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ANALYSIS OF SECONDARY WASTE FROM A PLASTICS RECYCLING PLANT FOR THE PRODUCTION OF CARBOXYLIC ACIDS

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ABSTRACT

The production of bio-based platform chemicals through the chain elongation of short-chain carboxylic acids to medium-chain carboxylic acids by ethanol-acetat fermentation can be a contribution to the circular economy. To avoid further waste, secondary waste that already contains short-chain carboxylic acids can be used. The potential for the production of bio-based carboxylic acids from a secondary waste of a recycling plant for plastic waste is examined in this paper. Therefore, practical experiments with the process water of a recycling plant for plastic waste were conducted in order to assess the potential for carboxylic acids production. At the end of the experiment, the concentrations achieved by chain elongation in the secondary waste result in 496 mg/L butyric acid and 87 mg/L caproic acid and the concentration in the extraction solvent is 933 mg/L caproic acid. To conclude, chain elongation of carboxylic acids in secondary waste, in this case the process water from a treatment plant for plastic waste, is generally possible. In order to estimate the total potential for the production, the fluctuations of the quality of the process water have to be considered.

1. INTRODUCTION

Primary fossil raw materials are limited and their demand is steadily increasing (BMBF & BMEL, 2020). According to the Organisation for Economic Co-operation and Development, the use of primary raw materials such as biomass, fossil fuels, metals and non-metallic minerals will double by 2060 (European Union, 2020, p. 4; OECD, 2019, p. 19).

The bioeconomy is defined in the national bioeconomy strategy of the Federal Government of Germany as "the production, development and use of biological resources, processes and systems to provide products, processes and services in all economic sectors within the framework of a sustainable economic system" (BMBF & BMEL, 2020, p. 10). The national bioeconomy strategy follows the Sustainable Development Goals of the United Nations and aims to ensure for example sufficient food, health, economic growth, sustainable consumption and production as well as humane work by 2030. For this purpose, raw materials from agriculture, forestry and marine management as well as biogenic residues and waste materials are to be used (BMBF & BMEL, 2020).

A transition from a linear economy to a circular economy is also required. As part of the European Green Deal, the New Circular Economy Action Plan was published in March 2020. It introduces new initiatives that consider the entire life cycle of products, modernise and transform the European economy and protect the environment at the same time. The aim of the New Circular Economy Action Plan is to take action to prevent and reduce waste (European Union, 2020).

A combination of circular economy and bioeconomy is described as circular bioeconomy. Stegmann et al. define it as follows: "The circular bioeconomy focuses on the sustainable, resource-efficient valorization of biomass in integrated, multi-output production chains (e.g. biorefineries) while also making use of residues and wastes and optimizing the value of biomass over time via cascading." (Stegmann et al., 2020, p. 5). Therefore, the development and investigation of existing secondary waste in relation to circular bioeconomy is important.

To contribute to circular bioeconomy, an experimental approach is utilized to produce bio-based chemicals from secondary waste. Secondary waste is waste that originates from a waste treatment process, e.g. residues from recovery and disposal processes (European Union, 2015). These include organic compounds with one or more carboxy groups (-COOH) (Federle et al., 2017) which are classified depending on the number of carbon atoms into short-chain (1-3 carbon atoms), medium-chain (4-10 carbon atoms) and long-chain (>10 carbon atoms) carboxylic acids (Hopp, 2018). These are conventionally generated by chemical synthesis from petroleum-based resources or by

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the synthesis of natural oils (e.g. coconut or palm kernel oil) (Anneken et al., 2012).

