

Energy Supply with Biogas – An Example of Curricula Innovation Research in the Field of Renewable Energy

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Abstract In school and university education, it is important to integrate current and innovative topics into the curricula. Curricular innovation research follows this line of research. Especially in the field of education for sustainable development, there is a great need to didactically prepare the topics on the basis of the Sustainable Development Goals and to convey them to pupils and students at an early stage. Energy supply is currently a highly complex and central topic from a climatic and political point of view. In this context, biogas production as a renewable energy source has become even more important. For example, more than 9000 biogas plants are currently in operation in Germany. The principle of biogas production has long been implemented in school experiments. However, it was recognized that the methods used in school experiments usually do not produce methane. Therefore, a new experimental setup was developed to ensure methane production in these experiments and to demonstrate biogas practically. Dried sugar beet was used as a substrate for biogas production. It was mixed with compost or garden soil, which contained the microorganisms required for biogas and methane production and served as inoculum. An inexpensive gas chromatograph was used to measure the methane concentration in the biogas produced. In a first attempt, to ensure methane production, sodium carbonate was added as a buffer to keep the pH of the fermentation broth in the optimal range (pH 7-8). To avoid the addition of buffer, the optimal ratio of compost to sugar beet was then investigated in collaboration with the University of Hohenheim. Based on these results, methane formation was observed after 8 days and methane concentrations of up to 65 vol% were measured. Overall, this trial was a practical way to demonstrate the anaerobic digestion process to students by production of biogas. This study also highlighted the great benefits of interdisciplinary collaboration in curriculum innovation research.

Keywords: Hohenheim Biogas Yield Test, Anaerobic Digestion, Methane, Biogas, School, Education, Curricular Innovation Research

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1. Introduction

1.1. Integration of Innovative Topics into the School Curriculum

A key concern of school education is to arouse pupils in science subjects. In the natural science particular, a "high level of proactivity" is required to achieve a successful outcome. In terms of popularity ratings, the subjects of chemistry and physics occupy the two last places [1]. Innovative concepts are one way to counteract this trend. In addition, it is important to integrate innovative topics at the cutting edge of science into the school curriculum in order to familiarize the young generation with research and development at an early stage. After all, they are the ones who will have to face the challenges of climate change, sustainability, a growing world population and

diminishing fossil resources. It will be up to them to find solutions for sustainable, ecological, and economic energy supply.

There is often no teaching material on innovative technological developments and subject areas. It is even more difficult to find experiments. It is therefore essential for innovative subject areas to be introduced and taught in schools in as practical a manner as possible. In the long term, they must also be integrated into (university) school curricula. One orientation of subject didactic research in chemistry is curricular innovation research according to Tausch [2,3]. It deals specifically with experimental and conceptual development of teaching materials. In curricular innovation research, the emphasis is on content and the methodological renewal and adaptation of teaching. In addition, future-oriented questions and current topics are examined and didactic concepts and new school experiments for innovative developments are established. On the one hand, it is important to present relationships

clearly and understandably. On the other, school experiments must be carried out with safe materials and substances that students and teachers can handle in the classroom. Furthermore, it is important that the costs of carrying out these experiments are within a normal school budget. Finally, the experiments must be feasible within the framework of a lesson or generally under school conditions. All these criteria limit the opportunities for experimentation. Often a didactic slimming down of the facts is necessary whereby a fine line must be drawn between required simplification and technical correctness [4]. For this reason, a close didactics exchange between the subject sciences and teachers is important. An example of this experimental- conceptual subject didactic research is presented below. It draws on a specific example taken from the field of sustainable energy supply, methane synthesis. In the context of the energy transition, this issue is of major importance. In Germany, for example, the goal is to increase the share of renewable energies (especially bioenergy, solar energy, wind energy, hydropower) in gross final power consumption to 80% by 2050 [5]. This envisioned goal can only be achieved if suitable and effective forms of energy storage exist and can be further refined, so that renewable energies can be used independently of time and place. In addition, supply periods must be bridged in which these energies are not available (e.g. wind calm).

Biogas production is one option for generating sustainable energy. Biogas can be produced by means of the anaerobic bioconversion of energy crops, agricultural by-products, and organic waste (e.g. manure, maize silage or sugar beet). It consists mainly of methane (50-65%) and carbon dioxide (35-50%) as well as small amounts of hydrogen, hydrogen sulfide, ammonia, and other trace gases.

