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Hydrogen as climate-friendly energy Source produced by fermentative microorganisms

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Abstract

The increasing global demand for energy from fossil fuels is opposed by the shortage of resources. In addition, the environment is polluted with carbon dioxide by the use of fossil fuels. A climate-friendly energy carrier is hydrogen based on renewable sources. The fermentative production of hydrogen has been investigated at DBI - Gastechnologisches Institut gGmbH Freiberg (DBI) for several years [1]. This technology is based on the anaerobic fermentation of biomass, which can be divided into the following four biochemical phases: hydrolysis, acidogenesis (formation of carbondioxid and hydrogen), acetogenesis and methanogenesis (formation of carbondioxid and methane) [2, 3]. In these phases complex organic matter is decomposed [4, 5]. Based on this knowledge a cyclic two stage fermentation process was established for the continuous and separate production of hydrogen and methane by using two bioreactors (Fig. 2). A challenge for the process management is the suppression of hydrogenotrophic archaea in the first (hydrolytic) phase. In form of a down scaled setup and under additional implementation of a heat treatment stage the established system was optimized. Due to the adjustments, the characteristic parameters could be significantly enhanced: the gaseous hydrogen content from 30 to 49 vol%, the molar hydrogen yield from 0.45 to 0.75 mole hydrogen per mole of glucose and the hydrogen yield from 62 to 213 L/kg sucrose.

1. Introduction

To overcome future problems associated with rapid industrialization and urbanization, environmental damage and the increasing demand and need of steady availability of energy, alternative sources will get more and more attention. Especially hydrogen is as a renewable, energy dense and carbon-neutral fuel an interesting alternative to fossil energy sources. Hydrogen can be generated in many ways (e.g. steam reforming and thermal cracking of natural gas, electrolysis, photolysis, thermolysis, a.o.). The main disadvantage of most industrial applicated techniques rests in their energy intensity and therefore high costs. An attractive way to avoid those disadvantages is the hydrogen formation via microbiological metabolisms like biophotoslysis of water (green algae, cyanobacteria), photosynthesis or dark fermentation (anaerobic bacteria and archaea). All of these can be conducted under low pressure and mild temperatures. Caused by the generally higher rate of hydrogen production and the possibility to use low cost substrates (such as waste products) and sources of microorganisms the dark fermentation under anaerobic conditions represents one of the most interesting alternatives. During the anaerobic digestion of macromolecular organic compounds short-chain volatile fatty acids and alcohols are produced alongside gaseous hydrogen and carbon dioxide (acidogenesis, figure 1). Acids and alcohols can be further decomposed to acetic acid, which is besides hydrogen the main substrate for methane producing microorganisms (methanogenesis, figure 1).

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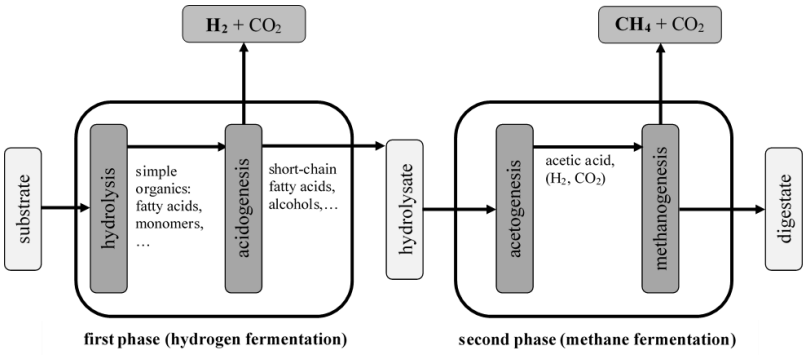

Figure 1. Simplified scheme of bio-hydrogen and bio-methane production

Carbohydrates embody the preferred carbon source for fermentation processes. The principle types of fermentation are summarized in table 1. Anaerobic and facultative anaerobic chemoheterotrophic bacteria generate predominantly acetic and butyric acids. Depending on the formed acid the theoretical molar yield of hydrogen production reaches 4 (acetic acid) or 2 mole H_2 per mole glucose. The formation of 2 mole propionic acid consumes 2 moles of hydrogen per mole of glucose. Therefore the propionic acid formation is a hydrogen consuming reaction and should be avoided. Lactic acid and ethanol formations do not yield hydrogen gas at all.

