Optimized use of biogenic waste streams through the combined production of bio-based products and bio-hydrogen

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Abstract

Since 2015, there has been a legal obligation in Germany for the districts and cities to collect biowastes separately, which are then treated in a composting plant or fermentation plant. However, in both aerobic and anaerobic biowaste treatment, a large part of the carbon contained in the waste is released in the form of carbon dioxide (CO2) without using the raw material potential it contains. Against the background of efforts to save climate-relevant gases and the scarcity of natural resources, the aim of biological waste treatment should be to make better use of the potential of bio-waste through innovations in the known treatment processes. These innovative processes should make better use of the carbon contained in the biomass and obtain higher-quality and economically profitable bio-based products from it, to substitute primary raw materials.

In a first step, the anaerobic process of dark fermentation initially produced short-chain carboxylic acids from organic waste streams. This process also produces a hydrogen-containing biogas that can be used for energy. In a secondary fermentation, the carboxylic acids are then to be lengthened and separated using a non-polar extractant. The extended carboxylic acids then serve as platform chemicals for the manufacture of various bio-based products.

Keywords: Bio-waste, anaerobic, dark-fermentation, carboxylic acids, bio-based products

1. Introduction

Every year large quantities of organic waste generate in Germany have been collected and treated separately. The treatment of this waste is largely in composting or fermentation plants. In 2017, this was 15.6 million tonnes (Statistisches Bundesamt, 2018). During composting, the organic matter is degraded releasing carbon dioxide (CO2), water and heat, and the resulting compost is used as fertilizer in agriculture or landscaping. Since large amounts of the carbon included in the waste are released into the atmosphere as CO2 without any benefit, this process has a high optimization potential. The fermentation of bio-waste is the second widespread treatment option and already known for better use of resources. The biogas produced during the fermentation process can be used for energy purposes and the digestate can subsequently be composted. But even with this method, a large part of the carbon is released into the environment in the form of CO2. The aim of the newly developed process for biological waste treatment is therefore to optimize the use of the carbon contained in the waste by producing products with higher value.

In the research project CarBioAb, funded by the European Fund for Regional Development (EFRD 2014-2020), the University of Duisburg-Essen, together with its partner INGUT GmbH, are investigating how the carbon contained in bio-waste can be transformed in bio-based chemicals by using the anaerobic process of dark fermentation.

2. State of the Art and Methods

To transform organic waste, first short-chain carboxylic acids are to be generated from the waste streams. A distinction is made between liquid (VS < 10%) and solid (VS > 10%) waste streams. The solid waste is first subjected to percolation in order to transfer as much organic matter as possible into the aqueous phase. The percolate obtained is then fed to the dark fermentation just like the liquid substrates. In this process step, polar organic acids are formed from the organic. This process also produces a hydrogen-containing biogas that can be used for energy-supply. In a post-fermentation, the carboxylic acids are then lengthened and separated using a non-polar extractant. The extended carboxylic acids then serve as chemicals for producing various bio-based products. The scheme of the process is shown in Figure 1:

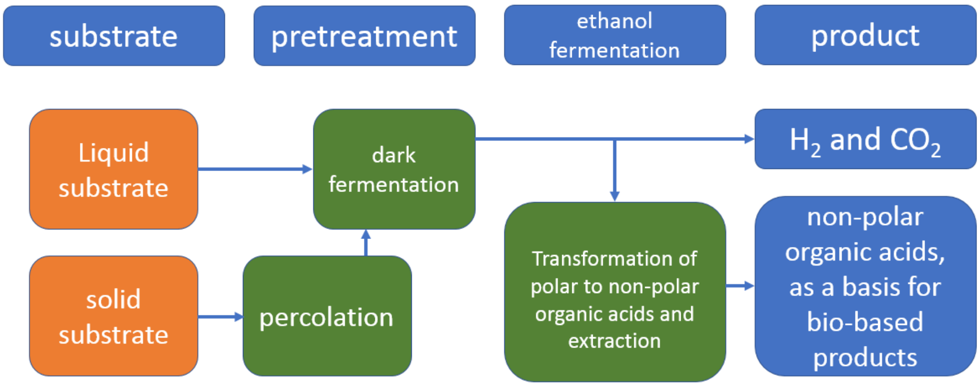

Figure 1. Schematic representation of the process for the production of non-polar carboxylic acids from biogenic waste.

