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R. Brunstermann, R. Widmann

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Development of a Combined Bio-Hydrogen- and Methane-Production Unit Using Dark Fermentation

R. Brunstermann, R. Widmann, University of Duisburg-Essen, Faculty of Engineering Sciences (Building Sciences), Department of Urban Water and Waste Management, Germany

Abstract

Hydrogen is regarded as a source of energy of the future. Currently, hydrogen is produced, predominantly, by electrolysis of water by using electricity or by steam reforming of natural gas. So both methods are based on fossil fuels. If the used electricity is recovered from renewable recourses, hydrogen produced by water electrolysis may be a clean solution. At present, the production of hydrogen by biological processes finds more and more attention world far. The biology provides a wide range of approaches to produce hydrogen, including bio-photolysis as well as photo-fermentation and dark-fermentation. Currently these biological technologies are not suitable for solving every day energy problems [1]. But the dark-fermentation is a promising approach to produce hydrogen in a sustainable way and was already examined in some projects. At mesophilic conditions this process provides a high yield of hydrogen by less energy demand, [2]. Short hydraulic retention times (HRT) and high metabolic rates are advantages of the process. The incomplete transformation of the organic components into various organic acids is a disadvantage. Thus a second process step is required. Therefore the well known biogas-technique is used to degrade the organic acids predominantly acetic and butyric acid from the hydrogen-production unit into CH_4 and CO_2 .

This paper deals with the development of a combined hydrogen and methane production unit using dark fermentation at mesophilic conditions. The continuous operation of the combined hydrogen and methane production out of DOC loaded sewages and carbohydrate rich bio-waste is necessary for the examination of the technical and economical implementation. The hydrogen step shows as first results hydrogen concentration in the biogas between 40 % and 60 %. The operating efficiency of the combined production of hydrogen and methane shall be checked as a complete system.

1 Introduction

The four steps of anaerobic digestion are shown in Figure 1. Only the last step, the methane production, is completely divided by eliminating methanogenic bacteria in the first process-step.

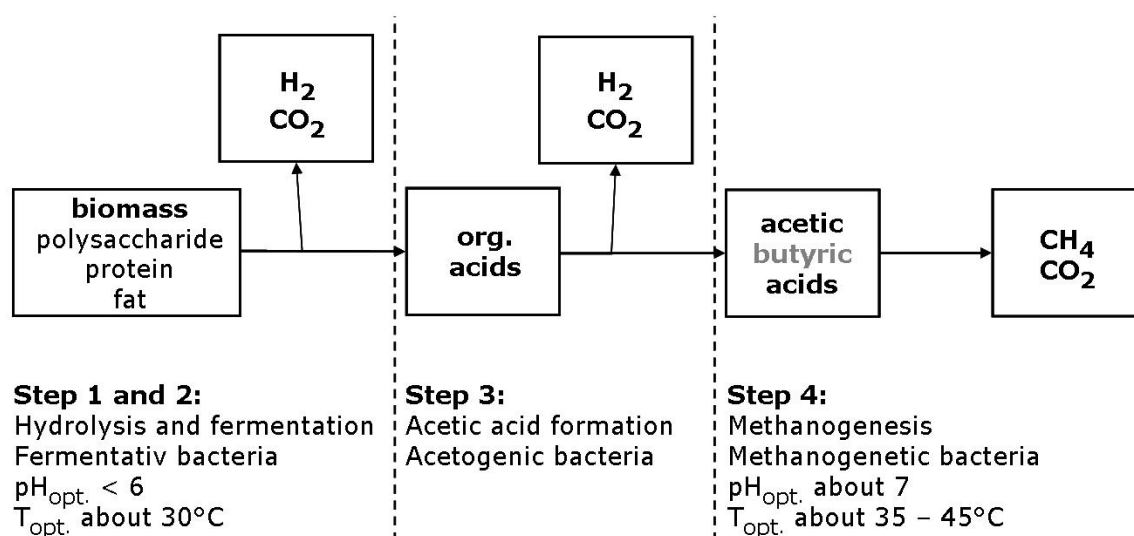


Figure 1: Four steps of anaerobic digestion.

According to [3], [4] hydrogen yields of 4 [mol/mol glucose] (Eq.1) at maximum are possible by dark fermentation with only 2 mol acetates as by-product. If only butyric acid accrue as by-product, the hydrogen yield decreases to 2 [mol/mol glucose] (Eq. 2). Typically, the end product of dark fermentation with mixed culture is a mix of different volatile fatty acids like acetic and butyric acid [2]; [5]. In consequence the stoichiometrical possible hydrogen yield is 2.5 [mol/mol glucose] (Eq.3).

