



Electrochemical Synthesis of Tailor-Made Hydrocarbons from Organic Solvent Free Aqueous Fatty Acid Mixtures in a Micro Flow Reactor

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Abstract

The process described in the current paper is an alternative route that allows running the Kolbe electrolysis under economically attractive conditions and thus bringing it closer to an industrial application through novel process conditions, novel reactor technology, and the utilization of low-cost excess renewable electricity. The process allows the conversion of fatty acids into hydrocarbons in aqueous electrolytes without applying organic solvents. Important process parameters such as electrode material costs, surface area, and energy requirements of an electrochemical reactor in MW scale have been calculated. Depending on the fatty acid mixtures chosen, tailor-made product equivalents of jet oil, lamp oil, and diesel fuels can be achieved at high Faraday efficiency and high conversion, yields, and selectivities.

Keywords Decarboxylation · Radical C-C coupling · High current densities

Introduction

There is a general consensus that existing fossil energy resources are becoming increasingly scarce and that their discovery and exploitation is becoming increasingly difficult, while it is associated with major environmental problems. The global climate changes pose a particular challenge to the world in terms of minimizing pollutant emissions, especially with regard to CO₂. Electricity generation from renewable energy sources such as sun and wind has already reached a significant amount of the electricity demand especially in Germany, the People's Republic of China, parts of the USA, the UK, the Benelux, and the Scandinavian countries. Through the fluctuating nature of these energy sources, options for energy storage are getting increasingly important. However, energy storage faces many unsolved problems. The conversion of electric energy into chemical energy allows storage in large quantities through water electrolysis. In the Soletair project, the first 200 l of synthetic fuel have now been obtained from solar energy and carbon dioxide from the air by Fischer-Tropsch synthesis [1]. A cheaper and less complicated

alternative process is the Kolbe's electrosynthesis of fatty acids from renewable raw materials or biomass.

Kolbe electrolysis is one of the oldest electroorganic syntheses. It was first observed in 1834 by M. Faraday when he studied the electrolysis of aqueous acetic acid [2]. This reaction was applied by H. Kolbe in 1849 for the synthesis of various hydrocarbons [3]. An important preparative breakthrough was achieved by Wurtz when he was able to show that two different carboxylic acids can be coupled together [4]. Despite its existence for more than 150 years, this synthesis path has never been used in industry. Therefore only a few scientific papers or patents that went beyond laboratory applications exist [5]. With the exception of a few references [6–12], all Kolbe and Hofer-Moest (non-Kolbe) electrolysis processes described in the literature that focus on hydrocarbon or alcohol synthesis from fatty acids utilize alcoholic electrolytes or alcoholic-aqueous mixtures or other organic electrolytes [13–21]. The good product solubility when using alcoholic or other organic solvents is accompanied by a complicated separation of the products from the unconverted feed and the solvent. Some of the solvents used (MeOH, EtOH, MeCN, DMF, etc.) are toxic or expensive, which represents an additional obstacle to the environment-friendliness and has financial drawbacks. Because the separation of the products is associated with high energy demand and equipment cost, which ultimately generates high operating costs, this process has not yet found an industrial application.

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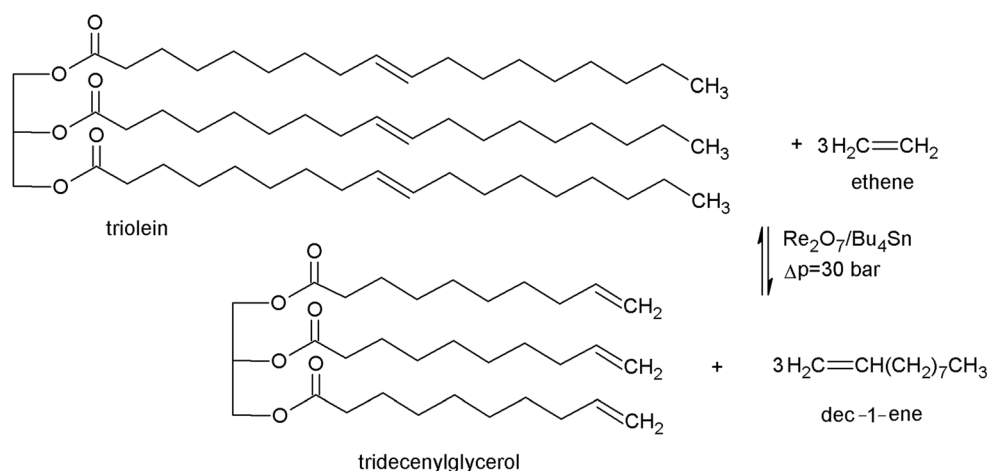


Fig. 1 Ethenolysis of triolein as a representative reaction of the unsaturated fatty acid esters in plant oils [24]

The current paper presents process alternative that allows operating the Kolbe electrolysis under economically more attractive conditions, namely the conversion of fatty acids into hydrocarbons in aqueous electrolytes without use of organic solvents. This process route has a number of potential advantages:

(a) It allows the utilization of excess energy from renewable sources.

(b) The more efficient utilization of raw materials, such as organic waste (used cooking oil, biomass, etc.) or other renewable raw materials after appropriate pretreatment to obtain alkanolic and/or alkenolic acids and/or their alkyl- and alkenyl aromatic substituents, such as 2-phenyl-acetic acid or 4-phenyl-but-2-enoic acid and their subsequent conversion into fuels.

(c) The application of the organic acids obtained under (b) as energy carriers for the direct storage of electricity in high-quality chemicals such as alkanes and olefins has not yet been realized.

There is a lack of inexpensive and efficient electrochemical cells (EC-reactors), as well as processes, that allow the effective utilization of regenerative electricity for the electrochemical conversion of organic acids into fuels or chemicals such as lubricants or lubricant mixtures or other substances and substance mixtures for the cosmetic and chemical industries.