The number of biogas plants in Germany grew rapidly as a consequence of a bonus payment provided for in the Renewable Energy Sources Acts (EEG) of 2004 and 2009. These acts guaranteed a bonus payment for a period of twenty years for power production from special agricultural substrates such as maize silage or manure. In 2019, a total of 9,527 biogas plants were in operation in Germany [6]. However, the Renewable Sources Energy Acts of 2014 and 2017 reduced these bonus payments. To ensure that the existing biogas plants could continue to operate profitably, new strategies were needed that either increased the efficiency of the process or rendered energy production more flexible. The goals were to supply energy to meet additional peak load and thus achieve higher prices for the electricity produced. Furthermore, the appropriate use of the generated heat gained importance. Research is currently underway on several additional topics, such as combining power-to-gas concepts and biogas production to make renewable energy storable in chemical form or using alternative substrates. The basic biogas process itself is simple to implement. It can help pupils understand biochemical processes and facilitates hands-on demonstration of renewable energy generation in the classroom.

The biogas process consists of several steps (see Figure 1). Basically, the four phases of anaerobic degradation run in parallel in a one-step process. However, the bacteria in the individual sub-steps make different demands on their

habitat (e.g. pH, temperature), which means that a compromise must be found in terms of process technology. Due to the slow growth rate, the methanogenic microorganisms are the weakest link in the biocoenosis and reacts most sensitive to disturbances. Therefore, the milieu conditions must, be adapted to the requirements of the methanogens [7]. A low pH of 5.2-6.3 is optimal for the hydrolysis, while the pH for methanogenesis should be between 6.5 and 8.0 [7]. This raises the question of how to set up an appropriate one-step process. Beside pH, microorganisms are also clearly affected by temperature. Consequently, a stable temperature during the process is important to avoid inhibition [8].

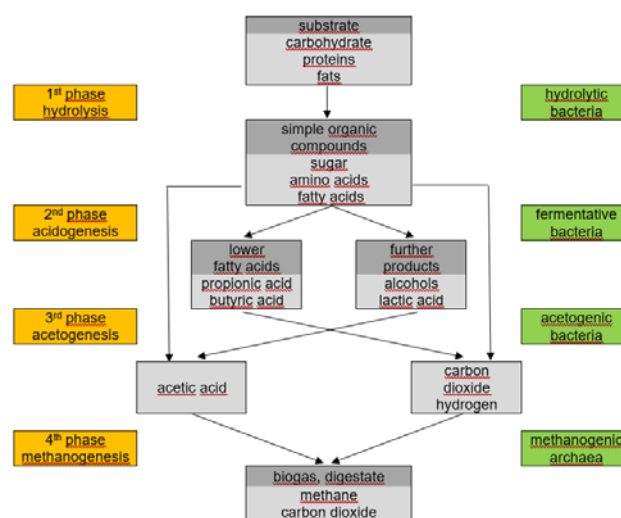


Figure 1. The four phases of anaerobic degradation [15]

The production of biogas is already a common experiment in schools. However, in almost all cases, no methane is formed, only hydrogen and carbon dioxide, because the low pH inhibits methanogenesis [9]. This is due to overloading of the process and a lack of analytical control and monitoring of the experiment. Optimized dosing of the added substrate quantities is crucial in this context.

The following study focused on the concept of curricular innovation research. It examined an experiment set-up for biogas generation in a school experiment. In most school experimental setups, the biogas produced likely consisted of only biohydrogen and carbon dioxide (test 1a). The addition of buffer substances ultimately resulted in the production of biomethane. This variation was next demonstrated in a laboratory experiment (test 1b). Subsequently, the optimal experimental conditions were investigated in a commercial batch test the Hohenheim Biogas Yield Test (HBT) (test 2). The experimental set-up for a school experiment was then tested under optimized conditions (test 3).

2. Materials and Methods - Biogas Synthesis in School

A core idea in curricular innovation research is that pupils should be introduced to current research content at

an early stage. The young generation faces particular challenges, as it is they who must develop intelligent solutions for a sustainable energy supply with renewable energies. In the next section, biogas production with its peculiarities in the school practice field.