If the liquid effluent of the H_2 -reactor is used as carbon source in a methane reactor, the organic acids become degraded to CO_2 and CH_4 . The theoretical methane yield that can be generated stoichiometrically depends on the liquid products of the hydrogen stage. The stoichiometric of possible bio-chemical reactions for the combined hydrogen and methane production with glucose as carbon source are given in table 1. The chemical equation for the degradation of glucose in a conventional fermentation is also given in this table (Eq 4) [6].

Table 1: Bio-chemical reactions of the bio-hydrogen and methane production.

	substrate	1 st reactor hydrogen	2 nd reactor methane
Eq. 1	$\text{C}_6\text{H}_{12}\text{O}_6 + 2 \text{H}_2\text{O} \rightarrow$	$2 \text{CH}_3\text{COOH} + 2 \text{CO}_2 + 4 \text{H}_2$ [3], [4] $2 \text{CH}_3\text{COOH} \rightarrow$	$2 \text{CH}_4 + 2 \text{CO}_2$
Eq. 2	$2 \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow$	$2 \text{C}_3\text{H}_7\text{COOH} + 4 \text{CO}_2 + 4 \text{H}_2$ [3] $2 \text{C}_3\text{H}_7\text{COOH} + 2 \text{H}_2\text{O} \rightarrow$	$5 \text{CH}_4 + 3 \text{CO}_2$
Eq. 3	$8 \text{C}_6\text{H}_{12}\text{O}_6 + 4 \text{H}_2\text{O} \rightarrow$	$4 \text{CH}_3\text{COOH} + 6 \text{C}_3\text{H}_7\text{COOH} + 16 \text{CO}_2 + 20 \text{H}_2$ [2]; [5] $4 \text{CH}_3\text{COOH} + 6 \text{C}_3\text{H}_7\text{COOH} + 6 \text{H}_2\text{O} \rightarrow$	$19 \text{CH}_4 + 13 \text{CO}_2$
Eq. 4	$\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow$		$3 \text{CH}_4 + 3 \text{CO}_2$ [6]

2 Materials and Methods

Continuous stirred-tank reactors (CSTR) were used. The hydrogen reactor had a working volume of 4 litres and the methane stage 30 litres.

For the hydrogen production several test-runs were made to verify optimal condition. In these experiments two seed materials (compost and heat treated digested sludge) at different conditions were tested. The temperature varied from ambient temperature of around 20°C up to 35°C, and the pH-value from 4.0 up to 5.5.

A nutrient solution according [7] was added to all reactors to provide optimal conditions for the mixed culture during the whole time of the test-runs. The hydraulic retention time (HRT) was decreased from 120 h to 24 h. By this, the organic loading rate (ORL) was increased. A survey of test runs discussed in this paper is given in Table 2.

Table 2: Survey of test-runs.

Reactor		Volume [L]	Temp. [°C]	pH [-]	HRT	Carbon source	Inocula	Duration [d]
R1	H ₂	10	without heating	4.5 - 5.2	15 – 26.5 h	Waste sugar	Heat treated digested sludge	200
R2	H ₂	3	30	4.5 - 4.8	48 – 30 h	Waste sugar	Heat treated digested sludge	50
R3	CH ₄	35	35	7.0	20 – 12.5 d	Output of R2	digested sludge	50

The pH-value of the hydrogen and methane reactors was regulated by using one molar NaOH-solution. During the tests the amount of produced gas was detected continuously with a gas meter and collected in a sample bag. The composition of the gas samples was detected once a day by thermal conductivity (H₂) and an infrared (CO₂ and CH₄).

The pH-value of the hydrogen and methane reactors was controlled by using one molar NaOH-solution. During the tests the amount of produced gas was continuous detected with a gas meter and collected in a sample bag. The composition of the gas samples was detected once a day by heat conductivity.

The experimental set-up of each reactor is shown in Figure 2 schematically.

