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UPGRADING POTENTIAL OF WASTE FERMENTATION-BASED C4-C5-C6 CARBOXYLIC ACID MIXTURES USING ELECTROCHEMICAL OXIDATIVE DECARBOXYLATION

TAMÁS RÓZSENBERSZKI[1], KATALIN KUCSERA[1], BOGLÁRKA BOCSKA[1], GERGELY FARKAS[2] AND LÁSZLÓ KOÓK[1]*

1 Research Group on Bioengineering, Membrane Technology and Energetics; University of Pannonia; Egyetem u. 10; Veszprém; 8200; HUNGARY
2 Research Group of Organic Synthesis and Catalysis, University of Pannonia, Egyetem u. 10, Veszprém, 8200, HUNGARY

Electrochemical upgrading techniques could provide a powerful tool to complement biorefineries processing waste materials, thereby making progress towards the electrification of these platforms. Among them, (non)-Kolbe electrolysis, that is, electrochemically driven oxidative decarboxylation of carboxylic acids, plays a key role as its product palette consists of alkanes (Kolbe products) as well as competing non-Kolbe products, including short-chain alkenes, alcohols, esters, ketones and aldehydes. The formation of alkanes takes place via the dimerization of radicals after the decarboxylation of carboxylic acids and requires relatively high acid concentrations (> 0.5 M) and a high current (> 200 mA cm^{-2}). In this work, the upgrading potential of VFA mixtures of C4-C5-C6 acids under conditions representing real waste-based fermentation effluents (lower VFA concentrations) and a suboptimal current density (100 mA cm^{-2}) was investigated. In addition, the effect of the initial VFA concentration ratios and the operation time (Faraday equivalents of FE = 0.25 and 1.0) on product selectivity and yields was studied. It was shown that mostly non-Kolbe products were formed – namely alcohols, esters and smaller amounts of ketones – in both experiments. An extended operation time favored ester and ketone formation, while alkanes (octane, nonane and decane) were presumably produced at the beginning of the electrolysis, since the process duration did not influence their yields. In addition, since butyric acid – the compound with the highest concentration in both model solutions – participated mostly in alcohol and ester formation, no butyrate radical dimerization (resulting in hexane) was observed. The results indicate that by not concentrating the VFAs in the fermentation effluents (via e.g. electrodialysis), the oxidative decarboxylation of VFAs at low/moderate current densities will likely result in non-Kolbe products.

Keywords: carboxylic acid, electrochemical upgrading, esters, Kolbe electrolysis, liquid alkanes

1. Introduction

The electrification of biorefineries is a strategy with enormous potential to achieve efficient Power-to-X for the utilization and (chemical) storage of excess renewable electricity. As a result, X can refer to various industrially interesting compounds such as hydrogen [1]-[3], methane [4], ammonia [5] as well as even food [6] and fuels [7]. State-of-the-art electro-biorefineries underline the importance of targeting components with high specific value since the main technological limits appear to be scaling up and productivity. Therefore, specialty chemicals and fuel components are of particular interest.

Although examples of studies related to specialty chemicals (e.g. the enantioselective bioelectro-synthesis of chiral alcohols for the pharmaceutical industry) are found in the literature [8]-[9], this approach assumes the use of pure (and often genetically engineered) cultures and specific reaction media / high process costs. Meanwhile, valuable compounds can be produced by mixed culture systems based on organic waste such as volatile fatty acids (VFAs) – referring to carboxylic acids containing 2-8 carbon atoms – via acidogenic dark fermentation (DF) [10]. In most cases, ethanol or lactate-driven chain elongation during DF facilitates the production of VFAs up to caproic acid (C6). After separation, the market value of the obtained VFAs is already remarkable, however, in a biorefinery platform, their upgrade to value-added chemicals is often considered via chemical, electrochemical and biological post-treatment processes. Among them, electrochemical methods could be considered as drivers to demonstrate electrified biorefineries.