Table 1. Types of fermentation (carbohydrates)

Type of fermentation	formula	mole H_2/ mole CO_2	mole CO_2/mole glucose	mole H_2/mole glucose
acetic acid	glucose + 2 H_2O → 2 CH_3COOH + 2 CO_2 + 4 H_2	2.0	2.0	4.0
butyric acid	glucose → 1 $CH_3(CH_2)_2COOH$ + 2 CO_2 + 2 H_2	1.0	2.0	2.0
propionic acid	glucose → 2 CH_3CH_2COOH + 2 H_2O – 2 H_2	-	-	- 2.0
lactic acid	glucose → 2 $CH_3HCOHCOOH$	-	-	-
ethanol	glucose → 2 CH_3CH_2OH + 2 CO_2	-	2.0	-

In case of hydrogenotrophic archaea, one of the general methane producing bacterial classes, the process of methanogenesis is directly coupled to the consumption of hydrogen, which makes it necessary to separate the two phases locally if targeting a high hydrogen production rate and yield. Therefore a cyclic two-stage setup is used in the here proposed technique to obtain hydrogen and methane in high gaseous concentrations via dark fermentation. During previous experiments at the DBI in the research project "MehrH2" [6] a cyclic two-stage-CSRT-system for bio-hydrogen and -methane production was established (working volume: 2.000 L, figure 2 left) [7]. The pilot-biogas-plant ran stable for six months while hydrogen (up to 30 vol% in first stage, Figure 2 right) and methane (50 to 60 vol% in second stage, data not shown) were continuously produced [1]. The aim of this study was to further optimize and evaluate process relevant parameters regarding high gas quality, – quantity and process efficiency.

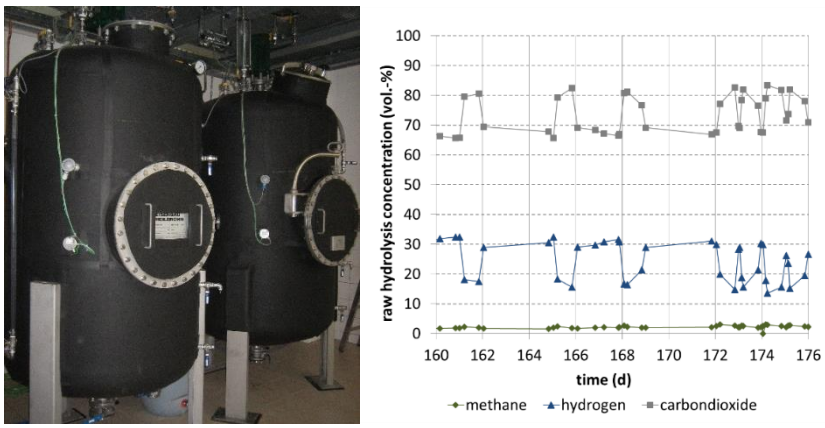

Figure 2. Experimental setup of already established cyclic two-stage biogas plant
for synthesis of bio-hydrogen and bio-methane (left) with steady state raw gas concentrations (right)

2. Material and Methods

2.1. Seed Sludge

Each reactor was inoculated with a methane-producing anaerobic sewage sludge micro-flora obtained from a mesophilic and long term stable reactor fed on sucrose.

2.2 Start up and feeding

The schematic description of the anaerobic digestion system used for the experiments is shown in figure 3. Two fermenter (CSTR, working volumes 2 L and 10 L) were inoculated with the same seed sludge (2.1) and immediately installed into the experimental setup. The system was fed on hydrolyzate (second stage) and sucrose/digestate (first stage), respectively. No active pH regulation was implemented. To obtain semi-continuously process conditions the volume transfer (sucrose, hydrolyzate and digestate) was conducted manually twice a day. Stable conditions were reached within six days. To investigate the influence of a thermal digestate treatment a third CSTR (operating temperature: 100 °C, working volume 400 mL) was implemented ("Heat treatment" figure 3).