The production described below is CO_2 neutral and can be applied in particular for the utilization of generated peak power.

The alkanes and olefins or mixtures thereof produced this way have comparable or superior properties such as low viscosity, lack of sulfur, and nitrogen compounds, which are harmful to the environment and health, and compounds with heteroatoms such as

oxygen or benzene compared with chemicals derived from fossil sources. Another advantage of alkanes and olefins and their mixtures ($\text{C}_6\text{-C}_{22}$) produced via the electrochemical route over biodiesel (fatty acid methyl esters) is their low viscosity and polarity, which allows their consumption even in extremely cold regions and their lower corrosivity. In particular, Kolbe electrolysis (electrochemical dimerization) is a kind of refinement of biodiesel. The electrochemically produced fuels, such as kerosene, can be produced free of aromatics, which prevents the emission of substances that are particularly harmful to the environment and health. Because they are almost identical to fossil fuels and their compatibility in contact with the fuel-carrying parts of the vehicles is better than that of biodiesel, it can be assumed that they are better accepted by vehicle manufacturers and owners.

Non-Kolbe electrolysis of saturated and unsaturated fatty acids also leads to valuable products such as long-chain alcohols or olefins.

Fatty alcohols, such as stearyl alcohol and cetyl alcohol, are used as non-ionic surfactants and can be used as the basis for many creams and ointments [22]. They are not miscible with water but can be converted into fatty alcohol sulfates by reaction with sulfuric acid. These fatty alcohol sulfates are very important as anionic surfactants in detergents. By ethoxylation, fatty alcohol ethoxylates can be obtained as nonionic surfactants, which are used in personal care products [23].

Unsaturated triglycerides or fatty acid alkyl esters can be converted to short-chain triglycerides or esters and olefins by catalytic ethenolysis as shown in Fig. 1 [24]. After hydrolysis

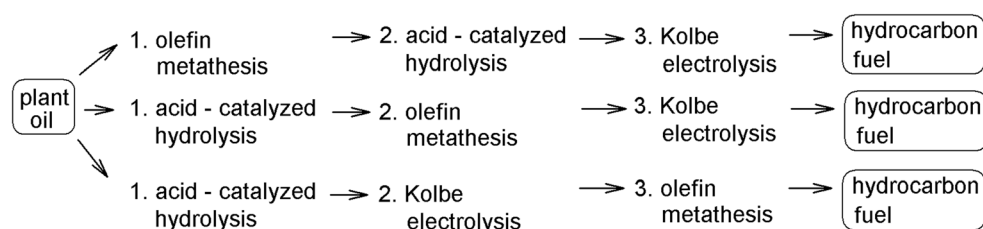


Fig. 2 Production of hydrocarbon fuels from vegetable oil and animal fat [25]

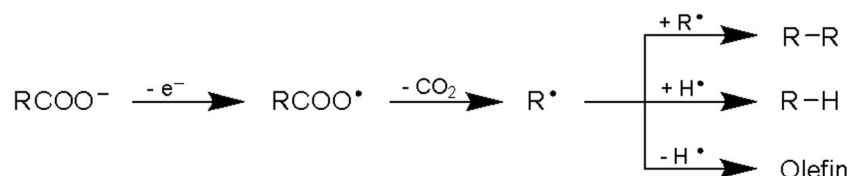


Fig. 3 Symmetric Kolbe electrolysis

of the short-chain (mostly C_{10}) triglycerides or esters, this method can be used for the inexpensive production of short-chain fatty acids with terminal double bonds. Kolbe dimerization then produces terminal dienes. Acid-catalyzed hydrolysis and subsequent olefin metathesis also lead to short-chain terminal olefins and fatty acids. The fatty acids can then dimerize through the Kolbe electrolysis to serve the corresponding terminal dienes. But it is also possible to dimerize the unsaturated fatty acid obtained after saponification of unsaturated triglycerides or fatty acid alkyl esters into long-chain olefins by Kolbe electrolysis and then to convert it into short-chain olefins by catalytic ethenolysis as shown in Fig. 2 [25]. Olefins can themselves or in mixtures with alkanes be used as fuels, converted to the corresponding alkanes by catalytic hydrogenation. They can also be used to produce fatty alcohols with carbon monoxide by hydroformylation (oxosynthesis) on cobalt and rhodium catalysts. The resulting aldehydes can be converted into alcohols by hydrogenation. The alcohols obtained in this way are also called oxo alcohols and can also be branched and odd-numbered by this synthesis route [26].

H_2 and CO_2 , which are produced in large quantities during the electrolysis, are not waste gases, but can rather be converted into other valuable fuels by catalytic power-to-liquid processes [26, 27]. The addition of up to 10% H_2 to the natural gas grid or its application as for hydrogenation reactions in chemical industry or the application of clean CO_2 in food industry are only examples.

The Electro-Decarboxylation of Fatty Acids

Kolbe Electrolysis

According to Kolbe, electrochemical decarboxylation of fatty acids (RCOOH) and in particular their carboxylates leads to radical intermediates (R^\bullet) [3]. The radicals mainly couple by a C-C-coupling to R-R dimer products as shown in Fig. 3 or in the case of a mixture of different carboxylates to a product mixture containing all potential combinations shown in Fig. 4. Depending on the conditions of the electrolysis, a further anodic oxidation of the radicals to cation intermediates (R^+) is also feasible [28, 29]. In a further step, the cation can either be

converted to an olefin by proton elimination or to alcohols, ethers, esters, etc. by the reaction with nucleophiles such as H_2O , ROH , and RCOOH as shown in Fig. 5.