Short-chain carboxylic acids (SCCA) in a secondary waste are converted into medium-chain carboxylic acids (MCCA) during a biotechnological treatment process with the help of specialised microorganisms and ethanol as a nutrient. This biotechnological treatment process is described as acetate-ethanol fermentation (Angenent et al., 2016). The separation of these carboxylic acids takes place during the treatment process as an in-situ extraction (liquid-liquid extraction) using a non-polar extraction solvent. These carboxylic acids can be used for the production of bio-based materials and thereby have a positive impact on the circular bio-based economy (bioeconomy). For example, precursors for lubricants and tensides can be produced (Sarria et al., 2017; Wang & Yin, 2022, p. 1). This type of waste management corresponds to material recycling according to article 4 number 1 c) of the European Waste Framework Directive (Directive 2008/98/EC).

In order to preserve primary fossil raw materials, it is essential to identify further secondary waste that can be used for the production of medium-chain carboxylic acids. A large number of different secondary waste types have already been analysed regarding the potential for the production of bio-based carboxylic acids. These include, for example, sewage sludge and municipal solid waste leachate (Wang & Yin, 2022). But also organic residues can be used, such as ethanol-containing secondary waste (yeast of beer production, wine fermentation residue (Groof et al., 2019), liqueur production (Wang & Yin, 2022), secondary waste from quark, yoghurt and cheese industry (Groof et al., 2019), swine manure or fermented sugar cane (Wang & Yin, 2022)).

In this study, the potential for a cascading utilisation of a secondary waste from a treatment plant for plastic waste is further considered, as the literature research revealed that such a secondary waste has not yet been analysed.

2. MATERIALS AND METHODS

2.1 Materials

For the experiments, secondary waste of a recycling plant for plastic films is considered. Here, the process water which is produced during the necessary washing process of the plastic films in the recycling process is used. After being treated, the process water is internally recirculated. The secondary waste already contains short-chain carboxylic acids and was used in the experiments without any addition of inoculum. A mixed bacteria culture is expected in the secondary waste, which is able to carry out ethanol-acetate fermentation. There were no detailed analyses conducted to characterise the bacteria cultures.

For the recovery of the produced medium-chain carboxylic acids a liquid-liquid extraction is applied with rapeseed methyl ester (SysKem Chemie GmbH; fatty acid methyl ester C16 - C18) as a solvent. Previous experiments at the University of Applied Sciences Darmstadt indicated that this solvent is suitable in combination with the biological process. Thus, it is added to the secondary waste in a volume ratio of 1:10.

Ethanol is also required as a nutrient for chain elongation (Carl Roth; ethanol 96% denatured) and is added into the secondary waste in a concentration of 9 g/L, since according to Sarkar et al. (2021, p. 8) the highest caproic acid production during chain elongation resulted from this concentration.

2.2 Experimental setup

2.2.1 Reactor setup

For the experiments, a stirred batch reactor with an integrated liquid-liquid extraction is used. The maximum capacity of the reactor is approximately 16 litres, with a final operating capacity of 14 litres. The reactor is airtight to allow an anaerobic milieu. The oxygen present in the headspace is displaced with inert gas at the beginning of the experiments. The stirrer motor (Brushless DC Motor, BPC Instruments AB) rotates the stirrer which consists of a combination of a diagonal flat blade stirrer and an anchor stirrer (Hemming & Wagner, 2017). The average rotation speed is 70°RPM.

There are two sampling devices for taking a composite sample of the secondary waste. Due to the integrated liquid-liquid extraction, the non-polar extraction solvent settles on the polar secondary waste. Since sampling takes place regularly, the filling level of the reactor is changing and thus also the sampling point of the extraction solvent. Therefore, a sampling device is required that can take a sample from the extraction solvent at any time. For this purpose, a floater is connected to a sampling device via a flexible tube. During each sampling, the volume that remains in the sampling device is to be discarded. For the regulation of the process temperature during the experiments the reactor setup is placed in a temperature-controlled room. Figure 1 illustrates the described experimental setup and the technical implementation.

2.2.2 Operating parameters

Four reactors with contents listed in Table 1 were used for the experiments. A double determination of the chain elongation with integrated liquid-liquid extraction (CE-LLE), one reactor without chain elongation but with liquid-liquid extraction (LLE) and one blind reactor with only secondary waste were used.

