

# Electrochemical Conversion of Lauric Acid through Kolbe Electrolysis for the Synthesis of *n*-Docosane

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Lauric acid (*n*-dodecanoic acid), a saturated compound derived from animal fats and vegetable oils, can be used as a feedstock for lubricant production. In this work, the production of *n*-docosane from lauric acid via Kolbe electrolysis was studied using two commercially available electrodes in order to optimize the procedure and also to assess the performance of such electrodes for the production of *n*-docosane. The optimization study was performed using a compact ElectraSyn 2.0 setup which is commercially available and easy to use. The utilization of the equipment with a regulated power supply, electrodes and other components makes the procedure easily repeatable. The effect of essential parameters influencing the yield of *n*-docosane was pinpointed in relation to the performance of two different commercial electrodes (platinum- and gold-coated copper). A green, cost-effective and safe electrochemical approach for the production of *n*-docosane with 45% product yield was obtained using Pt-coated copper electrodes. However, electrode damage and consequent declining performance were also observed during prolonged electrolysis. The confirmation through XRD analysis of the appearance of platinum, gold and copper particles in the solution indicates that such electrodes present a problem of limited durability when used as anodes in synthetic organic reactions.

## Introduction

Lubricants are agents that are used to lessen wear and friction between contacting surfaces (Gresham et al., 2000). The majority of conventional lubricants are mineral oils with a petroleum base, which raises environmental issues with regard to the extraction and use of petroleum, as well as biodegradability, ecotoxicity and carbon footprint (Bart et al., 2013). Most commercial lubricants are made of a base stock plus a number of additives (Ho et al., 2019). Different physicochemical properties produced by varying formulations have an impact on performance and appropriateness in a variety of applications. These qualities can be categorized into various groups: (1) general characteristics like viscosity and acidity (2) performance features like prevention from rust (Mobarak et al., 2014), (3) environmental characteristics like biodegradability (4) thermal and hydrolytic stability (5) thermal properties like volatility (6) cold flow properties like cloud point (Salimon et al., 2010). Commercial interest in bio-lubricants, also called green, seed-oil based, or bio-based lubricants, has developed significantly in recent years in response to increasing demand for lubricants combined with tougher environmental requirements (McNutt, 2016). Until now several books and reviews have been written about biolubricants, with a focus on the different feedstocks, modifications and additives for biolubricant synthesis (Salimon et al., 2014), areas of applications and implications in different fields (Wilson, 1998). A recent work (Syahir et al., 2017) investigated ionic liquids as biolubricants for various industrial applications. (Panchal et al., 2017) compiled a summary of the reaction conditions used in the literature for acid- and base-catalyzed transesterification to obtain biodegradable grease. Estolides, namely oligomeric structures containing fatty acid repeat units with secondary ester linkages, used as bio-based lubricants, are usually synthesized by conventional and well-established chemical processes.

There are different techniques for the production of lubricants on the commercial level, such as esterification and transesterification, hydrolysis, oligomerization, oxidative cleavage and Kolbe electrolysis. Kolbe electrolysis is the most attractive alternative because of mild working conditions, lower number of reaction steps, and no hydrogen consumption compared to other techniques. Kolbe electrolysis, by utilizing biomass and electricity, addresses the twelve principles of green chemistry and is therefore a viable technique in view of more and more stringent requirements for future sustainable industrial production (Anastas and Eghbali, 2010). Numerous scientific studies have been conducted on the applications of Kolbe electrolysis, with a particular emphasis on the production of biofuels and chemicals. One of these (R. dos Santos et al., 2015) presented the conversion of triglycerides and fatty acids to olefins and a mixture of olefins and ethers, while others investigated octane production (Nilges et al., 2012) or the synthesis of methoxymethyl ethers (de Kruijff and Waldvogel, 2019). Levulinic acid (Wu et al., 2017) was used for the production of polymers. Furthermore, different experimental parameters like effect of pH, temperature, solvent and different additives on the Kolbe electrolysis are also proposed by different researchers (Zhang et al., 2018). Further researches concerned product selectivity i.e., the formation of homocoupling vs cross-coupling products (Lund, 2002) as well as improvements in the Kolbe electrolysis (Yoshida et al., 2008). An electrolytic system based on solid-supported bases was developed (Kurihara et al., 2006) with a good yield of Kolbe product mixture. The effect of different experimental parameters on the Kolbe electrolysis of caproic and butyric acid,  $\gamma$ ,  $\beta$ -unsaturated carboxylic acid (Knolle and Schäfer, 1978) and malonic acid have been already clarified (Svadkovskaya and Voitkevich, 1960). Anyhow, efforts on the utilization and better efficiency of Kolbe electrolysis for good product yield is still ongoing.