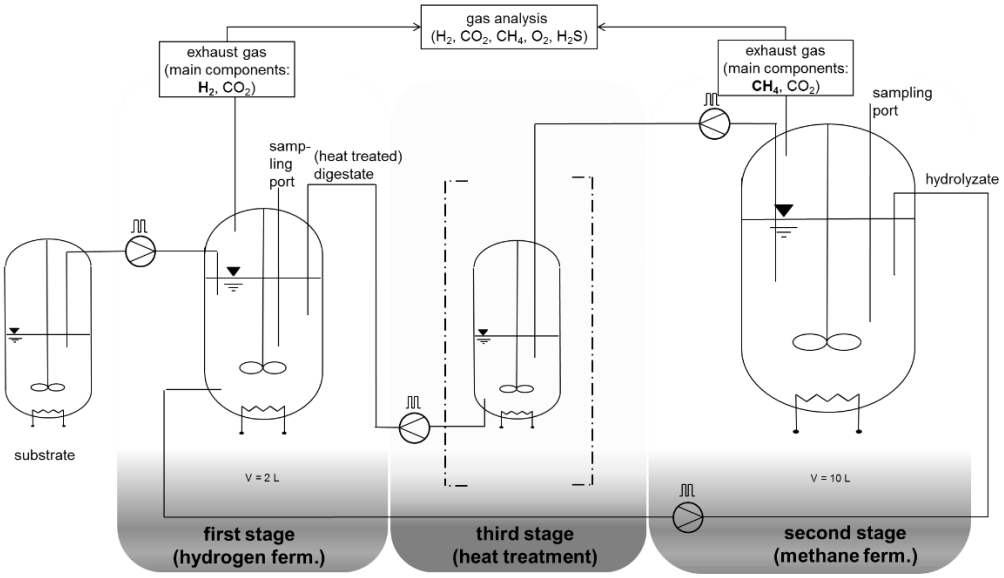

Figure 3. Experimental setup

2.3 Operation of the two-stage process

The investigated operational conditions of the system are summarized in table 2. The first stage (hydrogen fermentation) was conducted at a temperature range of 70 to 85 °C, a hydraulic retention time (HRT) of 2.5 d and a loading rate of 2.5 kg sucrose/(m^3d). The fixed values of HRT and loading rate were previously evaluated to secure the pH range of 5.0 to 5.5 (optimal hydrogen production [7]). In order to meet ideal cultivation requirements of aceto- and methanogenic microorganisms the second stage was conducted at 40 °C. The conditional implementation of the third ("heat treatment") stage was defined by an up heating of the digestate to 100° C and subsequent HRTs between 0 and 45 minutes. Each change of parameters was conducted without any previous starvation of the system.
The process was evaluated by analysis of quality and quantity of the gaseous phase. The produced gas flow of second and first stage was captured continuously by volumetric gas counters (MilliGascounter, Ritter). The gas composition was scanned offline at least twice a week, applied to standard conditions and calculated as weighted average in relation to the produced gaseous volume. Furthermore the pH value and the ratio of volatile organic acids (VOA) and total inorganic carbon (TIC) of the liquid phase was measured. VOA, TIC and pH were determined three times a week every other day and used as indicator of system stability.

Table 2. Experimental conditions of first, second stage and third stage

Exp. #	temperature first stage	temperature second stage	heat treatment duration [min]	hydraulic retention time first stage [d]	loading rate first stage [g Sac/Ld]
1	70 °C	40 °C	-	2.5	2.5
2	80 °C	40 °C	-		
3	85 °C	40 °C	-		
4	70 °C	40 °C	45		
6	80 °C	40 °C	45		
7	80 °C	40 °C	0		
8	80 °C	40 °C	15		
9	80 °C	40 °C	45		

3. Results and Discussion

Both fermentative stages were inoculated with unconditioned seed sludge (see 2.1). The required retention times and temperatures (c.f. table 2) were instantly applied. The efficiency of the first stage could be determined by the gas quality and quantity as well as the acid enrichment of the liquid phase caused by sucrose degradation. Therefore the unadjusted pH value was used to indicate the successful accumulation of acids. Due to the cyclic process the stability of the whole system was generally depending on acid formation of the first and degradation of the second stage. The optimal operational conditions of the stable process were estimated based on the maximum hydrogen fraction and formation rate within the first stage. The environmental demands for methanogenesis of the second stage had to be considered.