2.1. Biogas Synthesis as a School Experiment (Test 1)

Conventional laboratory equipment and low-cost medical technology materials were used for the experimental set-up (Figure 4). It is therefore suitable for low-cost use in schools. All organic substances can be used to produce biogas. However, for practical school use, it made sense to choose a reproducible setup with reaction conditions that were as constant as possible (type of substance, amount of substance, temperature, time). We therefore used garden soil as the inoculum and sugar beet pulp as the solid, which was prepared in a special water/solid-ratio.

Devices and chemicals: 250 mL wide-neck Erlenmeyer flask, three-hole stopper, m-adaptor, two three-way taps, plastic syringe at least 60 mL, gas bag, pH electrode, detector/ e.g. all-che-misst (view Figure 3), mortar and pestle, stirring fish, magnetic stirrer with hot plate, water bath, tripod with sleeve and clamp, dried beet pulp, compost, water, sodium carbonate (test 1b).

Measurements were performed with a low-cost gas chromatograph (thermal conductivity detector, AK Kappenberg, Münster, Germany). Simultaneously, measurements were also taken using a gas chromatograph mass spectrometer (GC / MS) (HP 8890, Agilent, Santa Clara, US and; MSD HP 5977B, Agilent, Santa Clara, US) in the analytical laboratory of the University of Tübingen. It shows a good correlation with the values measured with the low-cost school chromatograph. Despite its comparatively simple structure and low acquisition costs, the low-cost school gas chromatograph delivered good and sufficiently accurate results for practical school use, although some inaccuracy must be expected with this low-cost GC. The GC was useful for evaluating the reaction products. For quantitative analysis, biogas was compared with the reference samples of known volume concentrations.

Procedure: An Erlenmeyer flask served as the biogas reactor. It was sealed gas-tight with a suitable silicone or rubber stopper (Figure 2). Two holes were drilled into the flask. One hole was for inserting a pH electrode to monitor the pH during the biogas process. The second hole was for discharging the resulting gases through an m-adaptor with a three-way valve. An injection plug and a plastic syringe for storing the biogas were connected to it. Optionally, a third hole could be drilled in the stopper for simple material exchange. It was sealed with a small silicone or rubber stopper.

The combination of garden soil as inoculum and beet pulp as solid was prepared in a mixing ratio of 5:1 in an Erlenmeyer flask. In the fume hood, the test was set up using a magnetic stirrer with a heating plate, a water bath (37°C – the optimum temperature for mesophilic microorganism), and a tripod. Contaminants (such as stones) were removed from the compost soil, and homogenized by mixing. The dried sugar beet chips were

crushed in a mortar. 5 g of dried sugar beet chips and 25 g compost soil were then added into the reactor with 280 mL of warm water (37 °C). The temperature was maintained at 37 °C throughout the experiment with constant stirring in the water bath. The three-way tap was adjusted so that the resulting gas could be collected in the syringe. If possible, the gas volume in the syringe was read daily and examined with a gas chromatograph. If necessary, a gas bag could be connected via the three-way tap to facilitate the collection of a larger volume of gas. After 30 days or as soon as no more gas was formed, the experiment was stopped. The fermentation residues still present in the reactor could be tested for odor and appearance.



Figure 2. Three-hole stopper at the top of the biogas reactor used in a school experiment



Figure 3. Reactor for biogas production in a school experiment with pH monitoring

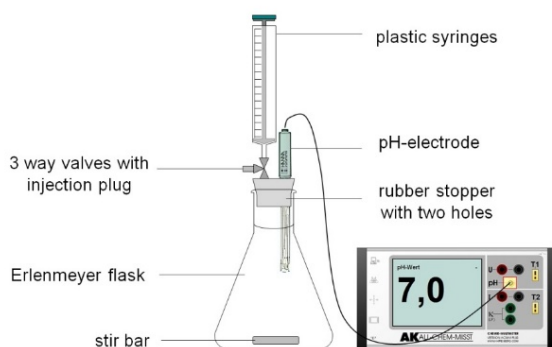


Figure 4. Experimental sketch of the reactor for biogas production in a school experiment with pH monitoring

2.1.1. Biogas School Experiment – State of the Art (Test 1a)

Firstly, the new experimental set-up was used to conduct the common school experiment. Gas quality was measured by the gas chromatograph and the gas was collected in the syringe. Gas was produced from the second day of the experiment. After 24 hours, evaluation of a 1:1 set-up (beet pulp / garden soil) showed a gas volume of 50% hydrogen and 40% carbon dioxide (Figure 5). The remaining 10% consisted of oxygen and nitrogen, which are not represented in this low-cost GC because air is used as the carrier gas. Quantitative evaluation was most accurately performed by comparing peaks of known amounts of substances.