The (bio)electrochemical reduction of VFAs, for instance, could be used to obtain the respective alcohols [11]. Another promising approach is the so-called Kolbe

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*Correspondence: kook.laszlo@mk.uni-pannon.hu

electrolysis, which involves anodic electrochemical decarboxylation. Oxidation of the VFAs leads to free radicals which, under suitable conditions, can dimerize to form linear alkanes with a carbon chain length of C(2*n*-2), where *n* denotes the number of carbon atoms of the VFA (for example, valeric acid, C5, results in octane, C8) [12]. On the one hand, Kolbe electrolysis has several major advantages such as the spontaneous separation of the alkane-rich phase from the aqueous VFA solution or the formation of excess H_2 at the cathode during electrolysis, thereby contributing to the hydrogen yield in addition to the DF. On the other hand, besides the necessity of using a Pt catalyst, several challenges limit the applicability of Kolbe electrolysis, including selectivity issues (the utilization of free radicals in non-Kolbe side reactions, e.g. alcohol, ester and ketone formation) as well as the requirement of usually high initial VFA concentrations (> 0.5 M) and current densities (> 200 mA cm^{-2}) [13].

In this work, the liquid alkane production selectivity and efficiency of Kolbe-electrolysis are investigated using model mixtures of C4, C5 and C6 VFAs representing acid ratios in real acidogenic fermentations, i.e. under suboptimal conditions. In addition, the effect of the operation time (or supplied charge) on the product composition is addressed.

2. Experimental

2.1. Model VFA solutions

Mixtures of butyric (C4), valeric (C5) and caproic (C6) acid (Merck, Germany) were prepared by diluting with distilled water. The applied ratios of initial concentrations of C4:C5:C6 acids were 0.23:0.11:0.083 M and 0.40:0.04:0.077 M in experiments A and B, respectively, based on the experienced titer range of previous fermentations (data not shown). The pH of the solution was set in both cases at 7 using 5 M NaOH.

2.2. Kolbe electrolysis tests

Kolbe electrolysis was carried out in a 100 mL customized Schott laboratory glass bottle reactor in experiment A containing 80 mL of a model VFA solution. In experiment B, the reaction took place in an 80 mL heart-shaped borosilicate glass reactor with ground-glass joints, enhancing how efficiently the produced gases were collected. The reaction media volume was 60 mL. The electrolysis was conducted using two Pt plate electrodes with a surface area of 2 cm^2 each. Galvanostatic control was applied by using a Keysight E3643A DC power supply (Keysight, USA), ensuring a fixed current density of j = 100 mA cm^{-2}. The reactors were connected to a 100 mL gas syringe by Tygon® tubing to measure gas evolution before the collected gaseous samples were transferred to 500 mL aluminum gas sampling bags.

In experiment A, the operation time was limited by the transfer of charge of Q = 1000 C, corresponding to t = 83 mins. In experiment B, the transferred charge was Q = 4000 C corresponding to t = 333 mins. These values represent Faradic equivalents of FE = 0.25 and 1.0, respectively, where FE represents the ratio of the charge required to achieve complete substrate conversion and the actual transferred charge.

2.3. Extraction and analysis of the organic phase

After electrolysis, the reaction media was transferred to a 250 mL glass separatory funnel before 40 and 30 mL of dichloromethane was added in experiments A and B, respectively. The mixture was then shaken vigorously and left to separate over 30 mins. After the bottom organic layer was removed, the procedure was repeated to ensure complete extraction was achieved. The collected extraction solution was analyzed via gas chromatography – mass spectrometry (GC-MS) using a Shimadzu GCMS-QP2010 SE (Shimadzu, Japan) spectrometer with an AOC-20i auto-injector. The injector (split) temperature was 250 °C and He (6.0) was used as the carrier gas. An Agilent J&W DB-5ms column (Agilent, USA) was applied. The heating program was set to 35 °C for 5 mins before being increased to 300 °C at a rate of 20 °C/min.