The experiment period is four weeks (28 days) at an operating temperature of 37°C ± 1. The pH-value of the secondary waste should range between 6.0 and 6.5 in order to inhibit the possible formation of methane. The pH-value is adjusted to 6.0 with hydrochloric acid (c = 2.87 mol/L) as required at the beginning of the experiments.

TABLE 1: Overview of composition in reactor (CE = chain elongation, LLE = liquid-liquid extraction).

reactor	secondary waste	extraction solvent	ethanol
CE + LLE 1	12 L	1.2 L	9 g/L
CE + LLE 2	12 L	1.2 L	9 g/L
LLE	12 L	1.2 L	-
Blind	12 L	-	-

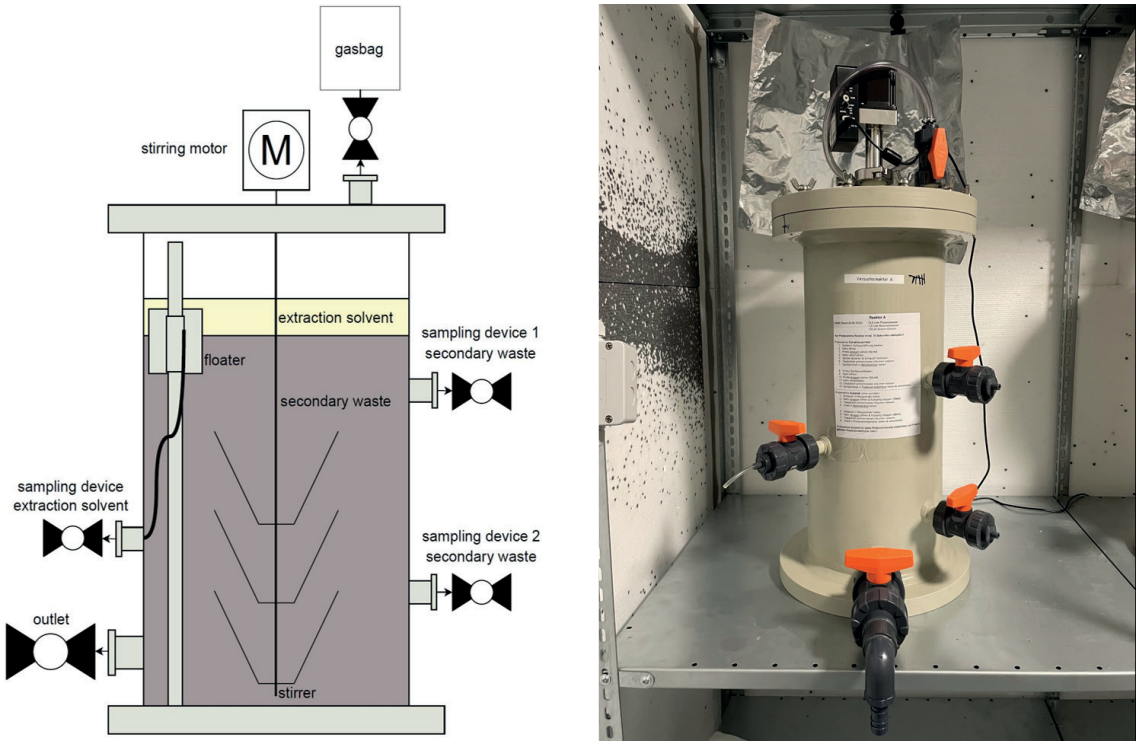

FIGURE 1: Schematic drawing of reactor setup (left) and technical implementation (right).

2.2.3 Technical sampling of secondary waste and extraction solvent

Sampling takes place twice a week. First, the stirrer is switched off one hour before sampling to ensure that the extraction solvent settles completely on the surface of the secondary waste. Firstly, 12 ml of extraction solvent is discarded, afterwards 10 ml of the extraction solvent is taken for each sample. This is followed by the sampling of the secondary waste. At first, sampling device 1 is sampled. 15 ml is discarded, and 20 ml secondary waste sample is taken. The procedure is repeated for sampling device 2. A composite sample is generated from the two secondary waste samples.