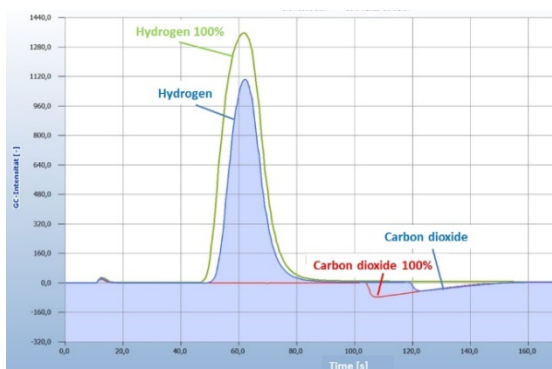


Figure 5. Gas chromatograph used in the school experiment to generate biogas (blue line – biogas, green line – 100% hydrogen, red line – 100% carbon dioxide)

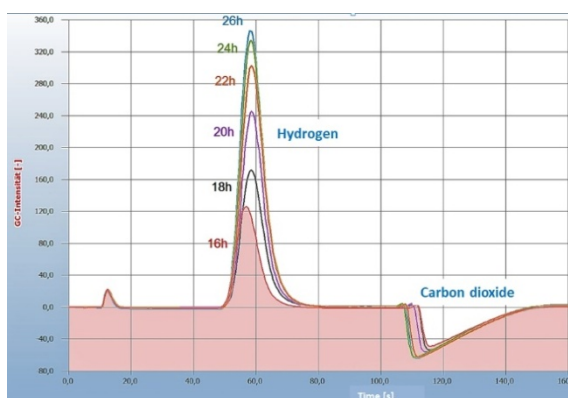


Figure 6. Comparative measurement by gas chromatograph of the biogas every 2 hours

The experiments showed that hydrogen and carbon dioxide can be produced from beet pulp and garden soil, but the key focus of interest was methane production. Unfortunately, no methane production could be detected (Figure 6). Analytical control and monitoring of the experiment were essential to determine the reasons. One possible reason could be inhibition of methanogenesis caused by a drop in pH due to acid production during acidogenesis. In agricultural plants, the buffer capacity of manure prevents a drop in pH, but soil may have less buffer capacity. To monitor this effect, a control of the pH value was necessary. Additionally, a drop in pH drop could be prevented by adding buffer during the experiment.

2.1.2. Biogas School Experiment with Additional Buffer (Test 1b)

The next step involved performing the experiment with pH control. The experimental setup and procedure were the same as for test 1a. If necessary, a neutral to slightly alkaline pH was set by adding a few spatula tips of sodium carbonate as the buffer. If the pH fell into the acidic range ($\text{pH} < 7$) during the test, the pH was adjusted by adding sodium carbonate again. The addition was made through the third hole in the stopper so that the oxygen input could be kept as low as possible. The experiment was stopped after 30 days or as soon as gas formation ceased. The fermentation residues still present in the reactor could be examined for odor and appearance. In the first few days of the experiment, acid-forming processes caused a significant drop in the pH (Figure 7) which meant that it had to be continuously adjusted so as not to impair the formation of methane.

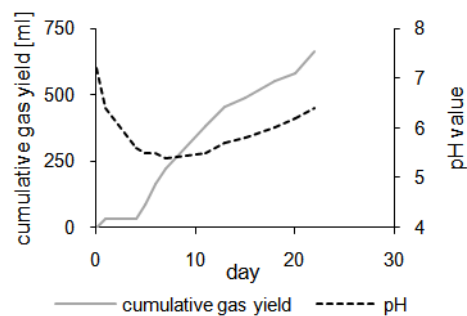


Figure 7. Development of the pH value and total volume in biogas production with continuous pH adjustment