Figure 4 summarizes the experimental data of steady state gas fraction distribution depending on the process temperature of the first fermentative stage and the application of a heat treatment of the digestate. Over all tested temperatures and system setups no hydrogen synthesis could be observed within the second stage.

3.1 Variation of fermenter temperature – first stage

To evaluate the optimal process temperature of the first stage, experiments were conducted with no further digestate treatment. The temperature was altered between 70 °C and 85 °C (figure 3: 70 °C, 80 °C, 85 °C). Whilst operating under 70 °C no hydrogen but methane formation (27 vol%) could be detected in the first stage. The application of a fermenter temperature of 80 °C led to 8.6 vol% gaseous hydrogen content and a significant decrease in methane formation (70 °C: 27 vol% CH_4, 80 °C: 18 vol% CH_4). Raising the system temperature up to 85 °C led to a complete cessation of the first stage gas production. The pH value of both fermenters leveled up and the gaseous methane content of the second stage dropped from 72 to 56 %.

The observed experimental results may be attributed to metabolic processes of hydrogenotrophic archaea, which generate methane under the consumption of hydrogen. At 70 °C a potential lack of inhibition of archaea leads to a complete conversion of bacterially produced hydrogen to methane. With an increased fermenter temperature of 80 °C the environmental pressure on archaeal microorganisms increased, which therefore lessened the hydrogen-conversion. At 85 °C the total breakdown of the first stage may be contributed to a complete inhibition of microbiological activity due to thermal overload and thereby transfer of undigested sucrose into the second stage. The undigested sucrose would lead to the decreased methane concentration. The results indicate a close connection between the production of hydrogen and the process temperature of the first stage. Without any additional process adjustments, hydrogen production was found to be linked to a very small temperature range of around 80 °C and reacted vastly sensitive regarding temperature changes between 80 and 85 °C. Furthermore the generation of gaseous methane in the first stage indicates an insufficient suppression of hydrogenotrophic archaea.