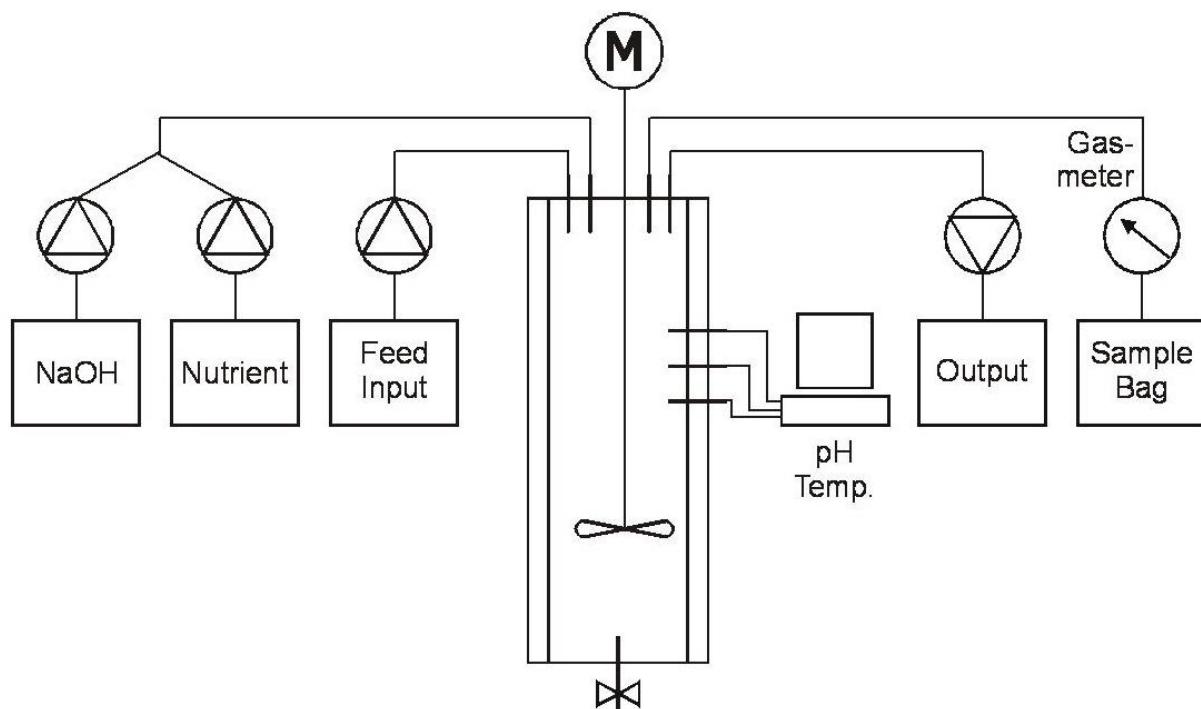


Figure 2: Experimental set-up for continuous hydrogen- and methane-production.

One H₂-reactor (R1) was working without heating at ambient temperature for 200 days. The temperature was only measured. Digested sludge of a wastewater treatment plant, which was boiled at 70°C for one hour, was used as seed material. The sludge was chosen, because of its consistency. The in- and output could be pumped with a peristaltic pump. A solution of a waste sugar with a concentration of 10 g/l and 15 g/l repetitively was used as carbon or rather hydrogen source in all hydrogen reactors.

The reactor R2 with a volume of 3 L was heated at 35 °C. The pH-value varied from 4.5 up to 4.8. Sugar solution was used as substrate. The output of this reactor was used directly as carbon source for the methane stage with a volume of 30 L (R3). So for the combined hydrogen and methane production the reactors R2 and R3 were directly connected with a tube.

Analysis of the sugar solution and the seed materials included the determination of dry matter (DM), volatile solids (VS) and total content of nitrogen and carbon (N, C). Furthermore, the analysis of the liquid end-products as well as the sugar solution included chemical oxygen demand (COD), dissolved organic carbon (DOC) and volatile fatty acids (VFA) measured as acetic acid.

3 Results and Discussion

Interesting findings of the continuous hydrogen production of R1 at ambient temperature are shown in Figure 3.

This figure shows, that gas yields of 2.5 [Nl/l*d] are reachable at hydraulic retention times (HRT) of 20 hours at 25 °C with a hydrogen concentration of approximately 58% (day 39 – 56).