The objectives of this paper are to describe a detailed optimization study on the production of *n*-docosane from lauric acid in view of a future application in lubricant production, and also to verify the viability of various type of electrode materials for this purpose. Lauric acid was chosen as the model substrate while KOH was chosen as supporting electrolyte. The effect of different parameters like concentration of lauric acid, concentration of KOH, current, time and the nature of the two electrodes were investigated. To the best of our knowledge there are no reports available related to the production of docosane by using ElectraSyn 2.0.

## 2. Materials

Lauric acid ( $C_{11}H_{23}COOH$ , 97 %, Sigma Aldrich), potassium hydroxide (KOH, 97 %, Sigma Aldrich) ethyl acetate (99.5 % Sigma Ald.) and methanol (MeOH, 99.5 % Sigma Aldrich) were used as purchased, without purification.

### 2.1 Electrodes

Two types of commercial electrodes (IKA for ElectraSyn) i.e., Pt-coated copper and Au-coated copper electrodes were used in all experiments. The dimensions (W x H x D) of both electrodes were (8 x 52.5 x 2 mm<sup>3</sup>) with a layer thickness of platinum and gold on copper of 400-600  $\mu$ m and a gap of 5 mm between working and counter electrodes.

## 3. Electrosynthesis using Lauric Acid

All the experiments were carried out using a galvanostatic/potentiostatic controlled ElectraSyn 2.0 (IKA®) system which is commercially available, compact and easy to use. For the electrolysis experiments, lauric acid as the main substrate was treated with KOH as the supporting electrolyte in MeOH as solvent. In a detailed procedure, a 15 mL vial with a magnetic bar was sequentially charged with lauric acid and with KOH in MeOH as solvent. The vial was then equipped with two electrodes and closed with a cap, and the reaction mixture was stirred for 5 minutes at 500 rpm. Next, the vial was connected with the ElectraSyn 2.0 setup, and the experiment was carried out at room temperature with the stirring at 600 rpm. After completion, the mixture was transferred quantitatively to a round-bottom flask, and the solvent was evaporated by rotary evaporator. The residues were then treated with acidified water, in order to transform laurate back into lauric acid, and then extracted with ethyl acetate; The organic phase, dried over anhydrous sodium sulfate and filtered, was then analyzed by GC-MS to determine the product distribution and yield. The quantitative analyses were performed on an Agilent 6850 chromatograph equipped with a 5975N mass spectrometer.

## 4. Results and discussion

Platinum has been widely employed as the anode material for Kolbe electrolysis due to its stability at high potentials. However, other electrode materials such as iridium, glassy carbon, graphite (Andreev et al., 2013),

and gold (Vijh et al. 1967) also catalyze the Kolbe radical generation. All the experiments using Pt-coated and Au-coated copper electrodes are discussed below.

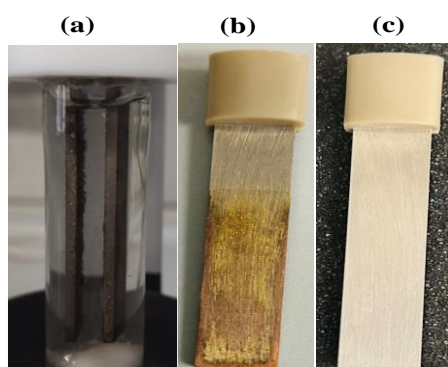
#### 4.1 Kolbe electrolysis of lauric acid on Pt-coated copper electrodes

A set of experiments was carried out utilizing Pt-coated copper electrodes for the decarboxylation of lauric acid, as shown in Table 1. The experiments were carried out with 0.4 or 0.7 mmol of lauric acid in methanol (12 mL) as solvent for 3 or 6 hours, with or without alternate polarity (AP). The amount of desired product was minimal in all the experiments conducted with a lower current, i.e. 20 mA and, as shown in entries 1-3, the unreacted starting material was almost completely recovered. The best result (45 %) was obtained when the current was increased to 85 mA by alternating polarity every 30 minutes (entry 4), a much higher yield than without AP (entry 5). Under these conditions the major product obtained was “one electron” Kolbe dimer *n*-docosane  $\text{CH}_3(\text{CH}_2)_{20}\text{CH}_3$ . In the experiment of entry 4 black particles began to appear inside the solution, due to the dissolution of the electrode, as shown in Figure 1a. After reaction completion, the color of the electrode was changed from its original metallic grey as shown in Figure 1b-c. Once selected the optimal current conditions, the effects of increasing amount of KOH were investigated. Varying amounts of KOH, i.e., 0.4, 0.8, 1 and 1.3 eq were examined while setting other conditions as follows: lauric acid 0.7 mmol, current: 85 mA and time 6 hours (entries 6-9). As the amount of supporting electrolyte was increased, a downward trend in product yield (21, 19, 14 and 4 % of docosane) was observed. Since an increase in electrolyte concentration causes an increase in the current through the cell, it is possible to attribute the slight decrease in product yield to the corrosion of the Pt coating. Moreover, the formation of a substantial amount of several side products was observed.