2.1. Dark fermentation

Dark fermentation is an anaerobic process to produce hydrogen (H_2), carbon dioxide (CO_2) and polar organic acids (acetic, propionic and butyric acid) from organic material. The basis of the dark fermentation is the four-stage anaerobic methane production consisting of hydrolysis, acidogenesis formation, acetogenesis and methanogenesis. The difference lies in the inhibition of methanogenic bacteria. As a result, the hydrogen and acetic acid produced during the process is not converted into methane and can be removed from the system (RECHTENBACH, 2009; BRUNSTERMANN, 2010). In order to inhibit methane bacteria during the fermentation, the operating parameters hydraulic retention time (HRT) and pH value are adjusted. On the one hand, the high sensitivity of the methanogenic bacteria to the pH value is exploited. The dark fermentation is carried out at a pH of 5.5 to 6.0, which is to low for methanogenic bacteria and inhibits their metabolism. On the other hand, the system is operated at a HRT of 0.5 to 2 days, which results in any methanogenic bacteria being removed from the system. (BRUNSTERMANN, 2010; JUNG et al., 2011)

2.2 Ethanol fermentation and acid extraction

This fermentation stage is followed by a process phase in which the short-chain, polar carboxylic acids formed in the dark fermentation are converted into non-polar carboxylic acids by the addition of ethanol. This is done according to the chain extension principle discovered by BARKER (1945). BARKER has proven that certain bacteria use ethanol and carboxylic acids for their own metabolism under anaerobic conditions and thereby expand the carboxylic acids chain by two carbon atoms. In this reaction, for example, acetic acid can be extended to butyric acid and this again to hexanoic acid. The following equation shows the principle of chain lengthening using the example of the extension from acetic acid to butyric acid (THAUER et al., 1967; STEINBUSCH, 2010):

$$CH_3COOH + CH_3CH_2OH \rightarrow CH_3(CH_2)_2COOH + H_2O$$

In a next step, the non-polar carboxylic acids contained in the liquid substrates are extracted. For this purpose, a non-polar solvent such as hexane or olive oil ethyl ester is added to the liquid substrates, whereby the formed non-polar acids are transferred from the aqueous, polar phase into the extractant. After the above-mentioned treatment stage, the last step is the back-extraction of the non-polar carboxylic acids from the extractant and the further processing of these acids into bio-based products.

3. Materials

The first research goal was to quantify the influencing factors that sufficiently describe the biological hydrogen and carboxylic acid production. For this, experiments are carried out in a laboratory scale and a semi-technical scale. For laboratory experiments, two hydrogen reactors (CSTR) with a working volume of 35 l were available. As substrates, waste streams were first used, which were incurred in the sugar and beer production. The aim of the laboratory tests is to determine the optimal operation for different substrates. In the next step the results of the laboratory tests are transferred to a semi-technical facility. For this purpose, a CSTR with a working volume of 60 L is available.

4. Results and discussion

The first laboratory tests have shown that dark fermentation can in principle be used to produce hydrogen and carboxylic acids from organic waste. It showed that especially the hydraulic retention time (HRT) is a critical design and operating parameters. It became particularly clear that the HRT mainly depends on the microbiological availability of the substrate used. During the investigations, an optimum HRT of 1 - 2 days for the investigated substrates was determined.
Based on the laboratory tests, the semi-technical plant was then operated with waste streams from the sugar industry. This has a low solids concentration (1 %-VS) as well as small concentration of organic acids (100 – 200 mg HAc / L). With an hourly substrate charge and a HRT of 1 d, an average of 58.56 NL / d of biogas could be formed. The proportion of hydrogen in the gas formed was on average 53 %. The concentrations of organic acids in the output of the hydrogen reactor ranged from 2,200 to 4,400 mg HAc / L. This shows that the concentration of carboxylic acids could be significantly increased by dark fermentation. Further studies showed

that predominantly short-chain acids such as acetic, propionic and butyric acid are formed.