In order to enlighten the reaction mechanism of acetic acid electrolysis, Kolbe postulated the theory of “active oxygen” formed by anodic water decomposition [3]. Kolbe’s theory of “active oxygen” was continued in 1896 in the “peroxide theory” of C. Schall [30], although 5 years earlier A.C. Brown and J. Walker had published the “discharge theory” [31], which was based on the well-known work of S. Arrhenius and W. Ostwald, but does not require “active oxygen” and explains the reaction with the direct conversion of the acetate ion at the platinum anode. From today’s point of view, the latter is regarded as “more modern” and differs from today’s interpretation only in the formulation of certain steps. The abandonment of the theories of the formation of “active oxygen,” however, leads to the need of explaining the suppression of anodic oxygen development at the platinum anode. High voltage (2.1–2.8 V vs. Standard Hydrogen Electrode, SHE) is required to generate the radical. At such critical voltage, oxygen development is inhibited. The oxidation of the solvent, which occurs at much lower voltage, is probably suppressed by a layer of carboxylates on the anode surface. Modern methods of electrochemistry, especially potentiostatic methods and cyclic voltammetry [32, 33] have made an important contribution to the understanding of these phenomena. A high current density (250 mA cm^{-2}) favors the coupling of radicals as shown in Figs. 3 and 4, while lower current density promotes further oxidation as shown in Fig. 5. Platinum or nickel electrodes favor radical coupling. Pd/Ti, Au, and non-porous graphite were also used in non-aqueous media. In particular, carbon as working electrode material (graphite, glassy carbon) favors the formation of cations by two-electron transfer, which by H^+ elimination lead to olefins or by nucleophilic addition of solvents such as methanol or water to the corresponding ethers or alcohols (non-Kolbe or Hofer-Moest electrolysis). According to literature [34, 35], Kolbe electrolysis is a 2nd-order reaction, which takes place at a platinum anode with smooth surface and high current density without foreign ions in an acidic medium. The α -position to the carboxylate acts as electron acceptor. In contrast, the Hofer-Moest electrolysis is a 1st-order reaction. The reaction works particularly well at graphite anodes with rough surface and low current density in basic

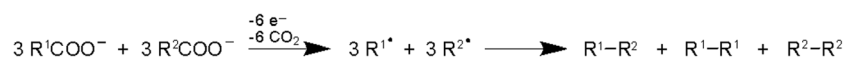


Fig. 4 Asymmetric or mixed Kolbe electrolysis

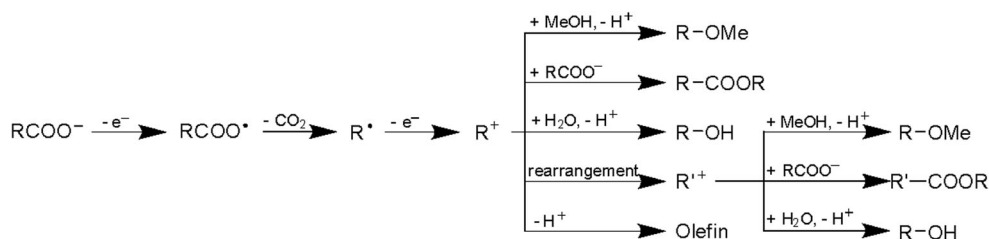


Fig. 5 Non-Kolbe (Moest-Hofer) electrolysis

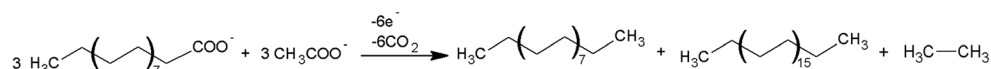


Fig. 6 Kolbe electrolysis of a stearate and acetate mixture

medium. The α -position acts as electron donor. Salt addition increases the yield and selectivity of the reaction. Generally neutral or acidic media are favorable for Kolbe coupling, whereas a basic environment favors the Hofer-Moest reaction [36]. The nature of the cathode is not critical. Since the reduction of protons is the main process, it is normally possible to work in undivided cells. At higher temperatures, mainly side reactions (disproportionation, esterification) occur and the yield of the desired product decreases. For radical coupling, foreign ions must be avoided, probably due to the formation of an oxidation layer on the electrode. Additives such as alkali bicarbonate, sulfate, or perchlorate favor the Hofer-Moest reaction. The structure of the carboxylic acid is also determining the nature of the products, which is dependent on the ionization potentials [37]. Radicals with an ionization potential larger than 8 eV result in coupling products (reaction scheme 3 and 4), while radicals with an ionization potential less than 8 eV are further oxidized (reaction scheme 5). α -Bromo-, α -chloro-, α -amino-, α -alkoxy-, α -hydroxy-, α -acyloxy-, α,α -diphenyl-, and β -silyl-carboxylic acids favor a two-electron process because the resulting cation is stabilized.

Depending on reaction conditions such as temperature, electrolyte composition, pH value for aqueous

electrolytes, electrolyte conductivity, reactant concentration, and electrode materials as well as operating conditions such as residence time and current density, the selective formation of certain products can be achieved. In Kolbe electrolysis, for example, the reaction conditions and electrodes are selected in such a way that the further electron transfer is minimized.

According to Fig. 4, the use of C_5 - C_9 or C_5 - C_{12} fatty acid mixtures leads to jet fuel or diesel-like products as shown in Table 1. To achieve a specific product quality, the required composition of fatty acids in the feed mixture can be determined by calculations and preliminary investigations. For long-chain fatty acid mixtures ($> \text{C}_{12}$), short-chain fatty acids are added in a ratio that suppresses the formation of long-chain dimers and promotes the formation of C-C coupling products from long- and short-chain radicals. For example, Kolbe electrolysis from stearate (C_{18}) and acetate can produce n-octadecane ($\text{C}_{18}\text{H}_{38}$) and the dimers $\text{C}_{34}\text{H}_{70}$ and ethane C_2H_6 as shown in Fig. 6.

While $\text{C}_{18}\text{H}_{38}$ is a component of diesel, $\text{C}_{34}\text{H}_{70}$ is a paraffin with high boiling point (482 °C) and viscosity, which is unsuitable as a fuel. In this case, correct adjustment of the feed composition will drive the reaction towards the formation of octadecane and suppression of the long-chain dimer.

