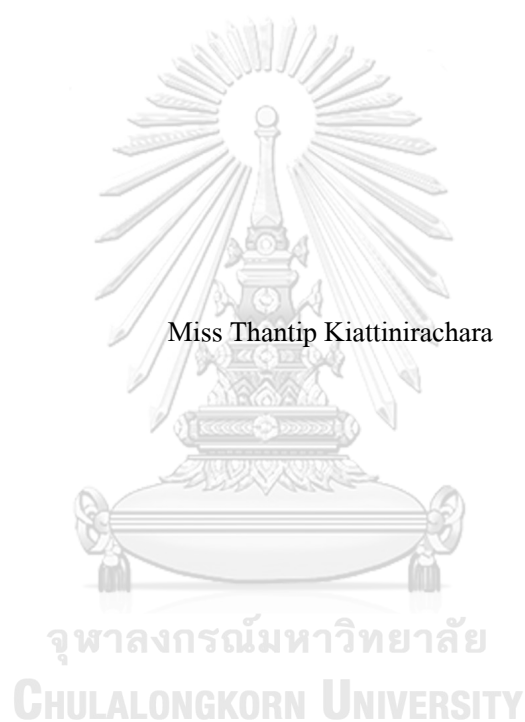


SYNTHESIS OF ALKANE FROM LAURIC ACID VIA ELECTROCHEMICAL REACTION
IN MICROREACTOR



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

FACULTY OF ENGINEERING

Chulalongkorn University

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

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 ศ. ดร. วรงค์ ปวรจารย์

งานวิจัยฉบับนี้ทำการศึกษาการสังเคราะห์แอลเคนจากกรดลอริก ด้วยปฏิกิริยาเคมีไฟฟ้า ในเครื่องปฏิกรณ์ขนาดไมโครที่ต่อเข้ากับแหล่งกำเนิดไฟฟ้า โดยขั้วแอโนดเป็นแกรไฟต์ และขั้วแคโทดเป็นสแตนเลสสตีล สารตั้งต้นจะไหลผ่านเครื่องปฏิกรณ์ระหว่างขั้วทั้งสอง ซึ่งในงานวิจัยฉบับนี้จะทำการศึกษาตัวแปรต่างๆ ได้แก่ ความเข้มข้นของสารตั้งต้น (กรดลอริก 30, 40, 50, 60 มิลลิโมลลาร์), เวลาในการทำปฏิกิริยาในเครื่องปฏิกรณ์ (100-400 วินาที) และ ความหนาแน่นของกระแสไฟฟ้า (6.67-37.04 มิลลิแอมแปร์ ต่อ ตารางเมตร) โดยจากผลการทดลองทำเพื่อศึกษาค่าอัตราการเกิดปฏิกิริยาเคมี และศึกษาพฤติกรรมของปฏิกิริยาจากผลของชนิดสารละลายที่แตกต่างกัน นอกจากนี้การถ่ายโอนไฮโดรเจนในระบบระหว่างการเกิดปฏิกิริยาจะอธิบายไว้ในงานวิจัยฉบับนี้



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In the present work, decarboxylation of lauric acid to undecane was conducted by Kolbe electrochemical oxidation process in a microreactor. The microreactor is widely used to study reaction kinetics as well as reaction mechanisms because of negligible heat and mass transfer resistances within the reactor. The reactor is also very effective in the control of residence time. The 250-micron thick reactor was formed between graphite anode and stainless steel cathode sheets. Reactive alkyl radicals were produced from the supplied electrical potential and their combination with proton produced alkane with the release of carbon dioxide. The experiments were conducted to study the effect of residence time in the range of 100-400 s, and that of current density in the range from 6.67-37.04 ampere per meter squared. Kinetic analysis and reaction behavior of the reaction was performed and presented in this work.



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Thantip Kiattinirachara

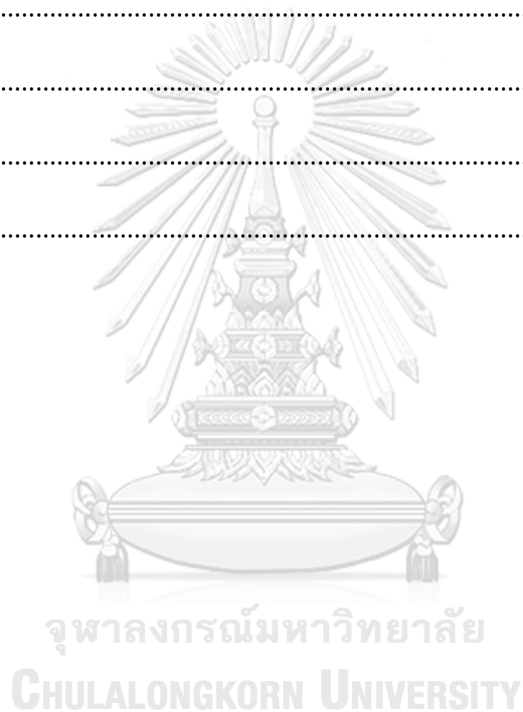


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CHAPTER 1

INTRODUCTION

The electrochemical conversion bio-derivable compounds have been interested and studied for many years. This method has been widely accepted to be one of the effective technologies for synthetic organic chemists. Additionally, electricity is an alternative energy that is a friendly environment and the reducing carbon monoxide and carbon dioxide release. One of the most famous that can converse fatty acids by the electrochemical reaction is Kolbe electrolysis or Kolbe dimerization. This reaction can be used to synthesis long-chain alkanes in mild conditions and has high efficiency. Due to the principle of Kolbe electrolysis, the long-chain alkanes that have an even carbon atom was produced.

Presently, the alkanes that have an odd carbon atom have much more demand and are more valuable. There are several applications more than mixed in lubricant as simple long-chain alkane but they can use as fragrance agents in cosmetics and perfume, etc. So, this research work is focused on the synthesis of odd-alkane as new desired products via an electrochemical reaction. Additionally, the experiment was used a microchannel reactor because of the special characteristic. The small size of this reactor makes a high reaction area per volume ratio that can reduce residence time, and extremely high mass and heat transfer. So, it suitable to study the kinetics of reaction because can negligibly heat and mass transfer in reaction.

This research work focuses on the synthesis of odd-alkanes as a new desired product from decarboxylation of fatty acid in a microchannel reactor via an electrochemical reaction. The preliminary mechanism of this reaction will start to examine the intermediate to explain the pathway of the reactions. The intermediate compounds of the reaction are identified. Additionally, to study reaction kinetics of alkane production and each step of the reaction. The various conditions consist of concentration, resident time, and current density was used in experimental design to find apparent rate.

Objective

The main objective of this research was to study the reaction behavior of electrochemical of carboxylic acid in three factors consist of system or type of solvent, current density, and residence time. The result can lead to the reaction pathway and explain the preliminary mechanism of the reaction. Additionally, the kinetics of the reaction also studies in terms of the apparent reaction rate constant (k).

Scope of this research

The scope of this research work is following :

1. The microreactor was used. The channel or volume of reactor equal to $6.75 \times 10^{-8} \text{ m}^3$.
2. The temperature is room temperature and at atmospheric pressure.
3. The experiment in various conditions consists of resident time in a range of 100-400s, the initial concentration of lauric acid as 30, 40, 50, 60 mM, and current density in a range 6.67-37.04 A/m².
4. The solvent consists of acetonitrile blended with methanol ratios of 0:10, 7:3, 1:9, and 10:0.
5. the reaction behavior about hydrogen transfer in system and the effect of any condition on conversion and yield of products

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Synthesis alkane

Currently, there are several reactions for the synthesis of alkane from fatty acid including hydrodeoxygenation, hydrodecarbonylation, and decarboxylation reactions. Based on the advantages and disadvantages, it can be concluded that the above reactions have highly efficient (high conversion and yield) but the reactions have occurred in harsh conditions (high temperature and pressure). So, many research focuses to survey another reaction to synthesis alkanes. One of the important reactions are name is the Kolbe reaction.

2.2 Kolbe reaction

The reaction was firstly proposed by Hermann Kolbe and Rudolf Schmitt in 1834. From the beginning, the name of the reaction is "Kolbe-Schmitt reaction". It is a carboxylation chemical reaction that proceeds by heating sodium phenoxide with carbon dioxide under pressure (100 atm, 125°C). Then, treating the product with sulfuric acid. The final product is an aromatic hydroxy acid (salicylic acid) as shown in Figure 1.