2.4. Analysis of aqueous samples

The VFA content of the aqueous phase after the electrolysis was determined via GC using a Shimadzu GC-2014 gas chromatograph (Shimadzu Corporation, Japan) with a flame ionization detector. Injection port and detector temperatures were 240 and 250 °C, respectively. The length and inner diameter of the DB-FFAP column were 10 m and 0.53 mm, respectively, with a film thickness of 1 µm. The column temperature was initially 50 °C over 2 mins before gradually being increased to 200 °C at a rate of 40 °C/min and maintained at 200°C for 2 mins. This device was equipped with an AOC-20i auto-sampler and N_2 was used as the carrier gas.

2.5. Calculations

The transferred charge was calculated according to the following equation, considering the applied current I_{appl} and the reaction time:

$$Q = I_{appl} \cdot t \quad (1).$$

The acid conversion (μ_{VFA}) and yield of product i (Y_i) were determined based on the initial ($n_{VFA,in}$) and final ($n_{VFA,fin}$) amount of VFA as well as the amount of dimer produced (n_{dimer}) according to the equations below:

$$\mu_{VFA} = 100 \times \frac{(n_{VFA,in} - n_{VFA,fin})}{n_{VFA,in}} \quad (2),$$

$$Y_i = 100 \times \frac{z \times n_i}{(n_{VFA,in} - n_{VFA,fin})} \quad (3).$$

where z denotes the ratio of product to VFA molecules (z = 1 for alcohols, ketones, aldehydes and alkenes but z = 2 for alkanes and esters).

3. Results and discussion

3.1. VFA conversion efficiency

The relatively short operation time (FE = 0.25) applied in the first experiment (A) is indicative of a limited degree of VFA conversion. From the results presented in *Figure 1*, it can be seen that the degree of conversion was indeed limited. The lowest value was obtained for butyrate (μ_{C4} = 19.3%), which was expected being the dominant component of the model solution and corresponds with Δn_{C4} = 3.56 mmol. Meanwhile, C5 and C6 acids yielded μ_{C5} = 24.1% (Δn_{C5} = 1.70 mmol) and μ_{C6} = 28.5% (Δn_{C6} = 1.28 mmol), respectively.

Experiment B (FE = 1.0) aimed to provide insights into rather suboptimal conditions for Kolbe electrolysis in terms of concentrations of VFAs – especially C5 and C6 acids – significantly lower than recommended in the literature. Nevertheless, such conditions represent potential compositions of real dark fermentation effluent without taking into consideration concentrating the acid content (e.g. by selective extraction or electrodialysis). As for the conversion of VFAs during electrolysis when FE = 1.0, high values were expected thanks to the longer operation time and lower concentrations. Indeed, conversions of C4, C5 and C6 VFAs up to 35.4, 70.1 and 72.4% could be achieved, respectively (*Figure 1*). The corresponding amounts were Δn_{C4} = 8.48, Δn_{C5} = 1.68 and Δn_{C6} = 3.34 mmol.

It could be observed from the results that absolute VFA conversion is proportional to the initial VFA concentrations in both cases. This shows that the electrolysis showed no notable degree of selectivity towards particular carboxylic acids. Therefore, electrooxidative decarboxylation takes place independently and in parallel for each VFA. Accordingly, the product composition can be estimated from the initial VFA content when the product selectivity of a certain VFA is known. This aspect is discussed in the next Section.