Table 1 Possible products or product mixtures by Kolbe electrochemical C-C coupling from fatty acids or fatty acid mixtures

No.	Fatty acid (n-alkanoate)	Educts	Product
a	$\text{C}_4\text{H}_9\text{COOH}$	a + a	n- C_8H_{18}
b	$\text{C}_5\text{H}_{11}\text{COOH}$	b + b	n- $\text{C}_{10}\text{H}_{22}$
c	$\text{C}_6\text{H}_{13}\text{COOH}$	c + c	n- $\text{C}_{12}\text{H}_{24}$
d	$\text{C}_7\text{H}_{15}\text{COOH}$	d + d	n- $\text{C}_{14}\text{H}_{30}$
e	$\text{C}_8\text{H}_{17}\text{COOH}$	e + e	n- $\text{C}_{16}\text{H}_{34}$
f	$\text{C}_9\text{H}_{19}\text{COOH}$	f + f	n- $\text{C}_{18}\text{H}_{38}$
g	$\text{C}_{10}\text{H}_{21}\text{COOH}$	g + g	n- $\text{C}_{20}\text{H}_{42}$
	mixture 1	a + b + c + d + e	Jet fuel equivalent
	mixture 2	a + b + c + d + e + f + g	Diesel fuel equivalent

Important Factors Affecting the Potential Industrial Applicability of Kolbe Electrolysis

In general, Kolbe electrolysis is performed on smooth platinum electrodes [7]. Calculation of the required electrode surface of a 2 MW electrochemical reactor under industrial operating conditions revealed that the demand for platinum would be uneconomical even for Pt electrodes coated with a Pt layer of only 20 μm thickness. The layer thickness has to be reduced further to 1–5 μm on stainless steel to reduce the material costs and to allow at current densities exceeding 150 mA cm^{-2} , the economic application of the process. Figure 7 shows the electrode surface requirement of an electrochemical reactor (ECR) with a power consumption of 2 MW for different current densities. Figure 8 shows the platinum costs of a 2 MW ECR at different current densities and a platinum price of currently (2019.08.09) 24.5 €/g including 30% electroplating bath surcharge on the platinum price. Figure 9 shows the required electric energy and current flow and different product flows as calculated for different cell voltages of a 2 MW ECR at 80% Faraday efficiency (FE).

Design Aspects of an ECR for Fuel and Chemical Production Through Kolbe Electrolysis

State-of-the-art syntheses of hydrocarbons or alcohols from fatty acids based upon Kolbe electrolysis or Hofer-Moest electrolysis are, with very few exceptions, carried out not larger than laboratory scale. Expensive organic electrolytes and inorganic or organic conducting salts are used, and divided electrochemical cells are usually applied [38–40]. These cells are divided by diaphragm or polymer electrolyte membrane into anolyte and catholyte space. Although these cells have the advantage of separating the products formed at the anode and cathode in the reactor already, they also have plenty

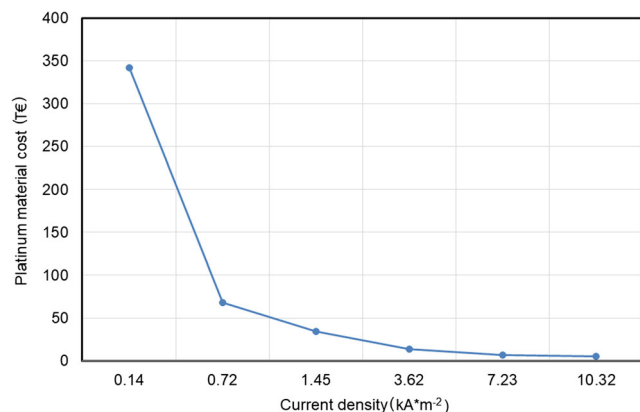


Fig. 7 Platinum costs of a 2 MW operated ECR at different current densities with an equivalent fatty acid concentration of 1 mol L^{-1}

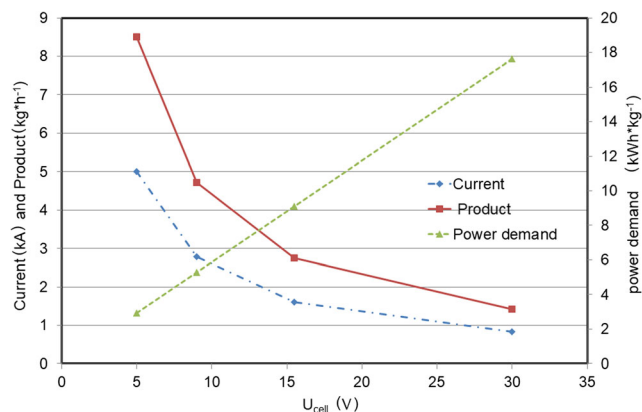


Fig. 9 Specific energy demand, required current flow for product quantities, for different cell voltages calculated for a 2 MW ECM operated with FE of 80%

of disadvantages. Divided cells work at higher cell voltages than undivided cells because apart from the potential loss in anolyte and catholyte, an additional potential loss occurs through the diaphragm or polymer electrolyte membrane, which can be calculated according to equation Eq. (1). The larger electrode space contributes to the high overall Ohmic resistance.

$$\Delta U = \frac{I}{A_e} \left(\frac{d_{AD}}{\kappa_A} + \frac{d_D}{\kappa_D} + \frac{d_{KD}}{\kappa_K} \right) = i \frac{d}{\kappa} \quad (1)$$

(ΔU Potential drop, I current, A_e electrode surface, d_{AD} distance between anode and diaphragm, d_{KD} distance between cathode and diaphragm; d_D diaphragm or polymer electrolyte thickness, κ_A anolyte conductivity, κ_D diaphragm or polymer electrolyte conductivity, κ_K catholytic conductivity, i current density, d electrode distance, κ total conductivity in the cell.)