2.3 Analytical methods

The on-site analyses include all parameters taken immediately after sampling. These include the pH-value, the redox potential and the conductivity in the secondary waste sample.

The pH-value indicates whether the ideal conditions for the microorganisms of chain elongation are present in the secondary waste.

The redox potential indicates whether there is an aerobic or anaerobic milieu in the secondary waste. If the value of the redox potential is below minus 330 mV (Wiese & König, 2007), the milieu is to be regarded as anaerobic. This is a necessary condition for microorganisms responsible for the biological chain elongation.

After the on-site analysis, the samples of secondary waste are stored at approximately minus 20°C until further analysis. The extraction solvent samples are stored at room temperature until further analysis.

To characterise the secondary waste in more detail, the samples are defrosted. The chemical oxygen demand (COD) is determined photometrically by using cuvette tests (LCK 514, 100 - 2,000 mg/L O_2 and LCK 014 1,000-10,000 mg/L O_2, Hach Lange GmbH). In order to monitor the degradation of the additive ethanol, its concentration in the secondary waste of the CE-LLE reactors is also determined photometrically by using cuvette tests (LCK 300, 0.01-0.12 g/L, Hach Lange GmbH).

The carboxylic acids in the secondary waste as well as in the extraction solvent are analysed by gas chromatography with flame ionisation detection (GC-FID). The gas chromatograph (Shimadzu GC2025) is equipped with a Thermo Scientific TG-WAXMS A capillary column (length: 30 m; inner diameter: 0.32 mm; film thickness 0.5 µm). Helium was used as carrier gas with a flow rate at 29.1 ml/min. For the samples of secondary waste 1 µL was injected into a split injector with a split ratio of 1:10. The following column oven programme was used for the samples of the secondary waste: heating up to 80°C for 2 minutes and continuing at a rate of 20°C per minute to 235°C for 5 minutes. For the samples of the extraction solvent 0.5 µL was injected into a split injector with a split ratio of 1:10. The following column oven programme was used for the samples of the extraction solvent: heating up to 80°C for 2 minutes, continuing at a rate of 10°C per minute to 180°C and with a rate of 5°C per minute to 235°C for 10 minutes. The samples of the secondary waste as well as the samples of the extraction solvent need to be prepared for the measurements. For this purpose, the samples of the secondary waste are acidified and diluted 1:10 and 1:100 with an acetone-water mixture (ratio 1:1). It is also necessary to filter the samples

with a PTFE syringe filter (pore size 0.45 µm) before the measurements. Whereas the samples of the extraction solvent need to be filtered with a PTFE syringe filter (pore size 0.45 µm) before the 1:10 dilution with n-hexane.

Furthermore, the composition of the collected gas in the gas bags are analysed by means of a biogas analyser (BM 5000, Geotech).

2.3.1 Analysis

For the analysis, only the carboxylic acids in the reactors with chain elongation and integrated liquid-liquid extraction (CE-LLE) are considered. The reactor without chain elongation but with liquid-liquid extraction (LLE) and the reactor without chain elongation and without liquid-liquid extraction (blind) are used as a monitor for the chain elongation by ethanol-acetate fermentation. The concentrations of carboxylic acids in the CE-LLE reactors are given as averaged absolute amounts. Therefore, the total amount of generated carboxylic acids is determined and a ratio of the amount of generated carboxylic acids in the secondary waste and in the extraction solvent is obtained.

3. RESULTS AND DISCUSSION

3.1 On-site analysis of secondary waste

During the experimental period, the temperature of the secondary waste in the reactors was measured continuously at 36.6°C ± 0.1.