3.2. Product selectivity and yields

Kolbe electrolysis results in alkanes after the dimerization of decarboxylation-originated C(*n-1*) radicals. However, the competing processes, namely the synthesis of non-Kolbe products, may significantly reduce dimer selectivity. Predominantly, alcohols as well as esters (via the reactions between alcohols and present carboxylic acids) form but aldehydes, ketones and short-chained alkenes can also be produced. Moreover, O_2 evolution on the anode is a known competing reaction. Overall, more hydrophobic VFAs, higher VFA concentrations and higher current densities promote the formation of the Kolbe product. In contrast, the present experimental setups focus on the composition of real

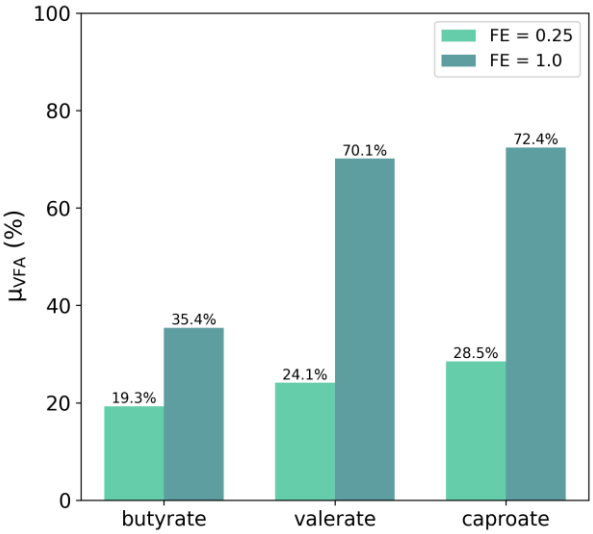

Figure 1: Conversion values of butyrate, valerate and caproate when FE = 0.25 and 1.0

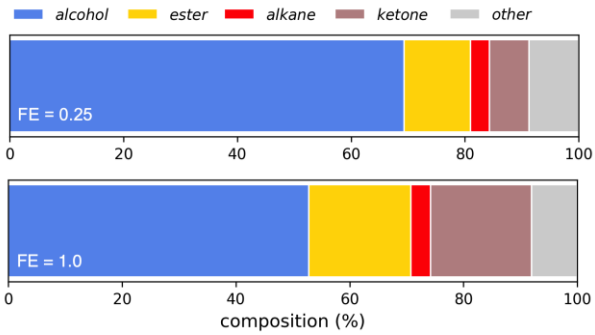

Figure 2: Final product composition in terms of main compound groups when FE = 0.25 and 1.0

waste-based dark fermentation effluents and intentionally investigate the process efficiency at lower current densities compared to in the literature.

As for the results for the tests when FE = 0.25 and 1.0, a fairly consistent product composition could be observed. Firstly, in the case of experiment A, almost 70% of the electrolysis products were identified as alcohols (*Figure 2*). Esters and alkanes accounted for 11.7 and 3.3%, respectively, moreover, a notable amount of ketones (7.0%) was identified in addition to minor components. Similarly, when FE = 1.0, alcohols were the dominant products accounting for 52.8%, while esters, alkanes and ketones accounted for 18.0, 3.4 and 17.8%, respectively (*Figure 2*).

It could be observed that alcohol production was predominant and, consequently, in the presence of excess carboxylic acids, considerable amounts of esters were formed, which was also observed when FE = 1.0 implying that, over time, the formation of esters exceeds the accumulation of alcohols. Similarly, the amount of generated ketones rose significantly as the operation time lengthened. Meanwhile, the final ratio of alkanes in the product mixture was nearly equal in both experiments regardless of the electrolysis duration suggesting that under the applied conditions, Kolbe-product formation

presumably occurs in the early phase of electrolysis and probably becomes suppressed as the non-Kolbe reactions proceed. This aspect, however, should be confirmed by follow-up experiments with more frequent sampling of the reaction media during the operation time. It is also important to mention that aldehyde formation was observed only in traces, while short-chain alkanes and alkenes were not detected in the samples.