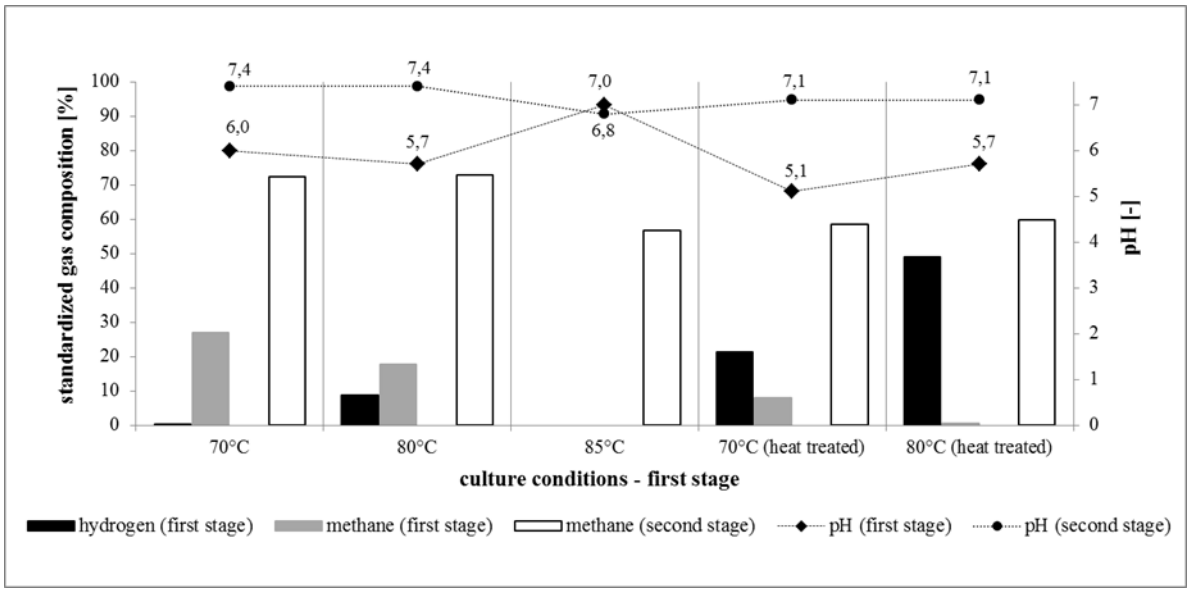

Figure 4. Comparison between gas composition and pH value of first and second stage in relation to varying culture temperatures of the first stage and with/without heat treatment of the digestate; first stage: hydrogen fermentation; second stage: methane fermentation

3.2 Integration of third stage – "heat treatment"

To stabilize and enhance the system efficiency, a third fermenter was integrated into the experimental setup (T=100 °C, HRT = 45 min; figure 2 (third stage)). Regarding the complete inhibition at 85 °C the investigated temperatures of the first stage were chosen to be 70 °C and 80 °C. The related data are shown in figure 4 (70 °C (heat treated), 80 °C (heat treated)). As anticipated, the thermal pretreatment of the digestate induced in both experiments a substantial increase of the gaseous hydrogen volume. Concentrations of 21 vol% (70 °C) and 49 % (80 °C), respectively, were achieved. However, it was noticed that only if conducted at 80 °C a complete suppression of methane production in the first stage could be ensured. This effect was reflected within the gas formation rates as well. Due to the elevation of the fermenter temperature from 70 to 80 °C the H_2-formation rate increased about 85 % from 133 to 247 L/(m^3d) (data not shown). The constant pH value of 7.1 and methane formation of nearly 60 vol% within the second stage implies the establishment of a stable steady state and no instabilities of the cyclic process due to the thermal pretreatment could be detected.

3.3 Improvement of third stage – HRT

To further optimize the efficiency of the digestate treatment and therefore inhibition of archaeal activity within the first stage the optimal hydraulic retention time (HRT) of the third stage was investigated. Based on the previous results (see 3.1 and 3.2) the cultivation temperature of the first stage was set at 80 °C. The determined data are shown in figure 5. The observed methane content in the first stage was at all times < 1 vol%.

The obtained results indicate no significant correlation between HRT of the third and the volumetric ratio of gaseous hydrogen within the first stage. The average H_2 percentage amounted for 49 % of the total gaseous volume. Assessing the methane content of the second stage, the heat treatment of 45 minutes caused in comparison to 0 and 15 minutes a decrease of 5 % from 65 to 60 % CH_4 (figure 5 top left). The energetic efficiencies in experiments with a HRT of 0 and 15 minutes were found to be 0.61 and 0.47, respectively. The difference may be related to the removal of short and therefore highly volatile organic acids during the prolonged heat treatment process. The potential sink of easily digestible acids would lead to a reduction of degradable organic carbon and therefore less H_2- and CH_4 formation. This hypothesis is supported by the under application of 15 min heat treatment compared to an HRT of 0 min about 160 mL/g sucrose reduced methane yield (349 mL/g suc) of the second stage (figure 5 bottom left). The lowest hydrogen yield of the first stage (136 mL/g suc) was determined in case of 45 minute heat treatment of the digestate. This could be attributed to the beginning of inhibition of hydrolytic bacteria due to the duration of thermal treatment. Further indication for reduced bacterial activity in the first stage lies within the decreasing hydrogen formation rate (figure 5 top right). Combined with a consequential transfer of undigested sucrose into the second stage and the therefore increasing CO_2 formation the reduced methane/CO_2 ratio of 1.48 could be explained (figure 5 bottom right). The pH value of the second stage was under all tested conditions within the optimal range of 7.0 to 7.5, which was taken as indication for a well working second stage.