The pH-value of the untreated secondary waste was pH 6.9. This was adjusted to pH 5.9 before the start of the experiments with hydrochloric acid. During the experiment the pH-value of the CE-LLE reactors decreased to pH 5.1. This may be caused by forming of carboxylic acids in the secondary waste. In the reference reactors, the pH-value increased to pH 6.6 for LLE and to pH 6.8 for blind. This may be responsible for the biogas formation in these reactors at the end of the experiment.

The composition of the collected gas took place at the end of the experiment period. The reference reactors produced about 3 L (LLE) and about 8 L (blind) over the entire experiment period. The LLE reactor produced 30 vol% of methane and 15 vol% of carbon dioxide. The blind reactor produced 50 vol% of methane and 20 vol% of carbon dioxide. The CE-LLE reactors produced about 1 L gas, which consisted mainly of the inert gas nitrogen at 85 vol%. It is assumed that this is due to the fact that the utilised bioreactor has a headspace volume of approximately three litres. At the beginning of the experiment, the headspace is filled with the inter gas nitrogen to ensure the necessary anaerobic conditions for the treatment process. If the biological process produces gas, at first the inert gas is led into the connected gas bag and is analysed.

There is no clear tendency in the redox potential determination. The analyses of the CE-LLE and LLE reactors do not indicate an anaerobic environment over the entire experiment period. In the blind reactor, predominantly anaerobic redox potentials can be recognised over the entire experiment period. The unsteady measurements of the redox potentials may be caused by the high salt content in the secondary waste. These are on average 22 mS/cm for the CE-LLE reactors and 23 mS/cm for the LLE and blind reactors.

3.2 Characterisation of secondary waste

At the start of the experiments, the chemical oxygen demand (COD) of the untreated secondary waste was 2.98 g/L O_2. With the addition of ethanol, the COD increased by a factor of five and reached on average 16.89 g/L O_2 in the CE-LLE reactors. The LLE and the blind reactor did not show higher values of COD (3.20 g/L O_2 and 3.01 g/L O_2) compared to the secondary waste at the start of the experiments. In the course of the four-week experiments, the COD remained almost constant. A slightly increased COD of the CE-LLE reactors to 17.21 g/L O_2 can be recognised. The COD of the LLE and the blind reactor decreased to 3.13 g/L O_2 and 2.29 g/L O_2 at the end of the experiments.

At the beginning of the experiments, 9.00 g/L ethanol was added to the CE-LLE reactors. Over the treatment period of 28 days, a degradation of the ethanol can be recognised. After the first three days of the experiment, an average of 7.00 g/L ethanol can be measured in the secondary waste. A continuous degradation of ethanol to 4.85 g/L at the end of the test period can be determined. This means that about 50 percent of the added ethanol was degraded. Due to the low production of gas in the reactors with chain elongation and liquid-liquid extraction, it can be presumed that the degraded ethanol contributed to the formation of the medium-chain carboxylic acids. The reduction of the ethanol during the experimental period is illustrated in Figure 2.

3.3 Potential for carboxylic acid formation

The carboxylic acids in the secondary waste and in the extraction solvent were analysed using GC-FID. In order to assess, if the secondary waste is suitable for forming carboxylic acid, the concentrations of acids were obtained and then allocated against the corresponding quantities to be able to compare the results. Therefore, the results refer to the 12 litres of secondary waste. Figure 3 presents the total amount of butyric acid (C4; in orange) and caproic acid (C6; in blue) summarized for secondary waste and extraction solvent over the experiment period in milligrams. Butyric and caproic acid were chosen as they showed the highest potential within the experiment.

The results show that there is no change in the amount of butyric and caproic acid until the tenth day of the experiment. Nevertheless, it must be mentioned that these results are only slightly above the lower limit of determination of 5 mg/L. An increase of butyric acid to 5,514 mg and caproic acid to 2,583 mg is noticeable by the tenth day of the experiment. Until the end of the experiment, these continue to rise to a maximum of 7,735 mg butyric acid and 3,786 mg caproic acid.