his consequently leads to high electrical energy consumption when using divided cells. Furthermore, due to their larger electrode surface, the diaphragm, the polymer electrolyte, the seals, the cost and power consumption of the additional

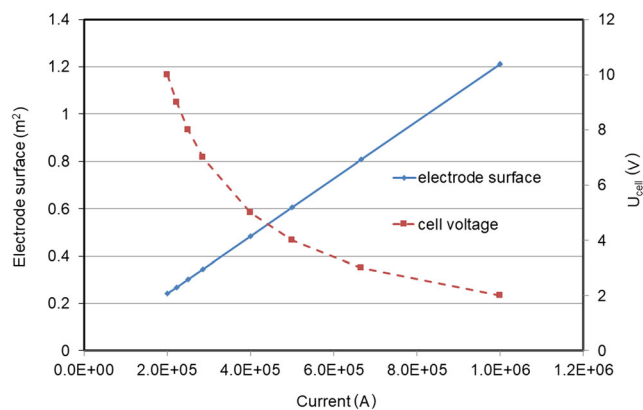


Fig. 8 Electrode surface area requirement in m^2 and clamping voltages (~cell voltages) of an ECR operated with 10.3 kA m^{-2} limiting current density at different current power

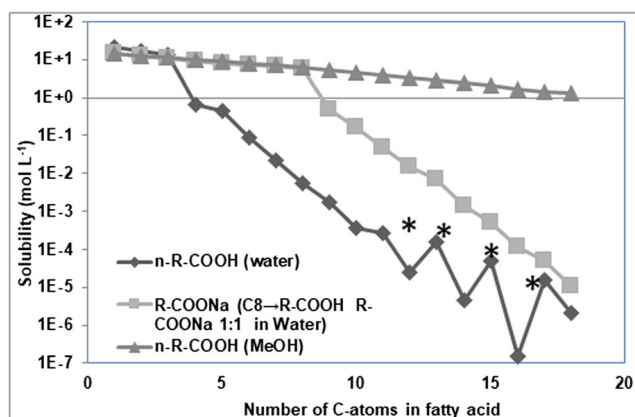


Fig. 10 Logarithmic plot of the molar solubility of C_1 – C_{18} n-alkanoic acids and their sodium salts in water and methanol at a pH of $7 \leq \text{pH} \leq 9$ and a temperature of 25°C . The values of undecanoate, tridecanoate, pentadecanoate, and heptadecanoate marked with asterisk (*) have been averaged

pumps and tanks for anolyte and catholyte, the frequent maintenance breaks, and reactors based upon divided cells are associated with high investment and operating costs.

From the Eq. (1), it becomes obvious that the voltage drop in an electrochemical cell is directly proportional to the current density i and the electrode spacing d and inversely proportional to the electrolyte conductivity κ_D .

Operation at high current densities requires as low as possible electrode spacing and high conductivity of the electrolyte. This places certain demands on the electrolyte and its composition. The electrolyte should consist of an inexpensive, environmentally friendly substance, and it should be as inert as possible and have a wide potential window and good solvent quantities for conductive salts and educts. The quality and simplicity of product separation also affects the selection of the solvent. The required conductive salt should also be inexpensive and easily soluble as well as show great electrochemical stability and ion mobility, which, in turn, affects conductivity and charge transport. Finally, the reactants used for the conversion should also be inexpensive, as soluble as possible, easily oxidable through low overvoltage, but with a minimal tendency to produce undesirable byproducts (esterification). After adaptation of the reaction conditions, the control of the oxidation products (Kolbe for alkanes, non-Kolbe for alcohols and olefins) should be easily feasible.

According to the requirements of the reaction system in focus and for the reasons mentioned above, the application of an undivided cell is regarded as much better suited for the continuous production of fuels chemicals.

The Solubility of Fatty Acids in Water

Fatty acids with chain lengths of less than 7 C atoms are classified as lower fatty acids, with 8–12 C atoms as medium and with chain lengths above 12 C atoms as higher fatty acids.

Higher fatty acids are highly soluble in organic solvents, but almost not soluble in water.

The solubility of fatty acids in aqueous media was described only rarely and inaccurately in the literature [41]. Figure 10 shows that the solubility of fatty acids in water decreases sharply with increasing number of C-atoms. In contrast, fatty acids in methanol are readily soluble even at higher concentrations.

At pH 7, the sodium salts coexist in aqueous solutions from C_8 in a 1:1 ratio with the corresponding free acids [42]. The values of undecanoate, tridecanoate, pentadecanoate, and heptadecanoate marked with asterisk (*) have been averaged.

It is also shown that for fatty acids, only the first three (formic, acetic, and propanoic acid) are miscible with water in any ratio due to the intermolecular hydrogen bonds. Then the solubility decreases almost linearly with the length of the alkyl group. As far as the corresponding sodium or potassium salts are concerned, their solubility decreases linearly only from sodium octanoate onwards (sodium salt of caprylic acid 966.6 g/L) and is 1225 times higher for caprylate (C_8) and 54 times higher for stearate (C_{18}) than for the corresponding undissociated acids (@ 25°C). At pH values above the equivalence point, the solubility is even higher [43].

With a pK_s value of 4.76–5, the $n\text{-C}_{2+}$ n-alkanoic acids belong to the group of weak organic acids. By titration with equimolar amounts of bases such as KOH, the fatty acids are only present in their salt form at an equivalence point of $\text{pH} = 8.66\text{--}9$ as shown in Fig. 11. At a pH value of approx. 7, the acids and their potassium salts are present in a 1:1 ratio.

The molecular solubility of the fatty acids was exceeded in every case in the experiments presented below. The solubility of rarely soluble fatty acids increases especially in mixtures with short-chain fatty acids and with increasing pH. This feature was utilized to produce concentrated aqueous solutions containing up to 2 M acid equivalents. Depending on the size of the fatty acids and molar ratios of mixtures, even higher concentrated solutions or emulsions can be produced. It can be assumed that emulsions form micelles, the polar part of which is surrounded by water molecules.