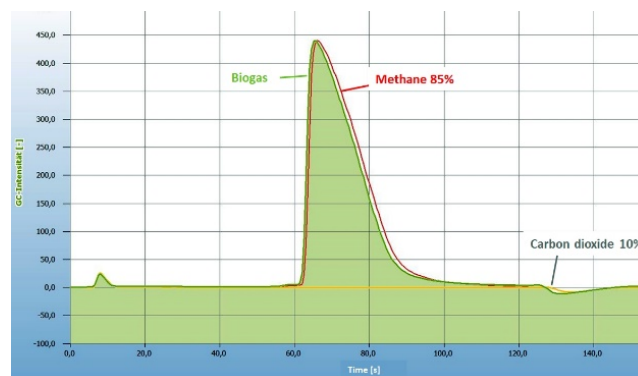


Figure 8. Quantitative evaluation of biogas after 24 days using the low-cost school gas chromatograph

The gas chromatography analysis showed methane content of around 85% in biogas after 24 test days (Figure 8). Setting the pH value actually enabled methane to be recovered in this experimental setup. In biogas plants, naturally occurring buffer systems, such as the hydrogen carbonate or ammonium buffer, ensure a stable pH value. With a suitable mixing ratio of compost and sugar beet pulp, the natural buffering capacity of the system is sufficient to regulate the pH, and it is not necessary to adjust the pH externally [10]. In cooperation with a university specializing in biogas research, this study focused on optimizing and simplifying the experimental procedure. To determine a suitable mixing ratio of compost and sugar beet pulp, the Hohenheim Biogas Yield Test (HBT) was conducted in the laboratories.

2.2. Optimizing the Ratio of Compost to Sugar Beet – Hohenheim Biogas Yield Test (Test 2)

A specific guideline (VDI 4630) served as the basis for obtaining a suitable mixture ratio of inoculum, in our case compost, and substrate, in our case sugar beet, in the HBT test. Further information is available in the supporting documentation.

Table 1. Test conditions and volatile solids (VS) ratio for the tests conducted in the Hohenheim Biogas Yield Test. For variations A-E a compost was used as the inoculum, and for the reference variation an inoculum cultivated under anaerobic conditions was used

Test	Methane ratio [vol %]	Specific gas yield [L kg ⁻¹ VS]	Specific methane yield [LCH ₄ kg ⁻¹ VS]
A	14 ± 2	70 ± 12	10 ± 2
B	16 ± 5	96 ± 30	17 ± 9
C	52 ± 1	559 ± 44	291 ± 29
D	52 ± 1	547 ± 79	283 ± 48
E	51 ± 2	685 ± 25	352 ± 23
Reference	51 ± 0	703 ± 7	359 ± 3

In the experiments, the test was carried out done in accordance with the VDI 4630 guideline for 35 days at 37°C. In each case, 400 mg of sugar beet pulp was used as the substrate (Table 2) as well as 30 g of the inoculum. But the composition of the compost inoculum varied. Based on volatile solids (VS), the compost to sugar beet ratio ranged between 5:1-25:1 and the compost mass between 2-10 g (Table 1). The compost was diluted with water to a total volume of 30 g. As a reference, another test was done using a standardized inoculum produced under control conditions in a 400 L laboratory digester at 37°C [11]. To establish the specific methane yield (SMY), the total solids (TS) and volatile solids (VS) were determined according to the guidelines DIN 12880 and 12879.

The results highlighted the importance of using a VS ratio of compost to sugar beet pulp higher than 12,5:1 (Table 2). For variations A and B, methane content of 14-16 % and a SMY of 10-17 L_{CH₄} kg⁻¹ VS were measured. Both clearly indicated inhibition of the process. In the second run, variations A and E were again tested, but this time the pH of the substrate was measured over a period of several days (Figure 10). The pH of test A declined to around pH 5. This was caused by the formation of volatile

fatty acids resulting from degradation of the biomass. This low pH led to effective inhibition of methanogenesis, because methanogenic bacteria prefer a pH between 6.5 and 8. At a lower pH, methane formation was inhibited [12]. This result supports the assumption derived from the first run.

Table 2. Average values and standard deviation after 35 days digestion in the Hohenheim Biogas Yield Test. For variations A-E compost was used as the inoculum, and for the reference variation an inoculum cultivated under anaerobic conditions was used. All volumes are given under standard conditions (p = 1013.25 hPa; T = 0°C)

Test	Water [mL]	Compost/inoculum [g]	Sugar beet [g]	VS ratio compost to sugar beet
A	28.0	2.0	0.4	5:1
B	27.5	2.5	0.4	6.25:1
C	25.0	5.0	0.4	12.5:1
D	22.5	7.5	0.4	18.75:1
E	20.0	10.0	0.4	25:1
Reference	0.0	30.0	0.4	2.25:1