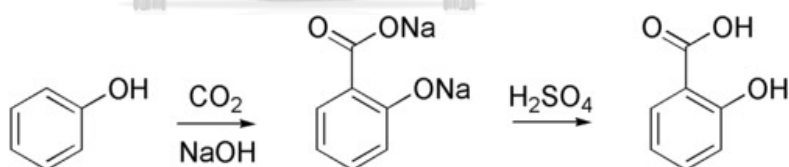


Figure 1 Kolbe-Schmitt in reaction

Meanwhile, M. Faraday [1] was studying the conductivity of acetates. He observed that an inflammable gas was produced at the anode. He reported this phenomenon but did not identify the gas. Then fifteen years later, in 1849, W.H. Kolbe [2] was reinvestigated Faraday's experiment. He found the gas produced in the reaction is ethane and notice the reaction similar to Kolbe Schmitt in a reverse way. So, he proposes a reaction that can synthesis ethane from acetic acids by electrolysis instead of traditional production methods. The reaction is anodic oxidation of carboxylate to radical

and called “Kolbe reaction or Kolbe electrolytic”. He has explained the mechanism of the reaction in Figure 2, the alkoxide ion is generated. Then, unstable alkoxides are motivated by the electrically assisted breakdown and occur decarboxylation reactions. The alkyl radicals that were produced are combined to form ethane at the anode.

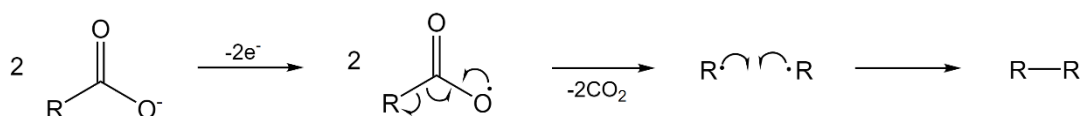
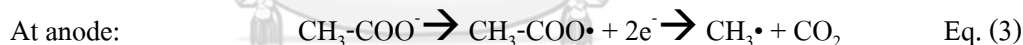


Figure 2 Electrochemical decarboxylation-dimerization (via free radicals) of carboxylic acids

*** R : methyl group

The acetic acids are treated with base to deprotonate and form sodium acetate in aqueous-solution. The combination to this form is symmetrical dimer or homocoupling products.



Although, the Kolbe electrolysis is a powerful method for the generation of C-C bonds under particularly mild conditions, the co-products were produced. Then, the different experiments of Kolbe electrolysis reaction have been studied in 1850-1990 [3-5]. The experimental factors studies in the Kolbe electrolysis are (i) current density, (ii) the pH of the electrolyte, (iii) ionic additives, (iv) the solvent, and (v) the anode material. All of these factors are affecting to yield, selectivity, and form of products in reaction. So, there have many theories and mechanism that were proposed and were reviewed in detail by Schafer in 1990 [6]. He concludes that the forms of products depend on the intermediate between alkyl radical and carbocation which occur in reaction.

The experimental conditions favor radical coupling.

- The high current density and concentration can increase the density of alkyl radical at anode. So, the high amount of alkyl radical can lead to dimerization. Besides, the low concentration of radical can support an electron transfer from the radical to the electrode to form a carbonium ion.

- Ionic additives to the electrolyte can negatively influence the Kolbe electrolysis. Anions other than the carboxylate should be excluded because they hinder the formation of a carboxylate layer at the anode, which seems to be a prerequisite for decarboxylation.

2.3 The form of products in reaction

Besides the aforementioned symmetrical dimers, other compounds can become the major products in the electrolysis of carboxylic acids. The intermediate form of alkyl can determine the pathway of reaction and products. The alkyl radicals lead to Kolbe products while cationic leads to non-Kolbe products.

2.3.1 Kolbe reaction products

2.3.1.1 The symmetrical dimers or homo coupling products.

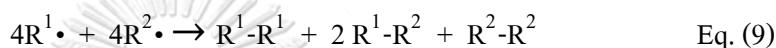
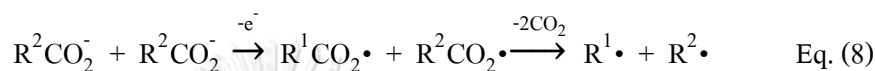
The first pathway is dimerization as original Kolbe electrolysis. The alkyl group of two identical carboxylic acids can be coupled to symmetrical dimers in the presence of a fair number of functional groups. Since free radicals are the reactive intermediates, polar substituents need not be protected. The step for protection and deprotection that are necessary. When electrophilic or nucleophilic C-C bond forming reactions are involved [7]. The experiments of Kolbe dimerization have been complied by performed at a platinum anode in water, methanol, ethanol, and ethanol/water blended.



*R is $\text{C}_n\text{H}_{2n+1}$

2.3.1.2 The unsymmetrical dimers or cross coupling products

In 1855, Wurtz [8] obtained unsymmetrical coupling products, when he co-electrolyzed two of different carboxylates. The different alkyl groups from two carboxylic acids can combine and form cross-coupling products. This reaction also known as the mixed Kolbe reaction. A disadvantage of this reaction is the statistical coupling of the intermediate radicals. The results, the reaction has the additional formation of two symmetrical dimers as major side products and unsymmetrical compounds.

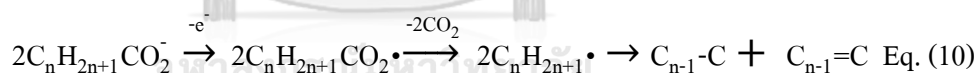


R^1 is C_nH_{2n+1}

R^2 is C_mH_{2m+1}

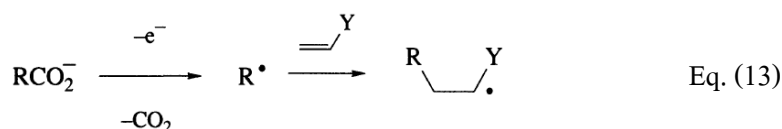
2.3.1.3 The disproportionation products

The disproportionation is a redox reaction in which one compound of intermediate oxidation state converts to two compounds, one of higher and one of lower oxidation states. The electron from the alkyl radical can move to other. Then, the radicals that lose electrons are formed into alkene and another radical can form to be alkane.



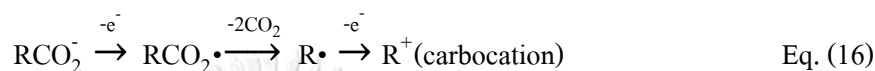
2.3.1.4 The addition products

The double bond or unsaturated compound can intercept the alkyl radical intermediate that is present in the electrolyte. So, the radical in a new form can combine with an alkyl radical or dimerize to form an additive dimer. Besides, the substitute with nucleophile and disproportionation reactions.



2.3.2 Non-Kolbe reaction products

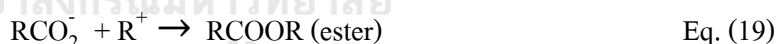
The radicals were oxidized to carbocation, which can form ethers and alcohols. These by-products were proposed by Hofer-Moest [9]. They studied Kolbe electrolysis in methanol (MeOH) and water solvent and found the solvent can break down by electricity.



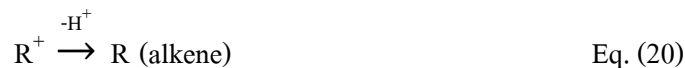
Then, the combination of alkyl carbocation with methoxy group or hydroxy group, which methanol splitting as substitution reaction. These are replaced by 3 types of reagents consist of nucleophile, electrophile, and free-radical.



Additionally, the alkyl carbocation can either react with a deprotonated acid leading to the formation of an ester as a side product.



Furthermore, the carbonium ion that does not react with another compound will be release H^+ . Then, the double bond has occurred at the end of the alkene.



All of the products that are produced from carbocation as intermediate have an effect from solvents to be a by-product. In the case of Hofer-Moest's experiment, aqueous or alcoholic solutions are supposed to be alcohol or ether also known as Hofer-Moest products.

Besides, the carbocation can occur rearrangement reaction is a reaction that has atoms or function group substituent moves from one atom to another atom in the same molecule. In the carbocation form, the hydrogen atom or methyl group to be a more stable carbocation form as isomers.



The example: pentyl cation can form to be 1-pentene, 2-pentene, or 3-pentene because of the stabilize carbocation. The stability of carbocations increases as we go from primary to secondary to tertiary carbons.