Experimental Section

Modification of ELMI

The electrochemical microreactor (ELMI) carries microchannels with a length of 32 mm and a width of 0.8 mm. The number of channels amounts to 27, the active electrode surface $A_e = 6.912\text{ cm}^2$, the electrode spacing $d = 200\text{ }\mu\text{m}$, and the active reactor volume $V_R = 0.138\text{ cm}^3$.

The stainless steel electrodes of the ELMI microreactor, whose explosion view is shown in Fig. 12 [44, 45], were

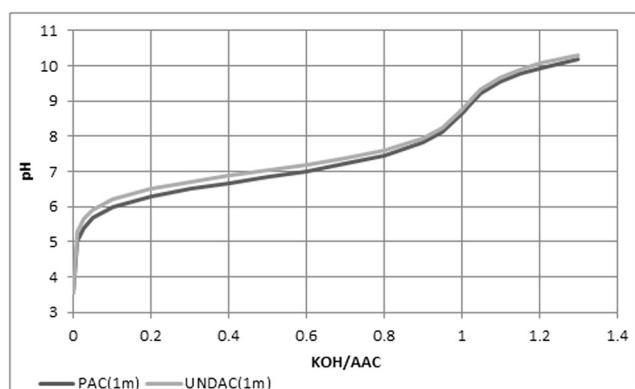


Fig. 11 Titration curve of 1 mol/L n-pentanoic acid (PAC) and n-decanoic acid (UNDAC) with KOH

modified by galvanic platinum deposition of 5.0- μm -thick layer in the micro channels. The two electrodes with integrated heat exchangers were used under thermally controlled conditions for a series of experiments applying Kolbe electrolysis.

In general, when an aqueous reaction mixture was applied, the product was separated in a simple separation tube into an organic phase floating at the top and an aqueous phase. The

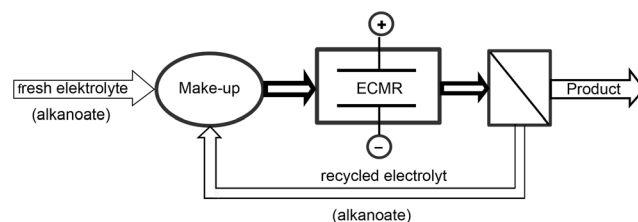


Fig. 13 Schematic of the experimental set-up for Kolbe electrolysis experiments performed in aqueous solution

organic product phase could be continuously removed without further treatment. The aqueous phase was recirculated through the reactor after continuous make-up with fresh alkanoate as shown in Fig. 13.

Experiments Performed with the Modified ELMI Reactor

Applying the modified ELMI® reactor initially n-octane synthesis was carried out by feeding a $\text{Co} = 1.0 \text{ M}$ solution of n-pentanoic acid in methanol at pH 6.8–7.5. The cell voltage at the beginning of the electrolytic process was 3.51–3.56 V. After quickly saturation of the methanolic electrolyte with

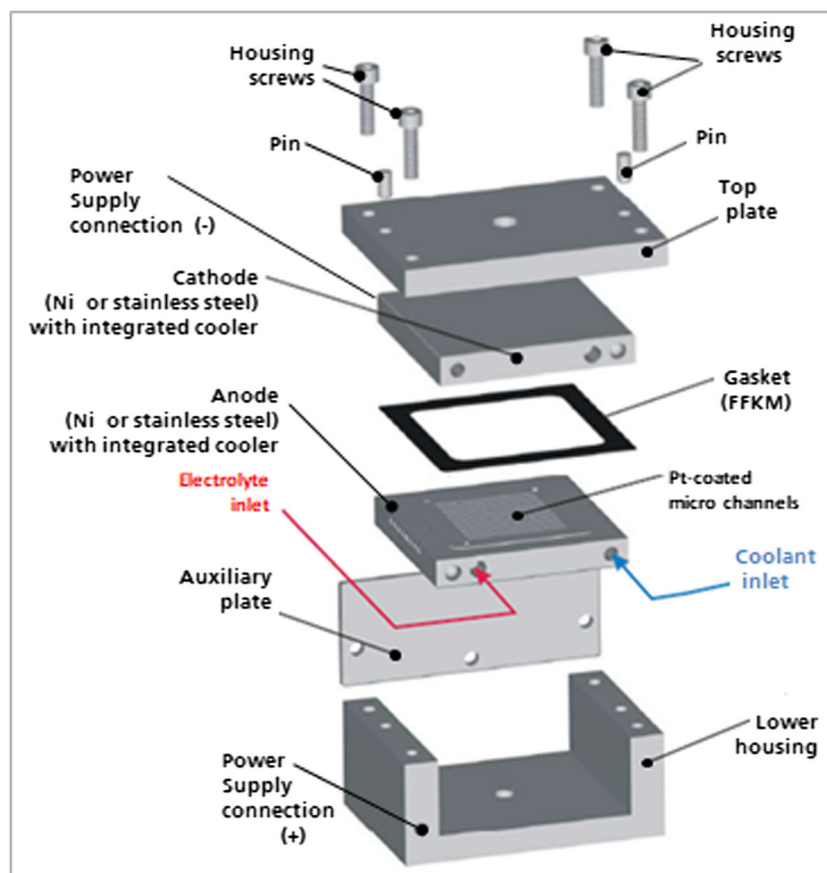


Fig. 12 Explosion view of the electrochemical microreactor ELMI® (source: Fraunhofer IMM)

Table 2 Electrolysis parameters and results of the n-octane electro-synthesis from 1 M pentanoic acid in methanol $E_{\text{cell}} = 4.5\text{--}4.9$ V