These results show in general, that forming butyric acid and caproic acid from secondary waste is possible. Furthermore, the potential resulting from the chain elongation of the carboxylic acids can be compared. Therefore the generated carboxylic acids in the secondary waste and in the extraction solvent (CE-LLE) were compared to those in the reference reactors (blind and LLE). An increase of

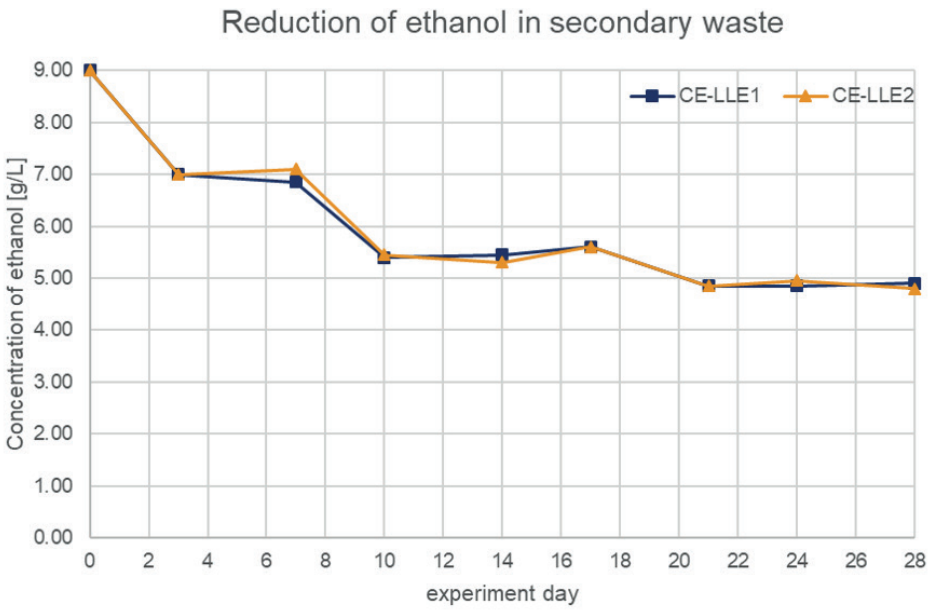

FIGURE 2: Reduction of ethanol in secondary waste in reactors with chain elongation and liquid-liquid extraction (CE-LLE).

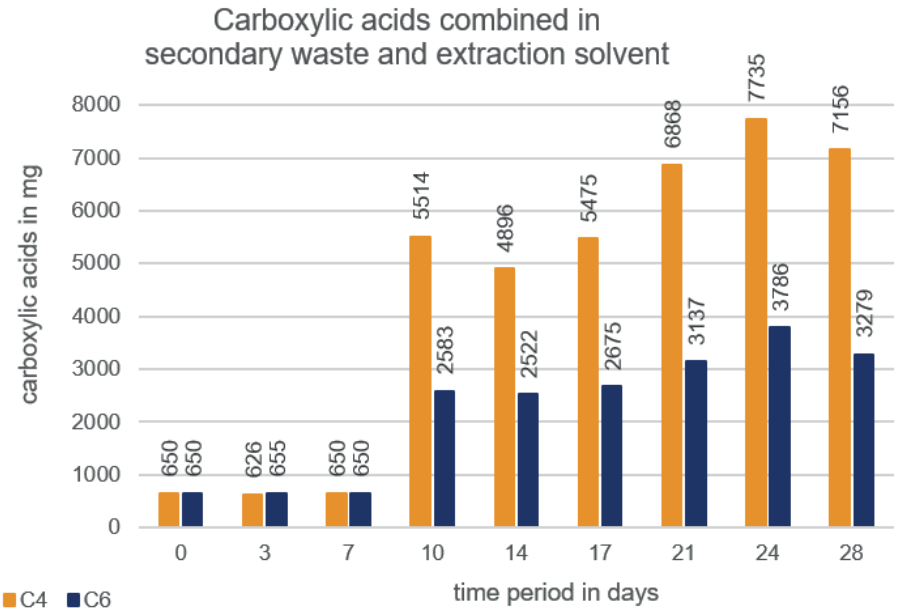

FIGURE 3: Total amount of butyric acid and caproic acid over the experiment period summarized for secondary waste and extraction solvent.

carboxylic acids in relation to the reference reactors is indicated. In this context, 100 percent refers to the reference reactors.