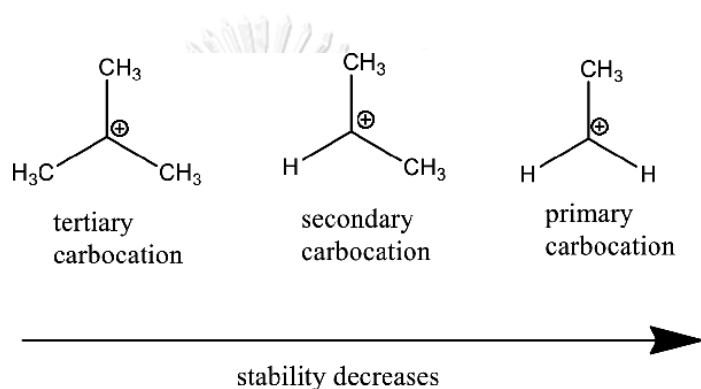


Figure 3 The decreasing stability of carbocations form.

All products that are produced from radicals and further oxidized to carbocation has shown in Figure 4.

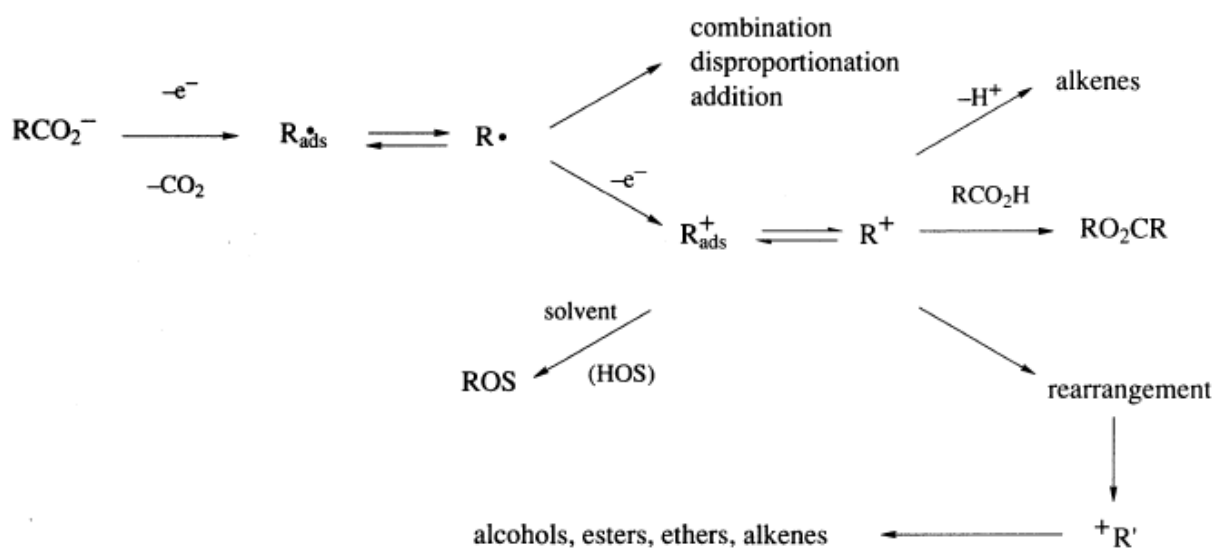


Figure 4 Formation of product that can be occur in Kolbe electrolysis [9]

Then, the effect of solvent on the reaction outcome gets more attention. Many research works were studied in a large of solvents and were concluded by Hammerich and colleagues in 2016[10]. They explain that mainly key to predicting the reaction outcome is the type of solvent. The nucleophilicity and redox potentials can be distinctly altered by different solvation and intermediates can be solvated more or less. Furthermore, the product can be protected from over-conversion and the selectivity and yield can be distinctly improved by choosing a suitable solvent system.

2.4 Solvents for electrochemistry

There are several well-known electro-organic syntheses in which the solvent employed has a significant impact on the reaction outcome. Although there are two main groups of solvents which are polar and non-polar, the non-polar is non-conductive. The polar solvents can divide into two groups consists of polar protic and polar aprotic solvents.

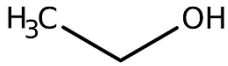
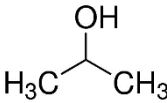
2.4.1 Polar protic solvent

Polar protic solvent is a solvent that has O-H or N-H bonds. It can build hydrogen-bonding and serve a proton (H^+) as acid which can form nucleophile in a reaction. The example of polar protic solvents is water (form OH^- as nucleophile), acetic acid, and alcohol such as methanol, ethanol (form MeO^- , EtO^- as nucleophile), etc.

Solvent properties are in important consideration in many chemical reactions, including nucleophilic substitution reactions. As strong hydrogen-bond donors, protic solvents are very effective at stabilizing ions. Therefore, they favor reactions in which ions are formed, such as the S_N1 reaction, and disfavor reactions where ions are reactants, such as the S_N2 reaction.

Table 1 Examples of a few common polar protic solvents used in organic chemistry

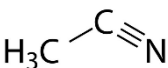
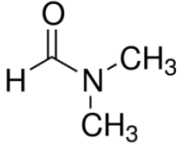
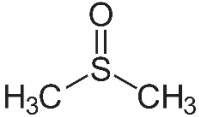
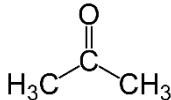

Solvent	Boiling Point, Celsius	Chemical structure	Dielectric Constant
Water, H_2O	100	$\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{H} \quad \text{H} \end{array}$	78.5
methanol, CH_3OH	65	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{O}-\text{H} \\ \\ \text{H} \end{array}$	32.6

Solvent	Boiling Point, Celsius	Chemical structure	Dielectric Constant
ethanol, $\text{CH}_3\text{CH}_2\text{OH}$	78.5		24.3
isopropyl alcohol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	82		18

2.4.2 Polar aprotic solvent

Polar aprotic solvent lacks O-H and N-H bonds and therefore cannot hydrogen bond with themselves. The example of polar aprotic solvents is acetone, dimethylformamide, acetonitrile, and dimethyl sulfoxide.

Table 2 Examples of a few common polar aprotic solvents used in organic chemistry

Solvent	Boiling Point (Celsius)	Chemical structure	Dielectric Constant
acetonitrile, CH_3CN	81.6		37.5
dimethylformamide (DMF), $\text{HCON}(\text{CH}_3)_2$	153		38
dimethyl sulfoxide (DMSO), CH_3SOCH_3	189		47
acetone, CH_3COCH_3	56.5		21
Pyridine, $\text{C}_5\text{H}_5\text{N}$	115.2		12.4

***dielectric constant : a measure of the amount of electric potential energy, in the form of induced polarization that is stored in a given volume of material under the action of an electric field.

The solvent system can influence product selectivity. Han, J. Schafer [9] firstly mixing methanol with water compare to another pure solvent and found that effect to reactive intermediate as Table 1.

Table 3 Anodic decarboxylation of cyclohexane carboxylic acid in different solvents

Solvent	Alkyl radical : Carbocation
H ₂ O/MeOH (30% v/v)	0.97:1
MeOH	1.76:1
MeCN	2.26:1
HCONMe ₂	4.32:1

As a result, the comparison of common solvents, the highest relative yields of the dimerization product are obtained from dimethylformamide and acetonitrile. For water and methanol are supporting the non-Kolbe product. The observation, mechanism of the electrochemical Kolbe reaction is related to the type of solvent, polar protic, and polar aprotic solvent. The ability of the solvent to form carbocation as reactive intermediate ; Water > protic solvent > aprotic solvent.

2.5 Odd-alkane

Originally, major sources of alkanes and alkenes are petroleum crude oil, which is found to be depleted. Kolbe dimerization is another way to respond to demand about fuel, lubricant, etc. the reaction can produce medium chained alkanes but cannot prepare alkanes that have an odd number of carbon atoms. Additionally, the medium-chained alkanes of odd carbon atoms over 17 atoms have higher cost than even numbers because of the specific use of the compound such as heptadecane used as the suspended extraction and concentration of essential oil, and nonadecane used as fragrance agent in cosmetic and perfume. Therefore, this research focuses on the method that can synthesis of odd-alkane from fatty acid.

As mentioned, both disproportionation reaction and cross-coupling reaction can produce odd-alkane but the addition formations are produced as co-products such as alkene in disproportionation reaction, and two of symmetrical dimers in cross-coupling reaction. Besides, the research work of Weiper, Ph.D. [11], he found that when one of two acids is used in excess, the yield of the reaction can be increased.