No.	Parameters		Results								
	Residence time τ (s)	pH (-)	Current density (kA m^{-2})	Faraday efficiency (FE) (%)	Conversion n-Octane (X) (%)	Yield (Y) (%)	Selectivity (S) (%)	By-products			
								Buten (%)	Methyl-pentanoate (%)	(2-Butyl)-pentanoate (%)	Butyl-pentanoate (%)
1	2.8	6.8	0.144	79	89	81	93	2.03	0.95	2.3	0.425
2	1.7	7	0.362	81	92	84	95	2.11	0.61	1.02	0.339
3	0.9	7.3	0.579	83	96	86	95	2.2	0.8	1.5	0.2
4	0.8	7.5	0.723	84	97	87.5	96	2.01	0.21	1.03	0.64

Table 3 Electrolysis parameters and results of the n-octane electro-synthesis from 1 M pentanoic acid in water

No.	Parameters		Results								
	Residence time τ (s)	pH	Current density (kA m^{-2})	Cell voltage (V)	Faraday efficiency (FE) (%)	Conversion n-Octan (X) (%)	Yield (Y) (%)	Selectivity (S) (%)	By-products		
									Butene (%)	(2-Butyl)-pentanoate (%)	Butyl-pentanoate (%)
1	1.656	7.5	0.75	5	70	92	80	92.1	3.2	2.03	1.6
2	1.104	8	1.5	4.8	73	96	82	94.3	2.9	1.08	0.9
3	0.92	8.5	1.75	5	79	99.5	84	94.3	2.8	1.2	1.1
4	0.83	9	2	5	84	100	87	95.3	2.4	0.9	1

Table 4 Reactant composition for the electrosynthesis of (a) jet oil and (b) diesel equivalent fuels

Alkanoic acid	(a) (mol/mol)	(b) (mol/mol)
C ₄ H ₉ COOH	0.0003	0.0458
C ₅ H ₁₁ COOH	0.4051	0.2914
C ₆ H ₁₃ COOH	0.2358	0.203
C ₇ H ₁₅ COOH	0.1827	0.1577
C ₈ H ₁₇ COOH	0.1334	0.1629
C ₉ H ₁₉ COOH	0.0428	0.0647
C ₁₀ H ₂₁ COOH	0	0.0745

CO₂, the conductivity became lower and the cell voltage was 4.5 to 4.9 V. Higher current densities increased the cell voltage to over 5 V. For this reason and to keep energy consumption low, the power source was set to a limited voltage of 5 V. Various residence times τ and current densities as shown in Table 2 conversion (X) up to 98%, yield (Y) up to 87.5%, and selectivity (S) up to 96% with a Faraday efficiency (FE) of 79–84% could be achieved.

However, Aspen simulations were performed, which revealed that for an industrial process, even at lowest material and investment costs, the energy demand for removing the solvent would be extensive, which makes the process clearly economically unattractive.

In order to avoid this problem and contrary to the acidic conditions claimed as necessary for the Kolbe electrolysis in the literature until today [46], a new process has been developed, which enables the reaction in basic electrolytes with high conversion, yield, and selectivity towards Kolbe products.

Table 6 Component distribution of the liquid product mixtures of (A) jet oil and (B) diesel equivalent fuels, obtained by the Kolbe electrolysis of 1 M reactant water solutions of the composition a) and b) shown in Table 4

n-alkane	(A) m-%	(B) m-%
C ₈ H ₁₈ (OCT)	0.001	0.128
C ₉ H ₂₀ (NON)	0.003	1.832
C ₁₀ H ₂₂ (DEC)	13.600	7.877
C ₁₁ H ₂₄ (UNDEC)	17.290	11.100
C ₁₂ H ₂₆ (DODEC)	19.790	13.491
C ₁₃ H ₂₈ (TRIDEC)	20.288	16.261
C ₁₄ H ₃₀ (TETDEC)	15.300	14.384
C ₁₅ H ₃₂ (PENDEC)	8.800	13.753
C ₁₆ H ₃₄ (HEXDEC)	4.932	9.348
C ₁₇ H ₃₆ (HEPDEC)	0.050	5.733
C ₁₈ H ₃₈ (OCTDEC)	0.001	3.872
C ₁₉ H ₄₀ (NONDEC)	0.000	1.384
C ₂₀ H ₄₂ (EIC)	0.000	0.838

Test Extension and Results of Kolbe Electrosynthesis in Aqueous Solution with the Modified ELMI

The syntheses described below were carried out in pure aqueous solution with 1–2 M n-fatty acids in the form of n-alkanoates at a pH-value of 7.5–10 (Tables 3 and 5).

The GC-MS analysis showed that the accumulated organic product phase consisted only of n-alkanes with content of lower 1-alkenes of 2.4–3.2 m-%, especially when the pH value of the electrolyte was higher than 9. After a series of tests under different conditions (flow rates, current densities, pH-values, see Tables 3 and 5) the best results for the

Table 5 Mixed Kolbe electrolysis in water: parameters and results of the two reactant compositions as shown in Table 4

No	Parameters	Results									
		Conc. C _A (molL ⁻¹)	Residence time τ (s)	pH	Current density (kAm ⁻²)	Cell voltage (V)	Faraday efficiency (FE) (%)	Conversion n-Alkanes (X) (%)	Yield (Y) (%)	Selectivity (S) (%)	By-products n-Alkenes C4-C9 (%)
1	Reactant	1	1.104	9	1.50	4.83	84	98	91	94.3	2.9
2	Composition	1.5	0.92	9.3	1.70	4.33	87	99.5	93	94.3	2.8
3	a)	2	0.83	9.3	2.00	4.82	91	99	94	95.3	2.4
4	Reactant	1	0.83	9.5	1.50	4.33	89	98	95	96	2.8
5	Composition	1.5	0.83	9.7	1.67	4.28	91	100	95	96	3.1
6	b)	2	0.83	10	2.00	4.94	90	99	95	95	3.2