*Table 1: Results from Kolbe electrolysis experiments for the decarboxylation of lauric acid using Pt-coated copper electrode.*

No.	Lauric Acid (mmol)	KOH (eq)	Current (mA)	Time (h)*	Docosane % <sup>a</sup>
1	0.7	1.5	20	3	1
2	0.7	1.5	20	3 AP	4
3	0.4	1.5	20	6 AP	4
4	0.4	1.5	85	6 AP	45
5	0.4	1.5	85	6	4
6	0.7	0.4	85	6 AP	21
7	0.7	0.8	85	6 AP	19
8	0.7	1.0	85	6 AP	14
9	0.7	1.3	85	6 AP	3
10	0.4	1.5	85	6 AP	10

\*AP = Alternate polarity every 30 minutes <sup>a</sup> % mmol respect to the initial amount of starting material



*Figure 1: Pt-coated copper electrode: (a) black particles appeared during electrolysis (entry 4), (b) corrosion effects after 24 h of electrolysis (the black particles were removed), (c) fresh Pt-coated copper electrode*

In order to gain information about the performance of the electrodes, the experiment of entry 4 was repeated after the electrodes had been utilized for 48 hours (entry 10). The product yield decreased from 45 % to 10 %, as shown in Table 1. After 54 hours of electrolysis time, the colour of electrode was totally changed into black. The XRD patterns in Figure 2 refer to used (red) and fresh (black) Pt-coated copper electrodes. The pattern shows the diffraction peaks of platinum at 39.6° and 46.1°, of copper at 43.1° and 50°, and of gold at 38°, 42° and 64.4° 2 $\theta$ . Surprisingly, a coating of gold is sandwiched between the copper substrate and the platinum coating. The XRD analysis indicates the stability of these commercial Pt-coated copper electrodes was decreased significantly due to electrode dissolution during the electrolysis. Recently, (Ranninger et al., 2022) associated the anodic damaging to direct dissolution of Pt in the form of Pt ions.

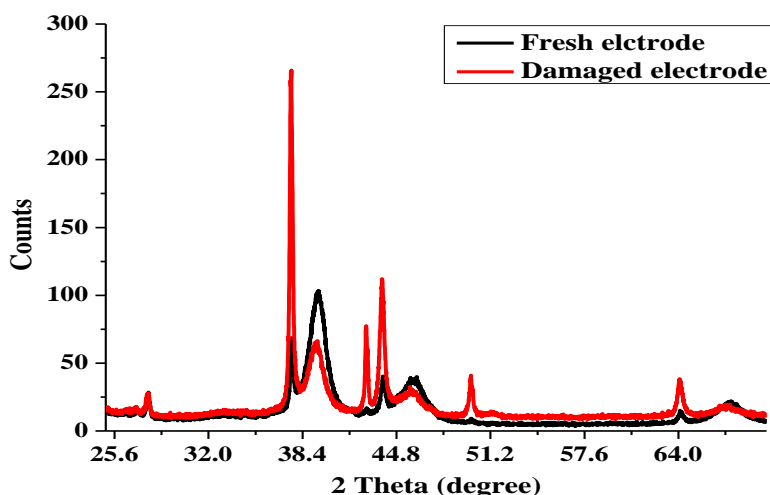


Figure 2: X-ray diffraction (XRD) patterns of fresh and damaged Pt-coated copper electrode.

#### 4.2 Kolbe electrolysis of lauric acid using Au-coated copper electrode:

Multiple experiments were carried out to examine the impact of Au-coated copper electrode on the electrolysis of lauric acid, as shown in Table 2. All the experiments were conducted with either 0.4 or 0.7 mmol of lauric acid and 1.5 eq of KOH as supporting electrolyte. In the first test, high values of the experimental parameters were used, including a constant current intensity of 85 mA for 6 hours of electrolysis, alternating polarity every 20 minutes. After completion of the experiment, 16 % of *n*-docosane was formed (entry 1). As expected, no Kolbe process product was observed when the current was then reduced below 85 mA to 10 and 20 mA for 3 hours (No.2-3 and 4).

Table 2: Results from Kolbe electrolysis experiments for the decarboxylation of lauric acid using Au-coated copper electrodes and 1.5 eq of KOH as supporting electrolyte.