Figure 4 illustrates the percentage deviation in secondary waste with chain elongation and without. Figure 5 shows the percentage deviation in the extraction solvent with and without chain elongation. As previously butyric and caproic acid were chosen for the comparison, based on the results of the experiments.

As already shown in Figure 3, there is no increase in butyric or caproic acid until experiment day ten. Figure 5 shows that on experimental day ten the butyric acid increased by 821% due to the chain elongation, which corresponds to 4,837 mg. In comparison to the reference reactor, caproic acid increased to 221% or 1,305 mg. During the experiments the deviation decreases. Due to the chain elongation, an increase of 512% or 5,846 mg more butyric acid can be detected at the end of the experiment. The deviation of caproic acid also decreases. At the end of the experiment, 90% or 1,026 mg additional caproic acid has been formed by the chain elongation.

Considering Figure 5, the delayed start is also noticeable. From day ten of the experiment, a deviation from the extraction solvent without chain elongation of 1,116% or 633 mg caproic acid can be seen. Only a small amount of butyric acid was transferred to the extraction solvent. On

experiment day 24 an increase of 206% or 108 mg butyric acid was extracted by the chain elongation. By the end of the experiment, the deviation rises to 2,069% or 1,059 mg caproic acid.

These figures illustrate that through chain elongation of short-chain carboxylic acids, medium-chain carboxylic acids can be formed in secondary waste and subsequently be extracted. At the same time, the results indicate that more butyric acid accumulates in the secondary waste and more caproic acid in the extraction solvent. This may be explained by the decreasing polarity of the carboxylic acids with increasing chain length. As a result, caproic acid is less polar and the transition into the extraction solvent is higher.

4. CONCLUSIONS

For the production of bio-based platform chemicals in the form of carboxylic acids, the process water from a treatment plant for plastic waste was examined as a secondary waste stream.

The experiments showed that the formation of carboxylic acids started with a delay of ten days. Specifi-

