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KombiGas: Combined Methane and Hydrogen Production for the Application in the Stationary Motor

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A combined hydrogen and methane producing process was developed in the laboratory. At first a characterization and selection of substrates was performed and brewer´s spent grains was used in the laboratory experiments. The hydrolytic fermentation was performed in a Semi-Continuously Stirred Tank Reactor and the subsequent methanogenic fermentation was done in a Fluidized-Bed-Reactor. The total biogas yield was 204.7–210.6 Nl Biogas/kg VS. The gas composition of the combined gas was first 75.4% CH_4, 23.5% CO_2 and 1.1% H_2 and after a parameter variation it changed to 72.6% CH_4, 22.9% CO_2 and 4.5% H_2.

1. Introduction

The application of biogas in the stationary cogeneration of heat and power is state of the art. The application's optimization is currently done by engine improvements; an optimization of the biogas is rarely taken into consideration. One aim of the presented project is the development of a biotechnical process for the generation of a hydrogen-rich biogas. By the application of this hydrogen-rich biogas in a stationary gas engine, a decrease of emissions and fuel consumption is expected. A further aim of the project is to discover influencing factors in the fermentation process leading to various hydrogen (H_2) yields.
In the current state of the project a selection of suitable substrates for the fermentation in the biotechnical process was done and the process was set up in the laboratory. Several fermentation runs were performed and in the present paper four runs and their evaluations will be presented. The combustion experiments in a stationary gas engine have not been performed yet and are not included in this paper.

2. Fermentation Process

In order to achieve a biotechnical process for a hydrogen-rich biogas production the four levels of the anaerobic biogas process need to be divided into two procedural coupled processes: hydrolysis and methanogenesis. The process step hydrolysis includes the activity of the hydrolytic, acidogenic and partly acetogenic micro-organisms. Its final products are gaseous H_2, carbon dioxide (CO_2), hydrogen sulphide (H_2S), acetate, long-chain fatty acids, dissolved H_2 and dissolved CO_2. The hydrolyzate

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of the first process step, containing acetate, long-chain fatty acids, dissolved H_2 and CO_2 and partly unconverted substrate, is directed to the second process step. The second process step includes parts of the acetogenesis and the methanogenesis. In this step the acetate is converted to methane (CH_4) and CO_2 and furthermore CO_2 and dissolved H_2 react to additional CH_4.

2.1 Set up

The first process step is conducted in a 3.2 L Semi-Continuously Stirred Glass Tank Reactor (CSTR). It has a (propeller) stirring device which runs periodically every 30 minutes for a period of 15 minutes. A controlled water bath heats the double jacket reactor constantly to a temperature of 60 °C. The produced gases are directed to a gas-drying bottle and then to a gas counter (Ritter). The feeding of the reactor is semi-continuous and takes place every six hours. It is done by a peristaltic pump which brings a charge of fresh crushed substrate and water in the fermenter and at the same time pumps the same amount of hydrolyzate out. The pH and the redox potential are continuously supervised and logged by a data log system (WTW).

The second process step is conducted in a 5.8 L Fluidized-Bed-Reactor (FBR), which runs in an upstream mode. It is partly filled with plastic carriers of different densities, leading to five different areas in the fermenter: (i) The bottom without carriers and with high concentration of solids (since the unconverted substrate is brought in there), (ii) a dense area with carriers, (iii) an area with a lower flow where flocks or granules are build, (iv) a porous area with carriers and (v) the top area without solids (see Figure 1). There is a circulation of liquid with a fluid flow of 750 ml/min. It is done by a peristaltic pump. The input of the circulation to the reactor is at the bottom and the output is in the top area. A controlled water bath heats the double jacket reactor constantly to a temperature of 37 °C. The produced gas is directed to a gas-drying bottle and then to a gas counter (Ritter). The feeding of the reactor is semi-continuously and takes place every six hours. It is done by peristaltic pump which brings fresh hydrolyzate from the first process step to the circulation line. At the same time the identical amount of effluent is pumped out of the fermenter by a second peristaltic pump. The pH and the redox potential are continuously supervised and logged by a data log system (Awite).