In a further trial phase, the hydrogen reactor was operated with a waste stream from brewing industry. In contrast to the previous substrate this had a higher solids content (4 %-VS) and already contained a larger amount of carboxylic acids (<1,000 mg HAc / L). Based on the results of the laboratory experiments, the reactor was operated at HRT of 2 d. Under these conditions, it was possible to extract on average of 76.2 liters biogas from the substrate and increase the concentration of organic acids to 6,000 – 8,000 mg HAc / L. Figure 2 shows the course of the concentration of organic acid in the substrate and reactor as well as the VS in the reactor over the test period. When operating the hydrogen reactor with percolate from the composting, the acid concentration can be increased from 34,840 mg HAc / L to 48,320 mg HAc / L on average by dark fermentation.

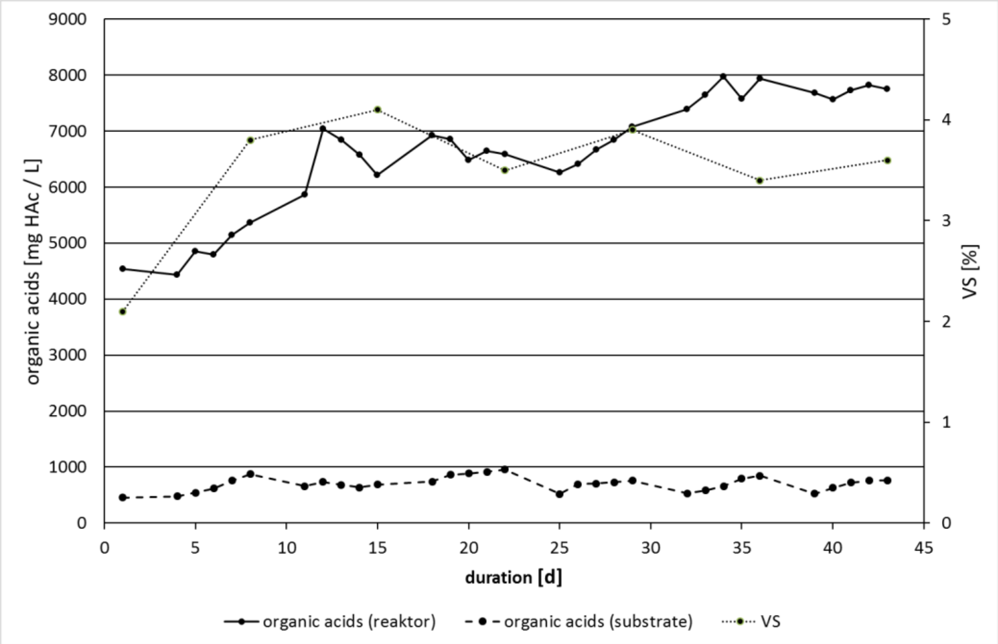

Figure 2: acid concentration in reactors and substrate and VS content over test period with brewing waste stream

5. Conclusions and perspectives

The experiments carried out so far demonstrate that it is possible to recover short-chain carboxylic acids from biogenic waste streams. In addition, dark fermentation offers the possibility of obtaining hydrogen as an energy carrier. In the next project phases, the short-chain carboxylic acids will be converted in an additional processing step, ethanol fermentation, to longer-chain acids. Additionally, further biogenic waste streams will be examined for their suitability for this process. For this purpose, biowaste with a high solids content should undergo a solid-liquid separation e.g. by percolation. The liquid is then examined for its suitability in the procedure.

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