To further evaluate product formation, the specific component yields are presented in *Figure 3*. Considering the alcohols, the most significant difference is that when FE = 0.25, a high yield of propan-2-ol (or isopropanol) was observed, while when FE = 1.0, this compound was not observed. It can be argued that thanks to the longer reaction time, propan-2-ol is completely consumed as a result of esterification. According to *Figure 3*, such a phenomenon may be supported by the fact that yields for butyric, valeric and caproic acid isopropyl ester were higher when FE = 1.0. In contrast, butan-2-ol (or sec-butanol) seems to accumulate over extended operation times. Moreover, it could also be observed that 2-butyl esters form only with butyric acid, i.e. butan-2-ol, does not present strong ester-forming reactivity. A similar trend was recorded for butan-2-on, which also accumulates over longer operation times of electrolysis.

As for the alkanes, mostly octane, nonane and decane could be obtained with yields of 1.67, 0.64 and 1.06% when FE = 0.25 as well as 1.64, 0.60 and 1.70% when FE = 1.0, respectively. Thus, a longer process time was beneficial with regard to dimer formation from caproic acid radicals. Octane, the dimer of valeric acid radicals, was not significantly influenced by FE nor nonane. This latter compound, formed by the coupling of a valeric and a caproic acid radical, is the only heterodimer produced observed in detectable amounts. Besides, it could also be concluded that C3 radicals from butyric acid decarboxylation presumably do not form homo- nor heterodimers as no hexane nor heptane could be found in the organic phase. This is also in line with the lower conversion rate of butyric acid as well as the higher amounts of propan-2-ol and isopropyl/n-propyl esters. Waste-based acidogenic fermentations with sufficient chain elongation usually result in an effluent particularly rich in C4 and C6 VFAs with varying C5 content (in addition to C2 acetic and C3 propionic acids). In the light of the presented results, it can be stated that at a low current density and moderate/low initial VFA concentration, Kolbe-product formation is significantly suppressed by mostly alcohol and ester production.

4. Conclusions

In this work, the upgrading potential of C4-C6 VFAs via electrochemical oxidative decarboxylation was investigated with model solutions representing the common concentrations of these compounds in waste-based acidogenic fermentation effluents. It was shown that effective VFA conversion can be achieved as a function of the operation time (and FE). Under the applied conditions – low/moderate current density, low

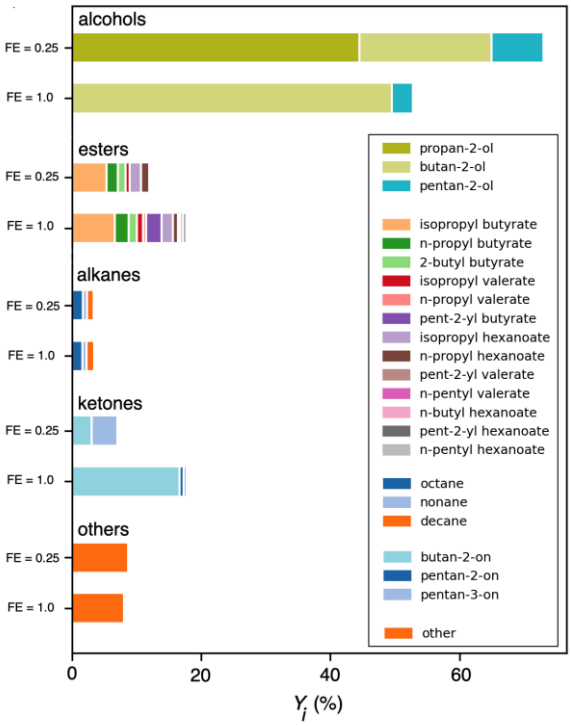

Figure 3: Yields of the identified components in the organic sample phase when FE = 0.25 and 1.0

VFA concentrations – predominantly non-Kolbe products formed, i.e. alcohols and a wide range of esters, as well as ketones. Kolbe dimers were formed with yields of only 3.3% and 3.4% for FE = 0.25 and FE = 1.0, respectively, consisting mainly of octane, nonane and decane. It could be assumed that butyric acid-derived radicals never or seldomly formed dimers. An extended operation time favored ester and ketone formation. Further research should address the time course of product formation to provide a more detailed picture of the competing processes.

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