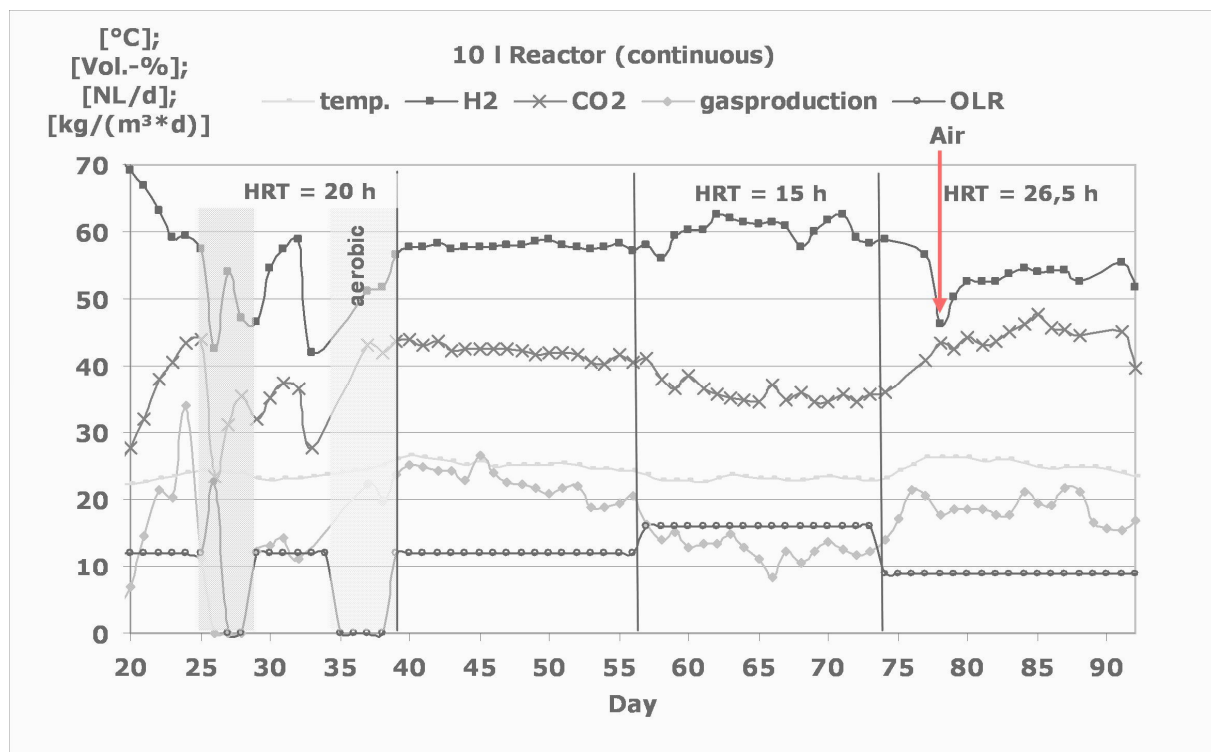


Figure 3: Effect of different HRT on continuous hydrogen production (Input feed: sugar water 10g/l).

Reduction of HRT (day 56 – 74) from 20 hours to 15 hours with according increase of OLR from 12 [g/L*d] to 16 [g/L*d] waste sugar, increased the hydrogen concentration to 63 %, but the gas yield decreased to approximately 1 [NL/l*d]. So the overall hydrogen yields decreased. Therefore the OLR was reduced to 9 [g/L*d] in accordance with a HRT of 26.5 hours. At these conditions the gas yield increased to 2 [NL/l*d] and the hydrogen content in the gas decreases to 55% on average (day 74 – 95).

Furthermore, Figure 3 shows the consequences from an overload of the digester caused by a pump fault between the 25th and the 28th day. The organic loading rate (OLR) suddenly became increased from 12 [g/L *d] waste sugar to 22.5 [g/L *d]. Due to this fault the hydraulic retention time (HRT) was reduced from 20 hours to 10.6 hours. As a result of overloading the gas production and hydrogen concentration went down. By switching off the pumps and therefore the temporary rearrangement of the continuous to the batch process the reactor recovered within a few days and the gas production started again.

The decrease of hydrogen concentration caused by continuous penetration of air into the anaerobic reactor at day 34, for several hours, was rearrange by switching to batch operation for a short period (2 days). The short aeration at day 78 caused by maintenance and repair did not affect the hydrogen production.

The gas production and composition of the test run with the connected reactor R2 and R3 are shown in Figure 4. In this test run the output of the hydrogen step was used as carbon source of the methane step. Therefore both reactors were connected by a peristaltic pump. The temperature of both reactors was maintained at 35°C.

The gray line (on the left) in Figure 4 represents the hydraulic retention time, which was reduced at day 32 from 48 h to 30 h. Causes by this the gas production (dark blue line with squares) decreased from 6 NL/d down to 1 NL/d whereas the hydrogen concentration (blue line with X) increased up to nearly 50 % (v/v). After day 40 the gas production of the hydrogen step stopped.