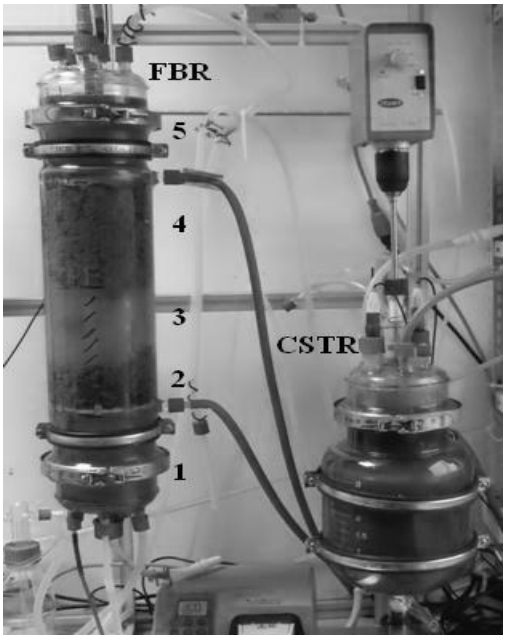

Figure 1: Set up of the biotechnical process.

2.2 Experiment performance

The hydrolysis and the methanogenesis were started separately in batch mode. After reaching the preliminary peak in productivity they were connected and the continuous feedings started. Due to longer reproduction rates of methanogenic bacteria, the second process step was started earlier than the hydrolytic process.

Hydrolysis: Two hydrolytic fermentation runs took place. Both used heat inactivated (80 °C and 30 min) digestion sludge from a biogas plant as inoculum and crushed vacuumed brewer´s spent grains as substrate. The dry matter concentration was 1% and the hydraulic retention time (HRT) was set to 3 days (Technical University of Hamburg-Harburg, 2008). In the first run the pH was adjusted to 5.5 (Massanet-Nicolau et al., 2008) by adding further heat inactivated sludge, whereas in the second run there was no pH control.

Methanogenesis: Two methanogenic fermentation runs took place. In order to start the first fermentation, digestion sludge from a biogas plant and 70 g crushed vacuumed brewer´s spent grains were added to the fermenter. After two weeks of batch performance, the constant feeding of fresh hydrolyzate from the first fermentation step started. The HRT in the fermenter was set to 5.7 days. For the second fermentation run, the sieved content from the first run was used as inoculum. There were also 70 g uncrushed vacuumed brewer´s spent grains added, but the connection to the first fermentation step was done after three days of performance.

3. Results and Discussion

3.1 Hydrolysis

The performed hydrolytic fermentation runs showed different results. In the first fermentation the total gas yield was 35 Nl/kg VS (standard liter per kilogram volatile solids). CO_2 was the highest among the detected gas components, followed by CH_4. There was an average H_2 yield of 1 Nl/kg VS. In the start-up phase the highest acetate equivalent (total amount of volatile fatty acids (VFA), calculated to acetate) of 2150 mg/L was detected. The most built acid was acetic acid, followed by butyric and propionic acid.

In the second hydrolytic fermentation run the average H_2 yield was 14 Nl/kg VS. The total gas yield was 31 Nl/kg VS. CO_2 was the highest among the detected gas components, followed by H_2. Only small amounts of CH_4 (2 Vol.-%) were detected. The highest acetate equivalent in this fermentation was 1880 mg/ L. The pH-drop to 4.5 changed the spectrum of VFA. Butyric acid was the most built acid, followed by acetic and propionic acid.

The different pH in the performed hydrolytic fermentation runs led to different yields of H_2 and different spectrums of VFAs. In the second run there was a lower total gas yield but a high yield of H_2, whereas in the first run there was a higher total gas yield, nearly no H_2 and a nameable yield of undesired CH_4. The drop of pH in the second hydrolytic fermentation run changed the spectrum of built acids and increased diffusion of H_2 to the gas phase. Furthermore it inhibited the methanogenic bacteria and nearly no CH_4 was built. This explains the higher H_2 yield. Nevertheless there is still a lot of H_2 dissolved in the hydrolyzate according stoichiometric calculations.

3.2 Methanogenesis

In the start-up phase of the first methanogenic fermentation run the average gas production was 45 Nl/kg VS. When the continuous feeding of hydrolyzate started, the gas yield constantly increased to 165 Nl/kg VS. The gas composition was 70–80 % CH_4 and 20–30 % CO_2.