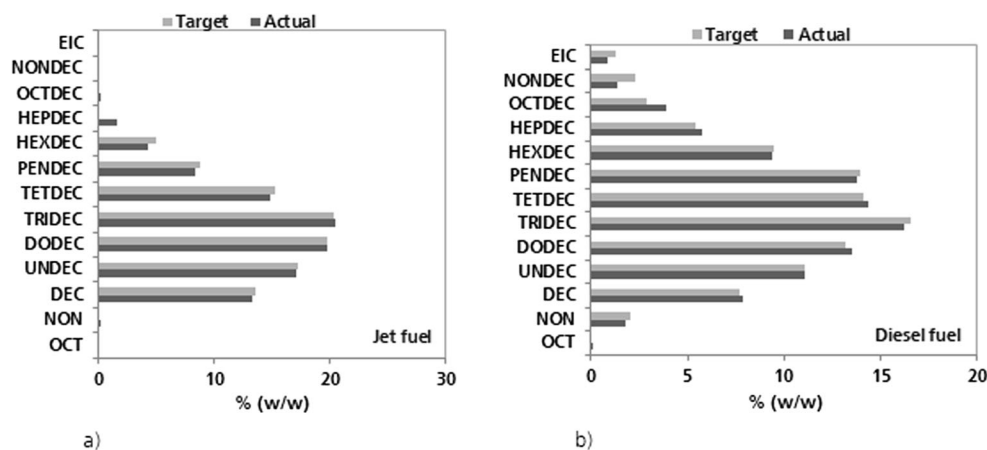


Fig. 14 Comparison between target composition and actual product composition for jet fuel (a, left) and diesel type fuel (b, right) alkane mixtures by asymmetric or crossed Kolbe electro-synthesis in aqueous solution using the modified ELM1®

electrosynthesis of n-pentanoate and of mixed n-alkanoates were achieved with conversions (X) in the range of 92–100%, Faraday efficiencies (FE) of 70–91%, yields (Y) of 80–96%, and selectivities (S) of 87–98%. By targeted and precalculated aqueous n-alkanoate mixtures as shown in Table 4, tailor-made n-alkane fuel equivalences could be produced by asymmetric Kolbe electrolysis as shown in Table 6 and Fig. 14.

The specific electrical energy consumption ω according to Eq. (2) is defined as the ratio of required energy per mass unit of product

$$\omega = \frac{zFE_{\text{cell}}}{M_p FE} \quad (2)$$

and amounts to approx. 1.745 kWh kg⁻¹ for jet fuel and approx. 1.5 kWh kg⁻¹ for diesel-type fuel.

Conclusions

The experiments revealed that the most important operating parameters to obtain tailor-made products of through Kolbe electrolysis can be obtained by:

Microstructured reactors including

- a microchannel-structured electrode with narrow electrode spacings (200 μm or less) to achieve laminar flow and homogeneous current density distribution,
- electrodes with smooth Pt layers only 5 μm thin coated onto the channels to achieve high product selectivity,
- a heat exchanger integrated into the electrode for effective heat exchange,
- cell(s) operated at elevated pressure of up to 100 bar in order to suppress gas coalescence,
- application of a precalculated feed composition,

- a pH value of 9–10 to achieve a good solubility of the fatty acids, good electrolyte conductivity, and saponification of esters potentially formed,
- short residence times of $\tau = 2$ s or lower to suppress consecutive reactions,
- precise control of the reaction temperature in the range of 10–25 $^{\circ}\text{C}$ by effective heat exchange and temperature control, and
- high current density in the range of up to 10 kA m⁻² to allow high throughput.

Summary and Outlook

A new method has been developed, which paves the ground for the industrial application of the Kolbe electrolysis. The electrolysis is performed in aqueous mixtures or emulsions without use of hazardous and expensive organic solvents at low-cost microchannel-structured and platinum-coated electrodes. Effective temperature control through integrated heat exchangers, a precalculated feed composition, low residence times, and high current densities provide excellent results in terms of Faraday efficiency, conversion, yield, and selectivity. The product phases can be separated very simply without further treatment, which reduces the production costs with regard to energy consumption waste deposition and product extraction. The process can be performed even more effectively if fatty acids from renewable resources produced by olefin metatheses of plant-oils or by fermentation of biowaste are used. The process gets economically attractive through the utilization of low-cost renewable electric energy from wind and solar sources. By these means, cost-efficient direct storing of surplus energy in high-quality products gets feasible through the novel process.

The observation described above provided the design parameters for the construction of a new and flexible

electrochemical micro reactor (ECMR) of larger scale. The new 3 kW ECMR, already manufactured by additive manufacturing, is currently in the validation phase. The results of this validation will be published in the near future.

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List of Symbols A_e , electrode surface $A_e = LW$ (m^2); C_o , concentration of reagent ($mol\ m^{-3}$) or ($mol\ L^{-1}$); d , inter-electrode gap (m); D , diffusion coefficient ($m^2\ s^{-1}$); E_{cell} , cell voltage (V); ECMR, electrochemical microreactor; ECR, electrochemical reactor; Eq, equation; F , Faraday constant ($96,486\ A\ s\ mol^{-1}$); FE, Faraday efficiency (-); i , current density ($A\ m^{-2}$); I , cell current (A); L , electrode length (m); M_P , molar mass of product P ($kg\ mol^{-1}$); Z , number of electrons involved ($equiv\ mol^{-1}$); ΔU_{ohm} , ohmic potential drop of the cell (V); X , conversion (-); S , selectivity (-); T , temperature ($^{\circ}C$); Y , yield (-); V_f , electrolyte volumetric flow rate ($m^3\ s^{-1}$) or ($mL\ min^{-1}$); V_R , reactor volume (m^3); w , electrode width (m)
Greek κ , specific conductivity ($S\ m^{-1}$); τ , residence time (s); Ω , specific electric energy consumption ($kWh\ kg^{-1}$)

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