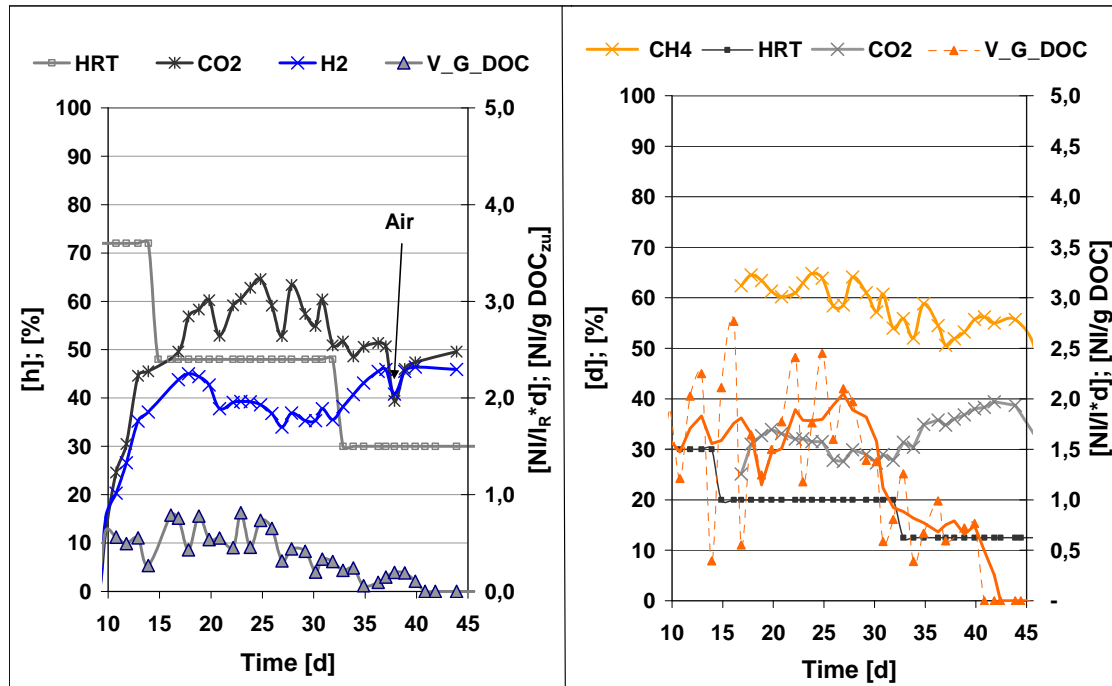


Figure 4: Gas production and –composition of the H₂-reactor R2 (left) and CH₄-reactor R3 (right).

The black lines with filled dots represents the hydraulic retention time (HRT), which was reduced at day 32 from 20 d to 12.5 h causes by reducing the HRT of the hydrogen step. This change influenced the methane concentration (orange line with X) slightly, but the gas production (orange line with filled triangles) was reduced by about a half. After day 40 the gas production of the methane step stopped like the gas production of the hydrogen step. This was caused by a leakiness of the tube which was connecting the both reactors. So both reactors were aerated.

4 Conclusions

The results show, that digested sludge pre-treated at 70°C for one hour include a stable mixture of bacteria, mainly of the family Clostridia, which are suitable for bio-hydrogen production by dark fermentation.

The results of R 1 exemplify, that a stabile hydrogen concentration in the range between 55 % and 60 % in the evolved gas at ambient temperature (23°C – 28°C) during continuous dark fermentation is possible. If the organic loading rate increases the hydrogen concentration in the gas increases too, but the gas production decreases. Furthermore a process break-down, caused by overloading the hydrogen reactor or flushing with air, could be repaired by turning the reactor temporally into batch process.

Results of experiments of a two stage test set up with bio-hydrogen production as first stage, followed by a “conventional” anaerobic digestion step with a tenfold volume show, that it is possible to combine these processes. By doing so, it is important to strictly divide both steps from each other because the methanisation stage can affect the hydrogen production negatively.

The combination of the two treatment steps bio-hydrogen production and “conventional” anaerobic digestion is a feasible option for example for the treatment of mono-charges, which is otherwise ensured by cost intensive enlargement of digester volume or massive reduction of organic load rate (OLR). However, further research is necessary to evaluate if the energy recovery with the combination hydrogen and methane with fuel cell is comparable to the conventional anaerobic digestion by using combined heat and power plants (CHP) to produce electricity.

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