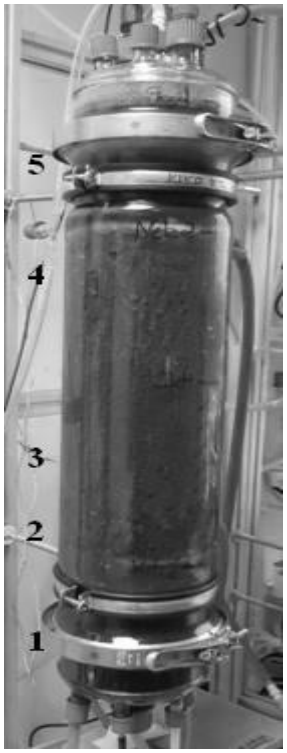

Figure 2: Methanogenic fermenter before formation of granules.

The second methanogenic fermentation run presents the continuation of the first run since the sieved liquid is used as inoculum. There was no lag phase observed because the majority of the bacteria were brought or even kept in the fermenter. When the continuous feeding of hydrolyzate started, the gas yield increased to 190 Nl/kg VS. 75–77 % of the produced gas was CH_4 and the majority of the remaining part was CO_2. In the third part of the fermenter a formation of granules was observed. In Figure 2 you can see the methanogenic fermenter before the formation of granules took place. There were flocks in the third part of the fermenter and several days later they were converted to granules (see Figure 3). After further days of operation, granules could also be found in the dense and porous fermenter beds.

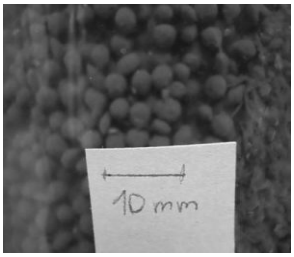

Figure 3: Granules in the methanogenic fermenter.

3.3 KombiGas – Evaluation of the combined hydrolytic and methanogenic fermentation runs

The first evaluation combines the first hydrolytic and the first methanogenic fermentation runs. Figure 4 depicts an increase of the total gas yield in this combined run. During the first twelve days of operation the highest amounts of H_2 in the gas were observed. At the same time the total gas yield accounted for only 80–90 Nl/kg VS. When the total gas yield reached its highest amount, there has only been a small hydrogen yield of 4 Nl/kg VS. The period starting on the 22th day, is the most representative period for making conclusion of the combined evaluation due to its constant performance. The average gas yields in the periods were: 210.6 Nl Biogas/kg VS, 158.9 Nl CH_4/kg VS, 49.4 Nl CO_2/kg VS and 2.4 Nl H_2/kg VS. This corresponds to a gas composition of 75.4 % CH_4, 23.5 % CO_2 and 1.1 % H_2.

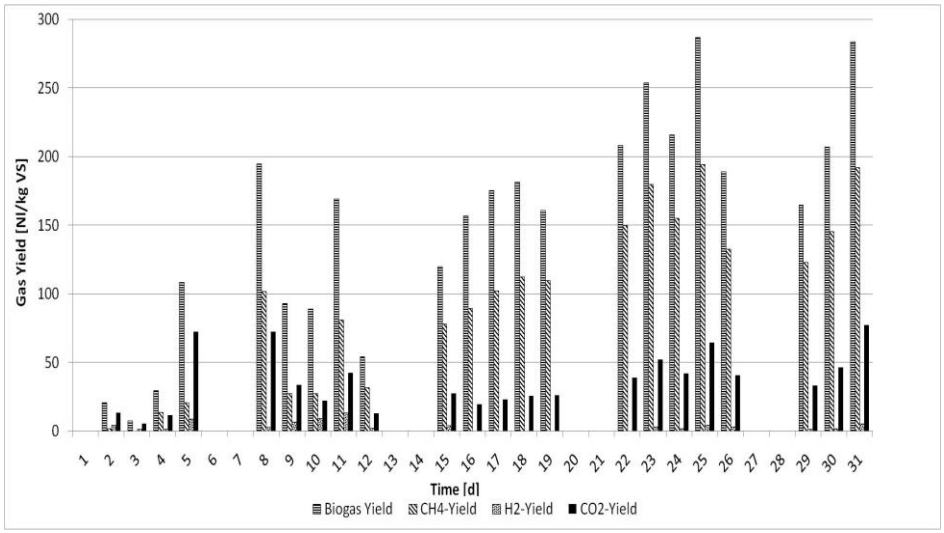

Figure 4: Gas yields of the first combined fermentation system.