Then, the research work of Koji Kimura and colleagues in 1973 [12], anodic oxidation of carboethoxy cyclopropane carboxylic acid in a differential solvent that is water + pyridine and methanol. For the result, both solvents can produce 2, 2', 3, 3'-tetracarboethoxy bicyclopopyl (A) that symmetrical dimer product and 2,3-carboethoxy groups cyclopropane (B) that haven't been mentioned as a co-product.

The 2,3-carboethoxy cyclopropane product was explained by the addition pathway also known as hydrogen abstraction reactions. Hydrogen abstraction is another important step in organic chemistry that is hydrogen in a molecule can split from the structure as radical. This is not deprotonation because radical provides only one electron to form the new hydrogen-alkyl bond. In deprotonation, the alkyl would provide both electrons for the new hydrogen-alkyl bond.

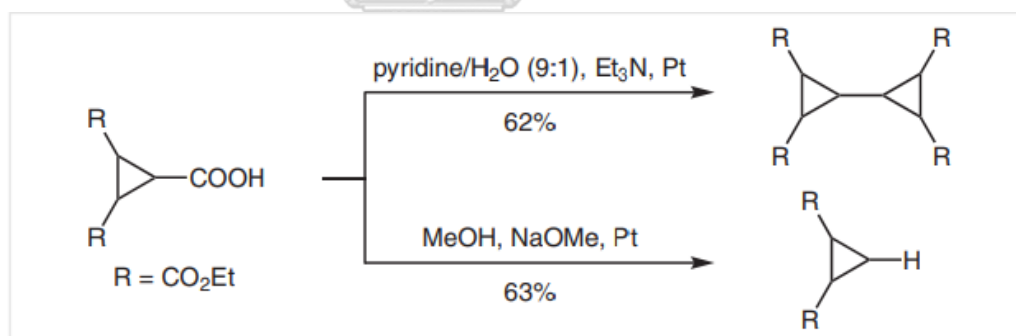


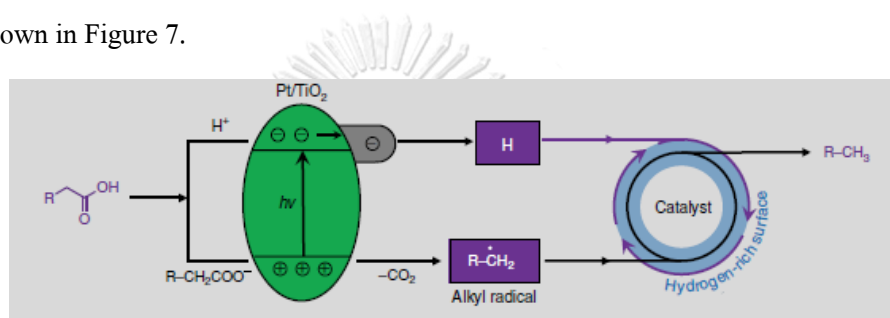
Figure 5 Solvent effect to product in Kolbe electrolysis

In the different system solvents, water + pyridine blended solvent has the main product contrast with methanol. They conclude that the main product was decided by the electron in the system. The amounts of an electron can force to form alkyl radical or carbocation, which can cause a substitute or non-Kolbe reaction.

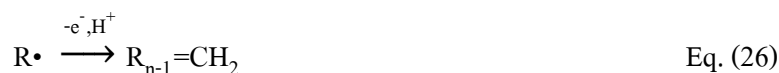
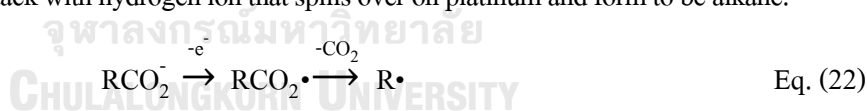
Table 4 Percent yield of coupling product and 2,3-carboethoxy groups cyclopropane

Product	Pyridine + H ₂ O	MeOH
Coupling product (A)	62.2	13.0
2,3- carboethoxy groups cyclopropane (B)	2.8	62.5

Additionally, in 2019, Zhipeng Huang and colleagues [13], focus on the synthesis of odd-alkane from a carboxylic acid via photo-catalyst reaction. They proposed the mechanism of this reaction shown in Figure 7.

**Figure 6** Photo-catalyst mechanism [13]

The reaction is the decarboxylation of stearic acid to heptadecane via photocatalysis and used Pt/TiO₂ as a catalyst and acetonitrile as solvent. They explain the alkyl radicals are generated by holes on TiO₂ that occur the hydrogen enrichment on Pt nanoparticle. Then, the alkyl radical after release carbon dioxide will attack with hydrogen ion that spills over on platinum and form to be alkane.



The mechanism of this research work is similar to the Kolbe reaction but the alkyl radical is attached by H (reducing H⁺ at conduction band) instead of dimerization of alkyl radical. This process is no adding base and used the different solvents with the Kolbe reaction. All of the products including heptadecane (main products), tetratriacontane (dimerization), and 1-heptadecene (alkene

formation). This process can convert carboxylic acid C_n to alkane 80-90% and have a high selectivity to C_{n-1} -alkane or odd-alkane.

2.6 Electrochemical

The electrolysis is consisting of two side names is anode and cathode. The electricity is used as the potential energy to force the electron to move from anode to cathode. The flow rate of electric charge that passes through a surface is called current and current density which are a ratio of electron value/surface area. The direction of the charge in the electrical circuit (electric current) is opposite to the conventional charge direction. The current and current density can be controlled by the force in terms of a volt.

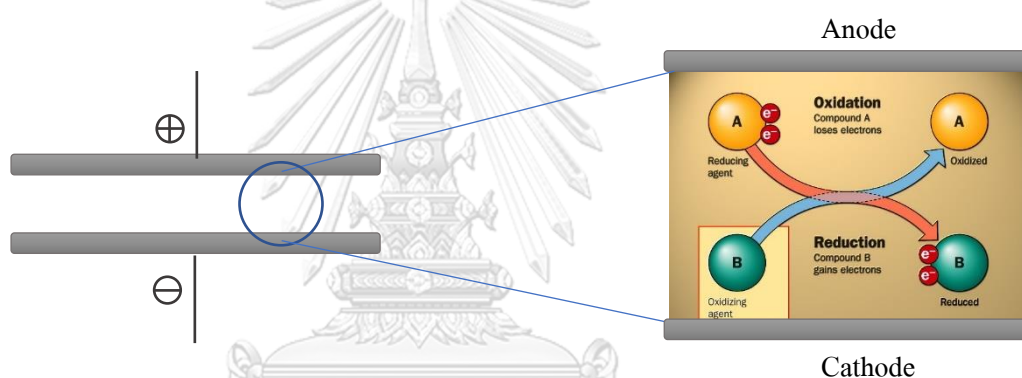


Figure 7 The redox that occur in gap of microreactor between anode and cathode

The anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction. Electrons from the negative terminal travel to the cathode and are used to reduce sodium ions into sodium atoms. The sodium will plate onto the cathode as it forms. The sodium ion is migrating towards the cathode. The negative Chlorine ions migrate towards the anode and release electrons as they oxidize to form chlorine atoms. The chlorine atoms will combine together to form chlorine gas which will bubble away.

Oxidation half reaction at anode





Reduction half reaction at cathode



The smooth platinum as foil or net in anode material of choice for Kolbe electrolysis. Additionally, in nonaqueous solvents, graphite, titanium and gold also used [14].

The nature of the cathode material is uncritical in the Kolbe electrolysis. The discharge of protons from the carboxylic acid is in most cases the only cathode reaction, which allows the convenient electrolysis in an undivided cell. For the electrolysis of unsaturated carboxylic acids, however, platinum as cathode material should be avoided, since cathodic hydrogenation can occur; in this case a steel cathode should be used instead.

The factor in electrochemical

1. Applied potential, electric potential or potential drop is the energy difference between two points, anode and cathode.

It's the energy per unit charge that make current flow in circuit. To find the energy output, we multiply the charge moved by the potential difference ($\Delta U=q\Delta V$). Many research works are studies about varies applied potential applies in the electrochemical reaction. The concluded, electrode potential is the determining factor for reduction reaction to take place and controls the redox gradient and the evolution rates of electron donor and acceptor.

2. Current density is the amount of electric charge per unit cross-section area.

Daniela E. Blanco and colleagues [15] were study about Optimizing organic electrosynthesis through controlled applied potential dosing and artificial intelligence. The organics electrochemical reaction is the difficulties to control the selectivity. Because of the difficulty in controlling multiple

reaction pathways but they found the current density is one of the most factor that have to control the selectivity

They use acrylonitrile (AN) in aqueous solution as feed stock of the reaction to produce adiponitrile(ADN). The pathway of the reaction has shown in Figure 9.