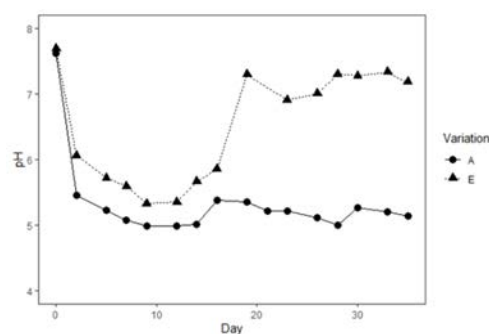


Figure 9. pH development of variations A and E during the second run

In contrast, variations C, D, and E had a higher methane content of 51-52 vol %, which were not significant compared with the reference measured in HBT (Table 1). The SMY of variation E and the reference did not show any significant difference from each other. In contrast, variations C and D had significantly lower methane yields than variation E and the reference. These results revealed that biogas production based on compost as the inoculum is possible as similar results to the standardized HBT test were obtained with a manure-based inoculum. However, the great importance of a high ratio of compost to sugar beet VS was also shown. To obtain comparable results, a ratio of around 25:1 is recommended. The effect of the ratio in the process was also supported by the measured pH (Figure 10). Unlike the pH of variation A, the pH of variation E declined first, but increased on day 20. The microbiome of the compost was not well adapted to the anaerobic condition. Although composting is an aerobic process, all the required anaerobic bacteria appear to have been present in the compost.

Primary fermentation and hydrolysis of the biomass began after a few days, as shown by the shift to pH 5.5-6.0. The methanogens needed more time to adapt and establish, but started methane production after several days.

The results were confirmed by the kinetics of methane production (Figure 9; Table 3). Methane production of variation E was delayed compared to the manure-based inoculum because of the lack of adaptation of the compost

inoculum. This resulted in a lag phase (λ) of 8.5 days compared to 1.6 days for the reference (Figure 10). Based on the results, a long retention time of more than 20 days was recommended in order to observe considerable methane formation in the experiments with compost.

However, the longer lag phase (λ) resulted in the students being able to get a better temporal experience of the anaerobic digestion process and a deeper understanding of the different steps of biomass degradation during anaerobic digestion.

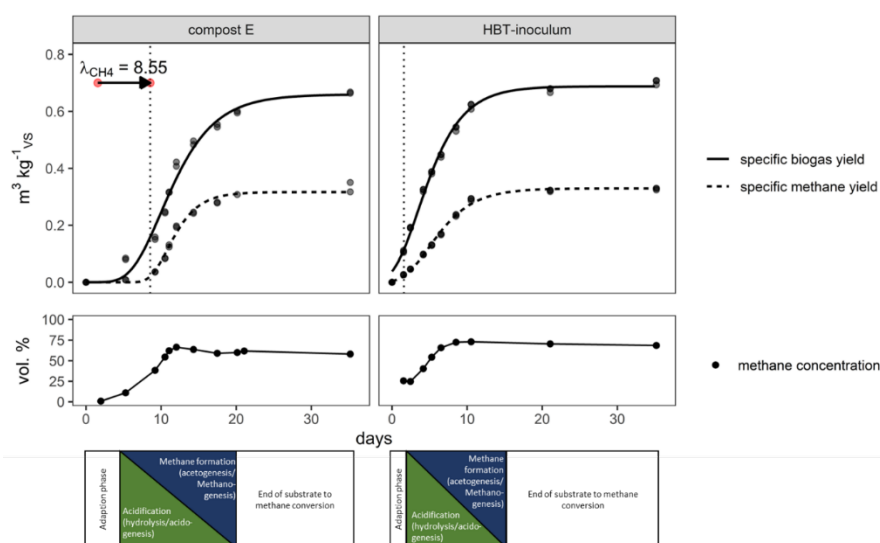


Figure 10. Kinetics of biogas and methane formation in the first run, comparison of variation E with the reference HBT inoculum and duration of the methane formation lag phase (λ_{CH_4}) shown as a dotted vertical line

Table 3. Parameters of the fitted Gompertz model with the upper asymptote as the methane production maximum (S), the production rate (Rm), and the lag phase (λ). Mean absolute error (MAE) was used to describe the quality of fit

Parameter	Variation	S [L kg ⁻¹ VS]	Rm [L kg ⁻¹ VS d ⁻¹]	λ [d]	MAE
CH ₄	E	316	50	8.5	13.36
	HBT inoculum	330	37	1.6	9.35
Biogas	E	659	61	6.0	13.17
	HBT inoculum	688	77	0.2	9.12

All measured gas volumes were corrected to standard conditions ($p = 1013$ hPa; $T = 0^\circ\text{C}$)

In a final step, the findings from the studies in Hohenheim were to be incorporated into the school experiment.