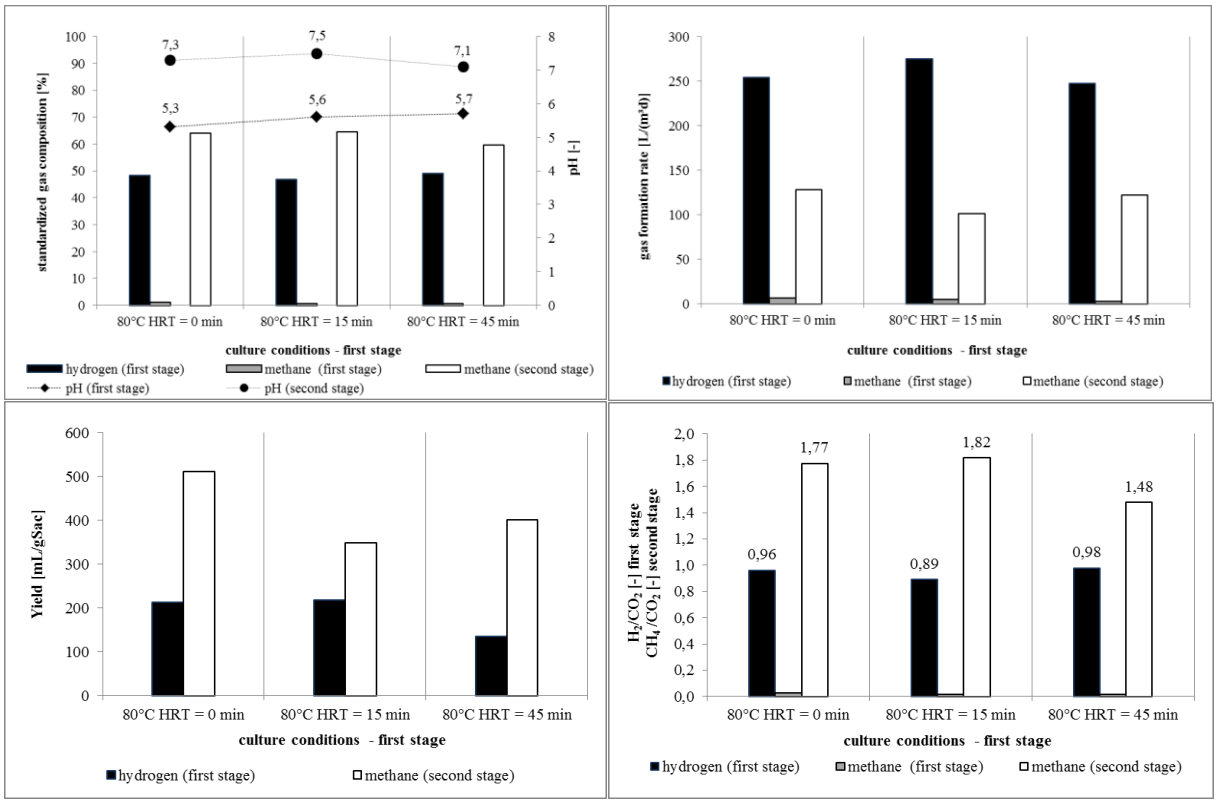

Figure 5. Comparison between standardizes gas composition (top left), gas formation rate of CH_4 and H_2 (top right), the Yield of CH_4 and H_2 (bottom left) and the ratio of CH_4 to CO_2 or H_2 to CO_2 (bottom right) of first and second stage depending on the duration of thermal digestate denaturation

In Table 3 the observed molar methane and hydrogen yield in relation to the investigated HRT of the heat treatment stage is displayed. The determined hydrogen yields of approximately 1 mole hydrogen per mole glucose indicate the presence of several different fermentative pathways. Apart from the generation of acetate and butyrate (≈ 3 mole hydrogen/mole glucose) a formation of acids, which do not yield any or even consume hydrogen is highly possible (cf. Table 1). Under this assumption the monitored molar yields of 1.67 to 2.03 mole CH_4 per mole glucose might be explained by the breakdown of the carbohydrate within the first stage. Compared to the maximal achievable yield of 3 mole CH_4 per mole glucose (conversion of glucose to methane), the fermentation of acids into methane reduce the reachable yields drastically due to the occurring carbon-elimination in form of carbondioxid within the acid formation.