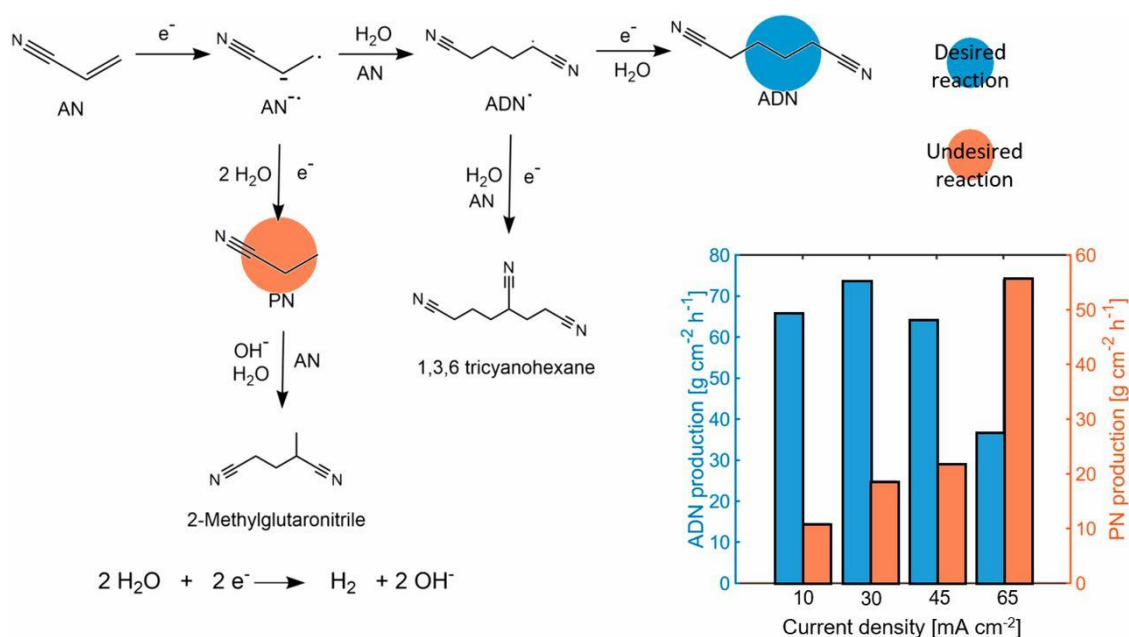


Figure 8 The reaction pathway to produce adiponitrile from acrylonitrile [15]

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CHULALONGKORN UNIVERSITY

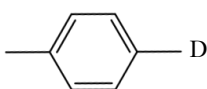
The initial, the acrylonitrile in aqueous solution has activated by electricity and breakdown. Then, it's can combine together and form to be an adiponitrile radical. first pathway, adiponitrile radical can occurred the hydrogen abstraction with solvent and another compound in solution to be adiponitrile as desired product. Another pathway, acrylonitrile breakdown can lose one more electron in the reaction and form to be propionitrile (PN) as undesired product. Additionally, from their experiment, the desired product or product that occur hydrogen abstraction are favor the low current density and have highest value at 30 A/m². They explain the high current density are relate to the electron in system. When increase the current density, the electron that loss from reaction is increase.

2.7 The hydrogen abstraction reaction

The hydrogen abstraction is different from deprotonation, the hydrogen can remove from molecule by a radical but the deprotonate is the hydrogen can remove from molecule in form of proton(H^+) and the molecule remain molecule is having negative charge as nucleophile.

F. M'Halla and colleagues [16] were study about hydrogen atom abstraction and solvent involvement in the electrochemistry of haloaromatics. The haloaromatic was separated during electrolysis. Then, the aromatic radical can attack and pull the hydrogen atom from another molecule. They used D_2O or water that replace hydrogen with deuterium in the experiment and study the effect of %water in system of solvent in the reaction. For the result, hydrogen abstraction of aromatic radical can occur with solvent. They found D in molecule of final product of the reaction. Additionally, the protonation of aromatic anions can occur to from the same product and it's depended on proton donor ability of solvent. When the ratio of water per solvent was increase, the kinetics of the reaction and amount of product from protonation reaction was increased.

Table 5 Deuteration experiments in acetonitrile and acetonitrile-3d

Solvent	% D_2O	Ph-CO 
CH_3CN	2	0
CD_3CN	0	93

From the table 2-5, deuterium in the final product is transfer from acetonitrile. The addition solvent, heavy water or D_2O have no effect about hydrogen transfer into products but it's can increase the rate of the reaction.

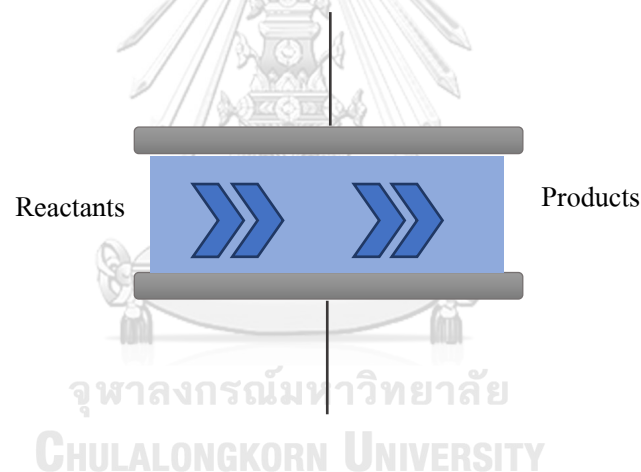
2.8 Microchannel

Microchannel reactors are small size reaction chambers. The dimensions of this reactor are typically in the range of micrometers (1-1000 μm) and volumetric capacity in the range of microliters (μL). The microreactor is widely used to study reaction kinetics as well as reaction mechanisms because of negligible heat and mass transfer resistances within the reactor. The axial

temperature, concentration, and velocity (that can occur while mixture stirred in the system) gradients appear in the fixed bed reactors which do not occur in the microchannel reactor module. Consequently, the microchannels reactor module was operated isothermally, and this can be quickly able to stable in continuous flow. This unit afforded a rapid and easy collection of data on reaction kinetics. Additionally, this reactor is very effective in control resident time. It is therefore this reactor can be easily identified as intermediate in the reaction. Moreover, the small size of this reactor which easy to control a high surface area to volume ratio and has faster reaction than conventional reactors.

2.9 Kinetics

Due to the substance was flowing through the Teflon channel between anode and cathode. The flow pattern in the micro-reactor is similar to the plug flow reactor. The small size of the reactor can negligibly heat and mass transfer resistances within the reactor.



Mole balance

$$\left[\begin{array}{c} \text{Molar flow rate} \\ \text{of species } j \\ \text{In at } V \\ \text{moles/time} \end{array} \right] - \left[\begin{array}{c} \text{Molar flow rate} \\ \text{of species } j \\ \text{Out at } (V+\Delta V) \\ \text{moles/time} \end{array} \right] + \left[\begin{array}{c} \text{Molar rate} \\ \text{of generation of} \\ \text{species } j \text{ within } \Delta V \\ \text{moles/time} \end{array} \right] = \left[\begin{array}{c} \text{Molar rate} \\ \text{of accumulation of} \\ \text{species } j \text{ within } \Delta V \\ \text{moles/time} \end{array} \right]$$

$$F_{A0} - F_A + \int_V \sum v_{Ai} r_i dV = \frac{dN_A}{dt} \quad \text{Eq. (31)}$$

At steady state

$$\frac{dN_A}{dt} = 0$$

Single reaction

$$r_1 = kC_A^n$$



CHAPTER 3

MATERIALS AND METHODS

3.1 Material and Equipment

3.1.1 Acetonitrile with purity of 99.5% was purchased from Duksan reagents, Korea.

3.1.2 Acetonitrile-3d with purity of 99.8% was purchased from Cambridge Isotope Laboratories, Inc., USA

3.1.4 Hexadecane (Industrial grade)

3.1.5 Lauric acid with purity of 99.8% was purchased from Krungthepchemi co., ltd., Thailand.

3.1.6 N,O-bis (trimethylsilyl) trifluoroacetamide, and trimethylchlorosilane mixture (99:1) for GC derivatization was purchased from Sigma-Aldrich, Switzerland.