2.3. Optimized School Experiment for Methane Production

The results of the experiments at Hohenheim University (Table 1) were integrated into the methodology of the school experiment. In the reactor, 4 g of dried sugar beet pulp and 100 g of compost (ratio compost to sugar beet VS 25:1) were added to approx. 200 mL of warm water (37°C). The temperature was set at 37°C in the water bath with constant stirring throughout the experiment. The three-way tap was adjusted to collect the resulting gas in the syringe. If possible, the gas volume in the syringe was read daily and examined by gas chromatography. If necessary, a gas bag could be connected via the three-way tap in order to absorb a larger volume of gas. After 30 days or as soon as no more gas was formed, the experiment was halted. The fermentation residues still

present in the reactor could be tested for odor and appearance.

Gas quality was again measured using the gas chromatograph (Kappenberg). For quantitative analysis, the biogas was compared with reference samples of known volume concentrations.

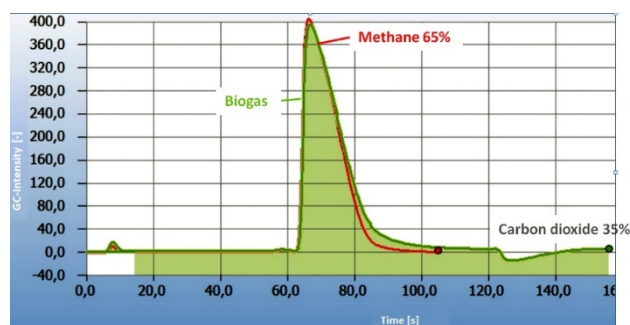


Figure 11. School experiment with optimised results (day 33)

2.4. Results

From the second day, gases were reported to be produced and collected in the connected syringe. Methane was produced in all set-ups. For compost, methane was detected in the biogas from day 8. In contrast, for garden soil, methane was observed in the biogas only on days 12-15. In some cases, it was easier to organize garden soil for schools. The observed differences could perhaps be explained by the heat pretreatment of the garden soil, which influences the microbiome in the garden soil. In both cases, a methane content of around 65% was measured (Figure 11). This constituted a high methane concentration in the gas compared to full scale anaerobic digestion plants, whose values are typically between 50-75 vol %. [10].

2.5. Conduct in Schools

For the experimental implementation of biogas production, a time frame of approximately 10-30 days must be set. This experiment can thus be conducted in an optimum manner in a school project. In addition, it is possible to set it up as an accompanying regular lesson and to discuss it with the students from time to time as part of those lessons. In this case, someone would have to control the experiment even on the days when classes are not in session. This can be done either by the teacher or by groups of pupils. As an alternative to the gas chromatograph investigations, comparative investigations of the gases based on combustion enthalpies or flame coloration are possible to determine the qualitative results [13,14].

3. Summary and Conclusions

In the thematic area of education for sustainable development, anaerobic digestion and biogas production offer many points of contact with classic topics of the educational curricula for chemistry and biology (e.g. hydrolysis, natural substances, chemical reaction). Until now, biogas school experiments have mainly produced hydrogen and carbon dioxide. However, the desired gas methane was not produced. The school experiment was therefore optimized by adding a buffer to show that methane could indeed be produced in the school experiment. Drawing on the findings from the studies on this experimental approach by the University of Hohenheim, it was possible to show that methane can indeed be produced at a soil-to-sugar beet ratio of 12.5:1 without the additional addition of a buffer. Furthermore, a comparable methane yield could be achieved with a soil to sugar beet ratio of 25:1. In this case, methane production began much earlier than in the school-based set-up with sugar beet pellets (after 8.5 days) and a standardized manure-based inoculum (after 1.6 days). This approach is an example of curricular innovation research which is

extremely important for current and innovative experimental chemistry teaching. In the further course of work, studies on the effectiveness of the developed and optimized experiments will be carried out and published in a timely manner.

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