acetate (~100 mM) and propionate (~25 mM) are present in significant amounts, whereas the concentrations of butyrate (~10 mM) and iso-butyrate (< 5 mM) are much lower. An increase of even-numbered fatty acids like butyrate or caproate was anticipated to account for significant increases in the carbon flux through the fermenter causing comparably smaller rates of acidification than acetate.

For theoretical yields it was calculated that 80 mmol of butyrate introduced should yield 200 mmol methane and 120 mol carbon dioxide, according to equation (1).

$$2\ \text{Butyrate}^- + 2\ H^+ + 2\ H_2O \rightarrow 5\ CH_4 + 3\ CO_2 \quad \Delta G'^\circ = -\ 88.5\ \text{kJ/mol butyrate (eq. 1)}$$

The observed productivity between 130 mmol to 161 mmol methane formed within 2 days, suggesting a conversion of butyrate to methane in the range of at least 40 %. This might be caused by immediate overflow after addition to the fermenter, as suggested by the measured butyrate concentrations. Evidently, the butyrate had an inhibitory effect on the formation of biogas from other VFAs. Thus, quantification of the methane formed from butyrate remains doubtful. However, for the measured maximum butyrate concentration of 60 mM, a conversion rate of about 68 % is theoretically reasonable. The observed gas yields, however, did not exceed 40% of the anticipated methane. It must be stated that part of the butyrate is consumed for biomass production and up to 25 % losses per day can be anticipated as wash-out of the fermenter caused by the ongoing background-feeding with cattle manure. Another interesting finding was the increasing gas quality, which is not readily explainable without further investigation.

The measured effects on gas production and VFA consumption turned out to be completely reversible: It is obvious that neither the butyrate oxidizing bacteria nor the methanogenic community in the reactor were significantly disturbed by addition of butyrate, although the biogas reactors organic load was increased from 10 g/(L*d) to 17 g/(L*d). This is reflected in the observation that gas volume and composition returned to the pre-experimental values within less than 72 hours after the last addition.

The response time to the following addition of butyrate was very short and within 24 h the amount of formed methane per hour roughly doubled. Although maximum performance with up to 3-fold increased methane yields was reached only after 4 days in the experimental setup, it must be stressed that gradually and controlled adjusted fermenters will likely reach the maximum performance of the microbial community within 3 days. The required period of 3 days to more than double the methane output of a given biogas plant is within the accuracy time of modern weather forecast. The speed of response provides, therefore, sufficient reaction time, to respond to bad conditions for the production of wind and solar energy.

This suggests that butyrate and probably also other even numbered volatile fatty acids are suitable for biogas process regulation and surplus production of larger quantities of biogas on demand: Fed with natural, comparable low yield substrates from waste streams, biogas plants can provide an important building block in a decentralized energy supply. The high energy substrate butyrate is easily formed from synthesis gas or hydrogen/CO_2 by acetogenic microbes. Thus, on windy, sunny days a surplus of produced energy can be stored in this compound. Likewise, butyrate is a common metabolic end product of lignocellolytic clostrial species, too. It is, therefore, easy to produce using biotechnological methods and can be stored save and easily at low costs.

To substantiate these findings in a technical context, the ongoing project “ACidestion” (funded by BMWi, grant no. 03KB084B) examines the effects of various ensiling strategies on the biogas process and the controllability via simulation by a simplified model.

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5. References

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