No.	Lauric Acid (mmol)	Solvent (12 mL)	Current (mA)	Time (h)*	Docosane % <sup>a</sup>
1	0.7	MeOH	85	6 AP	16
2	0.4	MeOH	10	3 AP	0
3	0.4	MeOH	20	3 AP	0
4	0.4	MeOH+H <sub>2</sub> O	20	3 AP	0
5	0.4	MeOH	85	2 AP	6
6	0.4	MeOH	85	2	2
7	0.4	MeOH	85	4 AP	0
8	0.7	MeOH	85	6 AP	4
9	0.4	MeOH	85	2 AP	5

AP\* = Alternate polarity after each 20 minutes, <sup>a</sup> % mmol respect to the initial amount of starting material

When electrolysis was carried out for 2 hours with and without AP, only 6 % and 2 % of yield along with side products were formed (entries 5-6). Worse products yield % was obtained with the Au-coated electrodes compared with Pt-coated electrodes. The result is consistent with observations in the literature on electrooxidation of carboxylic acids suggesting that parasitic Faradaic processes on Au electrodes are easier than on Pt, and, as a consequence, the Faradaic efficiency of gold anode is much lower than that of platinum (Ding et Orazov, 2023).

In entry 5, black particles appear in the solution, indicating that the anodic dissolution of gold is likely to occur. After completion of the experiments, the particles were collected through filter paper and then analyzed through XRD as shown in Figure 3a. The XRD pattern obtained indicates the presence of gold and copper particles.

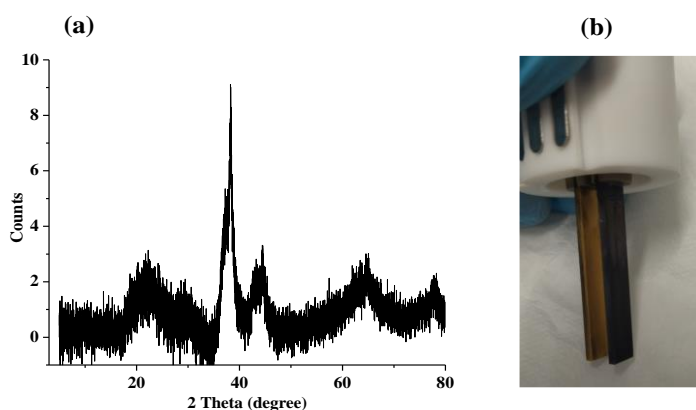


Figure 3: Au-coated copper electrodes: (a) XRD of black particles appeared during electrolysis (No. 5), (b) corrosion effects after 23 h of electrolysis.

The impact of operation time with current intensity of 85 mA was then studied. After using the same electrodes continuously for 23 hours, the performance was noticeably reduced, and the electrode color completely changed from golden to dark, as shown in Figure 3b. The experiments 1 and 5 were repeated with the deteriorated electrode, and the yield decreased from 16 % to 4 % and from 6 % to 5 % (entries 8-9). The yield of *n*-docosane progressively decreased with usage of the electrode. The comparison of the performance of Au-coated electrodes after different time of usage are shown in Figure 4.

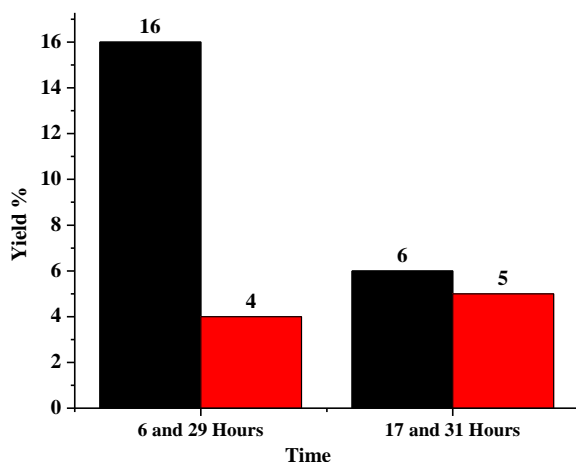


Figure 4: performance of electrodes after 6 and 29 hours (entries 1 and 8 in Table 2), 17 and 31 hours (entries 5 and 9 in Table 2) of usage. The values of docosane% is on the top of each histogram.

## 5. Conclusions

This study shows that an efficient process of electrochemical oxidation of lauric acid by Kolbe coupling reaction with 45% product yield of *n*-docosane can be conducted using Pt-coated copper electrodes. However, the service life of the Pt-coated copper electrode is short (< 30 h), because of surface dissolution effects. The performance for Au-coated copper electrodes was lower than that of Pt-coated electrodes. No further optimization was carried out for these coated electrodes, but experimental tests with massive electrodes are in progress.

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