3.1.7 Pyridine with purity of 99.8% was purchased from Sigma-Aldrich, Switzerland.

3.1.8 Silica gel

3.1.9 Undecane with purity of 99.9% was purchased from Dr. Eehrenstorfer, India.

3.2 Experiment Procedures

3.2.1 The reaction kinetic

The microreactor used in the experiment, the cross-section area is $2.7 \times 10^{-4} \text{ m}^2$ and high of space between anode and cathode is $250 \times 10^{-6} \text{ m}$ (Teflon thickness). This reactor consists of two sides of electrodes including anode is graphite and cathode is stainless steel. The middle of two electrodes is separated by Teflon that can customize the high of the channel of reactor by the thickness of Teflon's sheet. The anode and cathode sides of the reactor connected with DC power supplied to control applied potential and current density in the experiment that known the value by multimeter as shown in Figure 10.

For the substrate, the experiment has to prepared 4 level of concentration of lauric acid in acetonitrile solvent consist of 30, 40, 50, 60 mM. It is flowed into a microchannel reactor at controlled residence time by syringe pump.

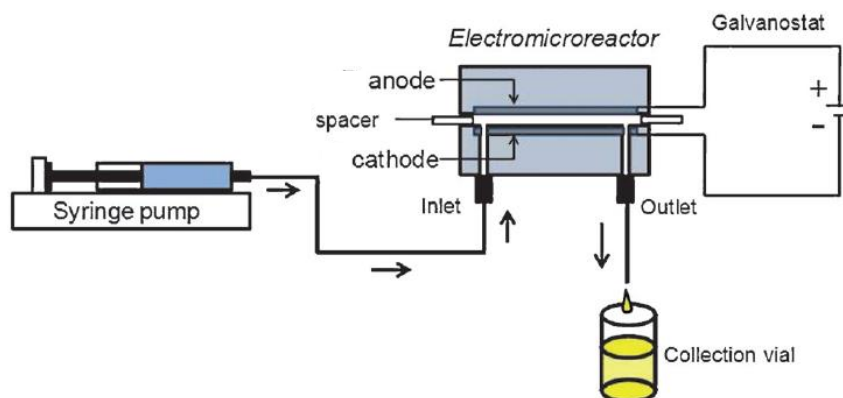


Figure 9 Schematic diagram of experiment setup

For analysis, the hexadecane (C16) was added in the precursor reaction as internal standard to confirm the concentration of each compound in products. For the liquid of product after the reaction, 100 μl of the derivatization solvent (N,O-bis (trimethylsilyl) trifluoroacetamide, and trimethylchlorosilane mixture (99:1)), and 200 μl pyridine was added. Then the mixture was heated in a water bath (60°C) for 60 minutes. Finally, the filtrate was used with a 0.22 μm Nylon syringe filter.

The products were identified by gas chromatography mass spectrometry (GC-MS, Agilent 7890A/5975C) with a HP-5 column. The injection temperature was 260 °C and the detection temperature was 280 °C. The column temperature was first held at 100 °C for 2 min and increased to 280 °C at a ramp rate of 10 °C per min. Highly pure helium was used as the carrier gas.

The liquid products were quantitatively analyzed by gas chromatography with a flame ionization detector (Agilent 7890 A) using a HT-5 capillary column. The injection temperature was 260 °C and the detection temperature was 280 °C. The column temperature was first held at 100 °C for 2 min and increased to 280 °C at a ramp rate of 10 °C per min; highly pure N₂ was used as the carrier gas.

The concentration of product and substrate were used to calculate conversion, selectivity, and yield.

$$\text{Conversion (mol\%)} = \left(1 - \frac{n(\text{lauric after reaction})}{n(\text{lauric before reaction})} \right) \times 100\% \quad \text{Eq. (32)}$$

$$\text{Yield (mol\%)} = \frac{\sum n(\text{iso-C11 product})}{n(\text{lauric acid converts in the reaction})} \times 100\% \quad \text{Eq. (33)}$$

$$\text{Selectivity (\%)} = \frac{\text{Yield(mol\%)}}{\text{Conversion(mol\%)}} \times 100\% \quad \text{Eq. (34)}$$

The apparent reaction rate constants are calculated by the solution 2nd order reaction in plug flow reactor (PFR).

$$r_1 = kC_A^2 \quad \text{Eq. (35)}$$

$$\frac{C_A}{C_{A0}} = \frac{1}{1+k\tau C_{A0}} \quad \text{Eq. (36)}$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = k\tau \quad \text{Eq. (37)}$$

Then, plot the graph between left term of concentration versus resident time in each of factor consist of current density, concentration. To find k, the slope is reaction kinetic values that were obtained with correlation coefficients higher than 0.98.

When the reaction order is 2nd order in plug flow reactor, C_A is the initial lauric acid concentration, C_{A0} is the final lauric acid concentration and k is an apparent rate reaction constant.

3.2.2 Reaction behavior

The reaction behavior of synthesis of alkane from lauric acid was studied to understanding the reaction pathway and lead to a preliminary mechanism. First, the previous section that study the kinetic constant, the main and by-products which occur in the reaction was found and identified. The concentration of each of the compounds depending on residence time, the main pathway has assumed.

Additionally, the acetonitrile-3d has used instead normal acetonitrile in substrate to studies hydrogen transfer in reaction. The solvent that has deuterium in hydrogen position. However, deuterium has same atom number and chemical properties as hydrogen but the higher mass than hydrogen. So, the transfer behavior of D was assuming to similar to H and can observe D transfer by GC-MS and NMR.

NMR or Nuclear magnetic resonance spectroscopy is technique to observe details of the electronic structure of a molecule and its individual functional groups. The product was added in thin NMR tube and placed in a magnetic field.



CHAPTER 4

RESULTS AND DISCUSSION

To study the individual effects of applied current density, the initial concentration of lauric acid, and resident time in micro-reactor on the Kolbe electrolysis of lauric acid using graphite and stainless steel as anode and cathode material, each experimental variable was varied while the remaining were kept constant. In the following, the observed lauric acid conversion and each product yield are discussed and compared among various experimental conditions. Additionally, the kinetics of the reaction was studied to interpret the reaction behavior.

4.1 Effect of current density on conversion of lauric acid and yield of product

Applied potential is one factor that is the amount of work energy needed to move a unit of electric charge also known as potential drop or electric potential. Ying-Shuang Liang and colleagues [17] were investigations of the applied potential effect on reaction mechanisms, this factor is the impact on the movement of electrons in the reaction. When increasing applied potential, the amount of electrons and charge is also increased.

The current density is the amount of charge flowing over the cross-section. The increasing current density in a system of the experiment can increase the number of electrons in the reaction. In chapter 2, many research works such as Daniela E. Blanco and colleagues [15] have concluded that the amount of charge or electron can support different pathway intermediate in reactions between carbocation and alkyl radical.

The experiments were performed at room temperature, 405s of resident time, and the initial concentration of lauric acid is 50 mM dissolved in pure acetonitrile. The amount of the lauric acid and product at each current density over 6.67 - 37.03 A/m² was measured by GC-FID. The products used to calculate the yield are undecane, 4-undecene, 5-undecene, propyl cyclooctane, methyl cyclodecane (all of iso-C11 products).

Base on the experimental data, the conversion and yield of product were calculated and shown in Table 6. A plot of the total conversion and yield versus applied current density is shown in Figure 11. The obtained results show that the conversion was increased by increasing

current density. On the other hand, the product yields were no significant changes (maximum and minimum value are 14.0, 8.06, respectively).