Table 3. molar H_2 and CH_4-Yields of first and second stage in relation to HRT of digestate heat treatment (third stage)

Fermenter temperature / heat treatment HRT	H_2-Yield first stage [mole/moleGlc]	CH_4-Yield second stage [mole/moleGlc]
80 °C / 0 min	0.75	1.67
80 °C / 15 min	1.15	1.75
80 °C / 45 min	0.77	2.03

4. Conclusions

Based on an already established cyclic, two-stage pilot plant (CSTR) designed for simultaneous bio-hydrogen and -methane production, an evaluation of possible gas quantity and –quality enhancing parameters was conducted. The scaled down lab-scale-system was tested under varying temperatures of the hydrolytic (first) stage, while all characteristics of the downstream situated methanogenic (second) stage were left constant. Induced by insufficient gas qualities of the first stage an additional heat treatment of the digestate was integrated (cf. Figure 3). The heat treatment was found to strongly enhance the process stability and efficiency. However, the duration of the denaturation process had a significant influence over methane and hydrogen formation rates and yields within the first and second stage of the experimental setup. In all tested system variations a pH value under 6.0 and higher than 5.0 could be linked to hydrogen production. Due to economical and process technical reasoning the preferred duration time was aimed to be as low as necessary to ensure an optimal relation between hydrogen formation rate, gaseous content and energetic efficiency.

Therefore the optimal process parameters were established as followed. The optimal hydraulic retention time of the heat treatment coupled to the process temperature of the first stage of 80 °C was found to be 0 minutes after reaching 100 °C. Under these conditions 49 vol% hydrogen in the gaseous phase (H_2/CO_2 ratio of 0.96), a hydrogen formation rate of 254 L/(m^3d), the hydrogen yield of 213 L/kg sucrose and a maximal yield of 0.75 mole hydrogen per mole glucose were achieved. Within the second stage 65 vol% methane (CH_4/CO_2 ratio of 1.77), the methane formation rate of 128 L/(m^3d), a methane yield of 512 L/kg sucrose and the molar yield of 1.67 mole CH_4 per mole glucose were observed. The energetic efficiency of the whole process was 0.61. System stability in every experiment was reached within maximal six days. The system could compensate intrusions such as a week-long downtime, a complete inhibition of the first stage caused by high temperatures and an acidic induced wash out of the first stage.

Compared to the pilot-scale-process [6] the integration of the optimized heat treatment stage led to a 19 vol% enhanced hydrogen content within the gaseous phase of the first stage (30 to 49 vol%). Furthermore the molar yield could be improved from 0.49 to 0.75 mole hydrogen per mole glucose. Also a significant enhancement of the hydrogen yield (with/without heat treatment: 213 / 62 LH_2/kg sucrose) was monitored. Relating the second stage of the system (methane fermentation) a light improvement of the gaseous methane content of 5 vol% (60 to 65 %) and enhancement of the molar yield from 1.48 to 1.67 mole methane per mole glucose could be noticed.

Further potential for optimization lays within the active control of the fermentative pathway due to active pH control or variation of the ratio HRT/loading rate within the first stage. The observed ratio of H_2 to CO_2 (0.96) suggest predominant acetate/butyrate fermentation. Caused by the molar hydrogen yield of 0.75 mole H_2 per mole glucose the presence of another more unfavorable fermentative pathway under no CO_2 production is expected. Pure acetate/butyrate fermentation would lead to a yield of 2 to 4 mole H_2 per mole glucose. Therefore a significant formation of lactate and propionate is highly probable and should be avoided in the future (see table 1). This adjustment may lead to an acceleration of both hydrogen yield and production rate. An optimization of the volume ratio between first and second stage could lead to a more efficient carbon converting within the stages. Eventually the optimized parameters should be transferred and validated by the already established pilot scale process.

5. References

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