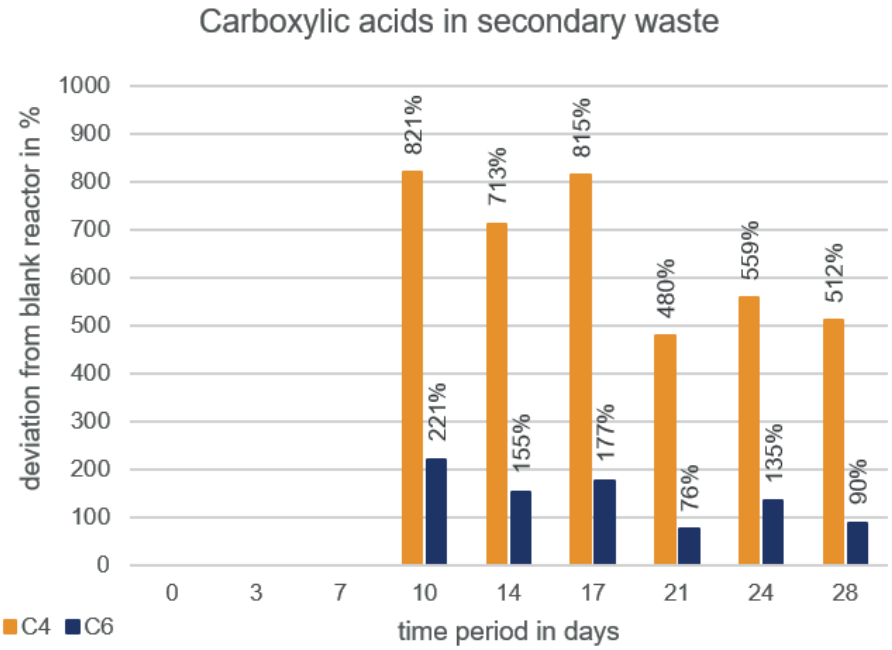

FIGURE 4: Percentage deviation of generated butyric acid and capronic acid in secondary waste with and without chain elongation.

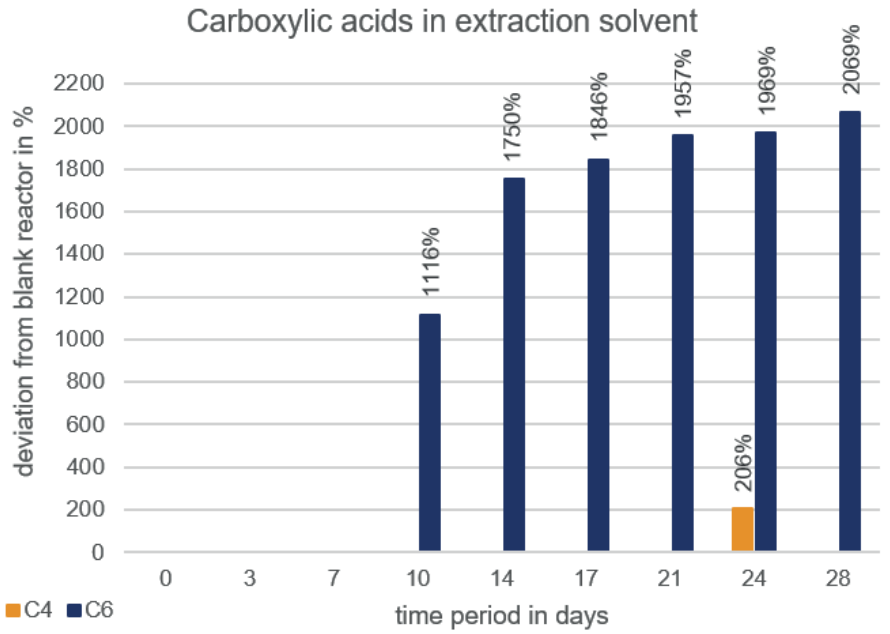

FIGURE 5: Percentage deviation of generated butyric acid and capronic acid in extraction solvent with and without chain elongation.

cally, the formation of butyric acid and caproic acid were considered. By the end of the experiment, 5,846 mg additional butyric acid were formed in the secondary waste compared to untreated secondary waste (reference reactor blind). On the other hand, 1,026 mg caproic acid was detected in the secondary waste at the end of the experiment. Additionally, 1,059 mg caproic acid was extracted. These amounts of carboxylic acids refer to the 12 litres of secondary waste treated in the experiment by consuming 3 kW of electrical energy and about 50 grams of ethanol. Therefore, the concentrations achieved by chain elongation in the secondary waste at the end of the experiment result in 496 mg/L butyric acid and 87 mg/L caproic acid and the concentration in the extraction solvent is 933 mg/L caproic acid.

To conclude, chain elongation of carboxylic acids in secondary waste, in this case the process water from a treatment plant for plastic waste, is generally possible. However, due to fluctuating concentrations of carboxylic acids in the original material in these experiments, the amounts of carboxylic acids detected are comparatively low and thus the potential of the examined secondary waste also is very low. Preliminary tests have shown higher concentrations. Therefore, in order to estimate the total potential for the production, the fluctuations of the quality of the process water have to be considered.

Furthermore, the experiments were realised without an inoculum. The use of already existing microorganisms in an inoculum could probably increase the potential.

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