Table 6 Effect of current density on the conversion and yield of experimental data

Current density (A/m ²)	Experiment 1#		Experiment 2#		Average	
	Conversion	Yield	Conversion	Yield	Conversion	Yield
6.7	48.52	11.75	47.20	11.00	47.86	11.37
11.5	57.85	14.61	54.39	12.57	56.12	13.59
15.6	60.63	16.75	61.50	13.97	61.07	15.36
20.4	66.99	15.16	65.94	16.12	66.46	15.64
37.0	82.12	8.48	78.28	8.97	80.20	8.72

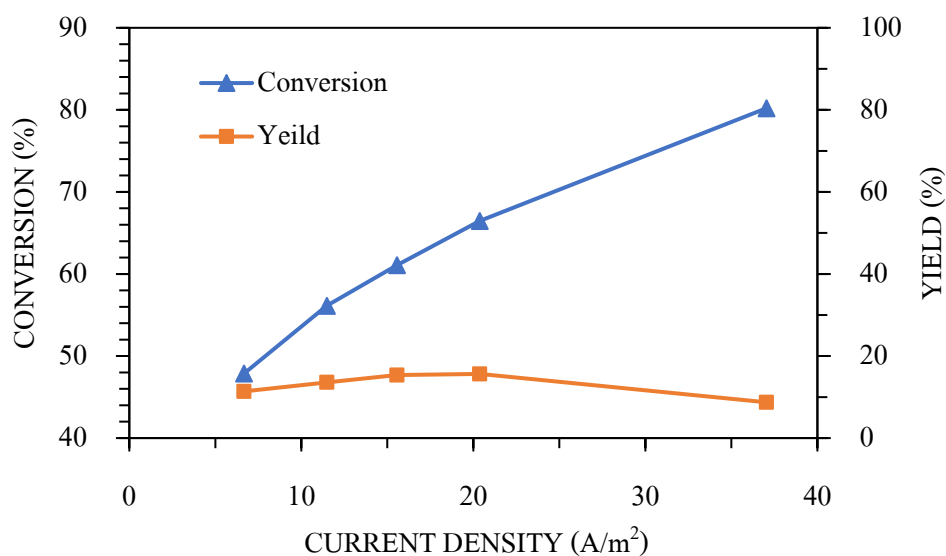


Figure 10 The lauric acid conversion and yield versus current density at resident time = 405s; initial concentration of lauric acid = 50mM in acetonitrile solvent

Additionally, the product distribution in Figure 11. The increasing three main by product was noticeable consist of docosane, 2-undecanol dodecanoate, and dodecanoic acid undecyl ester. The amount of by-product was increased as applied potential and conversion increased. When

the reaction used low current density about 6.67 A/m^2 , the docosane was not occurred. So, iso-C₁₁ can occur in range of $6.67\text{-}37.04 \text{ A/m}^2$ but docosane must have high current density over 11.48 A/m^2 .

The trends was similar to Daniela E. Blanco's work [15]. He concluded the intermediate in form of radical can transform to cation by lose addition electron at high current density. So, the product radical can reduce as side reaction.

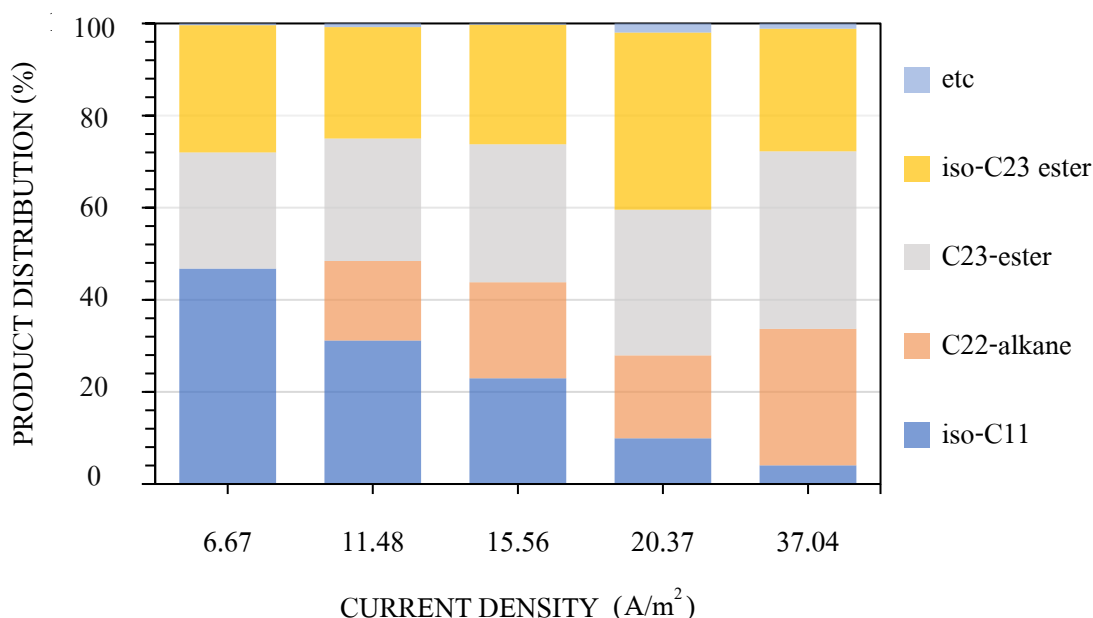


Figure 11 The product distribution versus applied potential at resident time = 405s; initial concentration of lauric acid = 50mM in acetonitrile solvent

4.2 Effect of the initial concentration on conversion of lauric acid and yield of product

The effect of the initial concentration on conversion of lauric acid and yield of iso-C₁₁ products has studies in conditions: varies concentration of lauric acid over 40-70 mM, current density = 8.2, and 11.9 A/m^2 , and resident time = 405 s. The conversion of lauric acid and yield of iso-C₁₁ products data was shown in Table 7 and plotted as a function of initial concentration in Figure 12. It is obtained that the conversion rose as current density increased by 10 mM from 40-

70 mM but has no significant change on the yield. The concentration is related to the molecules in the system. When the reaction has higher molecule in system, it's can increase the chance of molecular collisions.

Table 7 Effect of the concentration of lauric acid on the conversion and yield of the experimental data at 40, 50, 60, 70 mM

Concentration (mM)	Experiment 1#		Experiment 2#		Average	
	Conversion	Yield	Conversion	Yield	Conversion	Yield
40	34.2287	16.1825	46.2382	19.0426	40.2335	17.6125
50	42.2004	27.2415	57.7273	22.2634	49.9638	24.7524
60	51.3655	17.4783	69.3875	20.5673	60.3765	19.0228
70	57.0851	15.9656	77.1138	18.7873	67.0995	17.3764

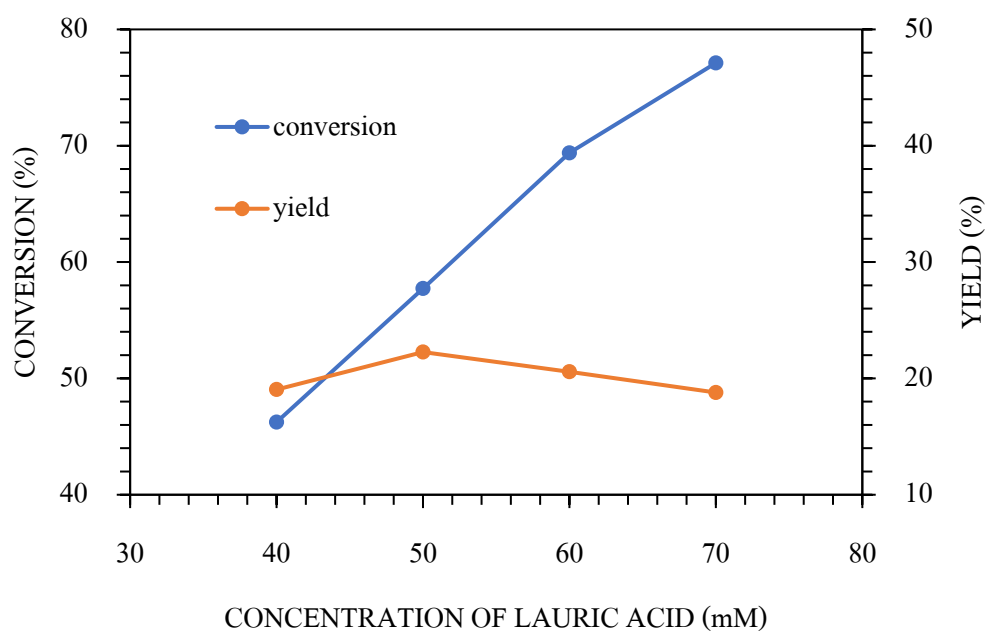


Figure 12 The lauric acid conversion and yield of product versus concentration at applied potentials 6 V; current density = 8.2 A/m^2 ; resident time = 405 s

4.3 Effect of resident time on conversion of lauric acid and yield of product

The effect of the resident time in the reactor on the conversion of lauric acid and yield of iso-C₁₁ product in the presence of 50 mM lauric acid in pure acetonitrile, current density is 8.2 and 11.9 A/m². As seen from Table 8 and the corresponding Figure 13 and Figure 14. The conversion increased with resident time in reactor. Additionally, observing the current density, the low current density (8.2 A/m²) has a lower rate of increase conversion of lauric acid than high current density (11.9 A/m²). But the increasing residence time over 980s, the conversion at 8.2 A/m² have higher conversion than the conversion at 11.9 A/m² that can conclude the current density have high effect in the first time and less effective when the time increases over 980s. Additionally, the effect of residence time on yield of product as shown in Figure 15. The slope is raised as residence time increase. So, the product is stable and not occur the reversible reaction.