The changes in the second hydrolytic fermentation run (lower pH) and the formation of granules changed the gas composition of the combined gas. The average gas yields of the second combined fermentation run were: 204.7 Nl Biogas/kg VS, 148.6 Nl CH_4/kg VS, 46.9 Nl CO_2/kg VS and 9.2 Nl H_2/kg VS (see Figure 5). This corresponds to a gas composition of 72.6 % CH_4, 22.9 % CO_2 and 4.5 % H_2.

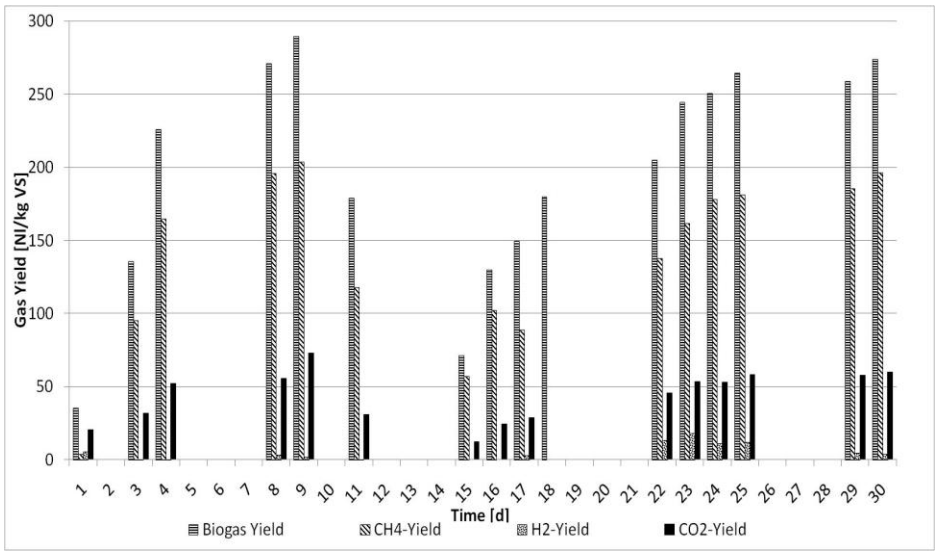

Figure 5: Gas yields of the second combined fermentation system.

4. Conclusion

The performed combined fermentation runs had a total biogas yield of 204.7–210.6 Nl Biogas/kg VS. The adjustment of pH in the hydrolytic fermentation process changed the gas and VFA yields of the single fermentation steps and then the composition of the combined gas. A low pH of 4.5 increased the H_2 release in the hydrolytic fermentation step and led to a combined gas with a measurable H_2 concentration of 4.5 % and a CH_4 concentration of 72.6 %. If a higher pH of 5.5 was adjusted in the hydrolytic fermentation run, the H_2 release was lower, leading furthermore to a reduced H_2 concentration of 1.1 % in the combined gas. On the other hand the CH_4 concentration increased to 75.4 %. The CO_2 concentration in both combined gas was approximately the same.

The drop of pH to 4.5 led to a significant H_2 release in the hydrolytic process and simultaneously unwelcome CH_4 production was reduced. It is obvious that a low pH inhibited methanogenic bacteria that were brought into the fermenter with the substrate. When pH was adjusted to 5.5 methanogenic activity was not inhibited and H_2 and CO_2 were converted to CH_4.

The gas yields obtained from both fermentation runs were lower as the biogas yield of a one-step digestion test, operating in batch mode for 30 days in our laboratory. Its biogas yield was 301 Nl/kg VS, but the CH_4 concentration was only 61 %. As a conclusion the two-step fermentation generated less biogas with a higher CH_4 concentration.

The HRT of the combined process was nine days. Compared to the production of the digestion test, the HRT was reduced by 70 %. One influencing factor leading to this reduction was the retention of biomass in the methanogenic fermenter. After a period of 21 d first significant flocks were found in the fermenter. Granules were even built after 41 d of operation. The Fluidized-Bed-Reactor (FBR) showed a good performance in the retention of biomass and reduction of HRT.

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