Table 8 Effect of resident time on the conversion and yield of experimental data at current density = 8.2, 11.9 A/m²

Current density (A/m ²)	Resident time (s)	Conversion (%)	Yield (%)
8.15	1215	79.51	57.10
	810	70.14	40.12
	486	64.54	36.79
	405	57.73	22.26
	243	45.08	17.73
11.85	1215	76.93	44.33
	810	70.14	20.14
	486	64.54	16.79
	405	62.57	15.29
	243	56.63	10.59

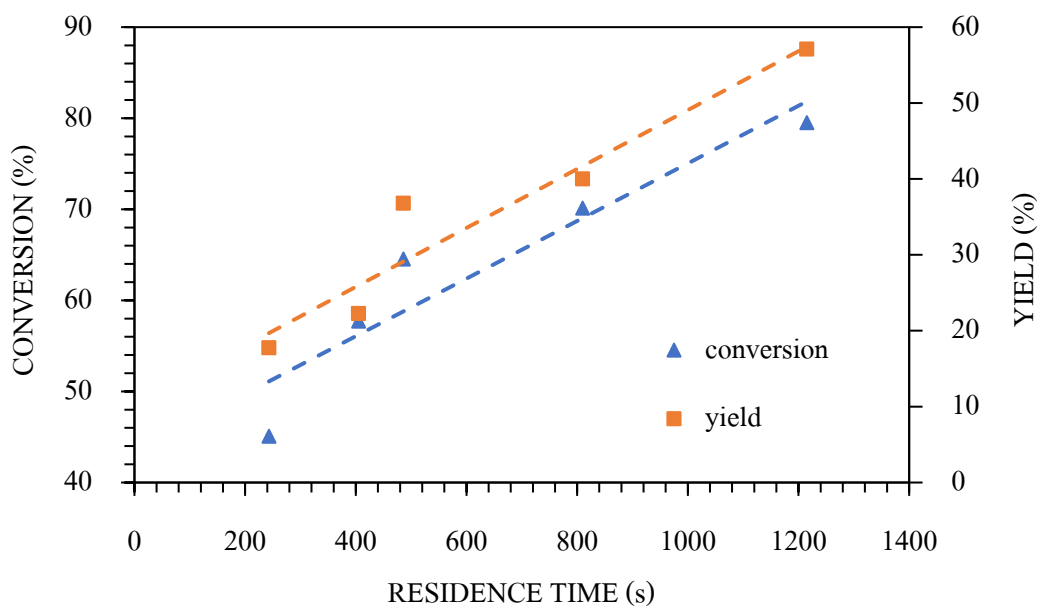


Figure 13 The lauric acid conversion versus resident time at current density = 8.2 A/m^2 ; concentration of lauric acid = 50mM in acetonitrile solvent

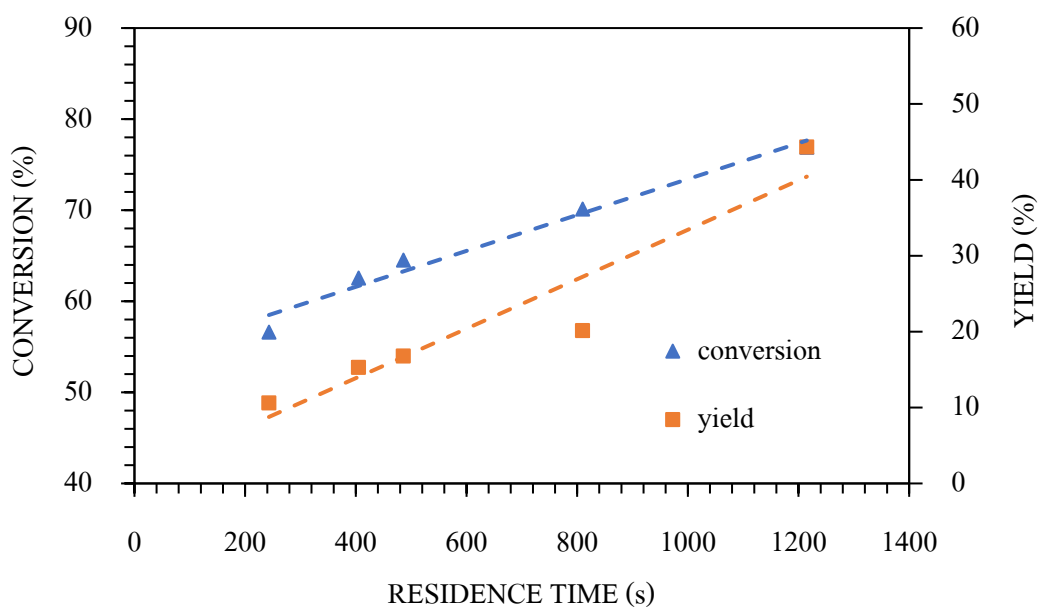


Figure 14 The yield of product versus resident time at current density = 11.9 A/m^2 ; resident time = 405s; concentration of lauric acid = 50mM in acetonitrile solvent

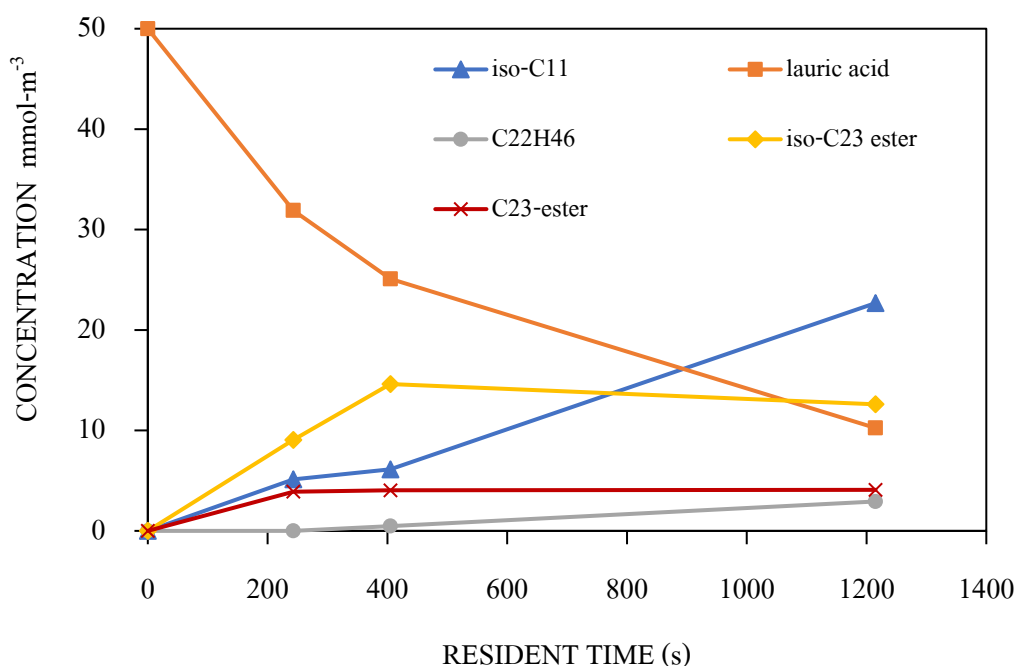


Figure 15 The lauric acid concentration of any compound versus resident time at current density = 11.9 A/m^2 ; resident time = 405s; concentration of lauric acid = 50mM in acetonitrile solvent

For Figure 15, the first part of concentration of any compound was obtained in term of resident time, the experiment is residence time in range 0-405s, the amount of lauric acid was drop sharply, the product was continued to increase. Next part, the slope of concentration was decreases. The reaction rate was lower than before and both of $\text{C}_{23}\text{O}_{46}\text{O}_2$ and isomer was stable. For the assumption, both of $\text{C}_{23}\text{O}_{46}\text{O}_2$ are intermediate that occur from lauric acid and can breakdown to be another compound in long time but the rate of combination and decomposition reaction maybe close to other. Additionally, the docosane ($\text{C}_{22}\text{H}_{46}$) is continue increases for 1200s. The docosane and undecane is alkane that saturated and stable that hard to breakdown or decomposition.

From all of assumption, the reaction pathway can draft in Figure 20 that used to be main in studies behavior of the reaction.

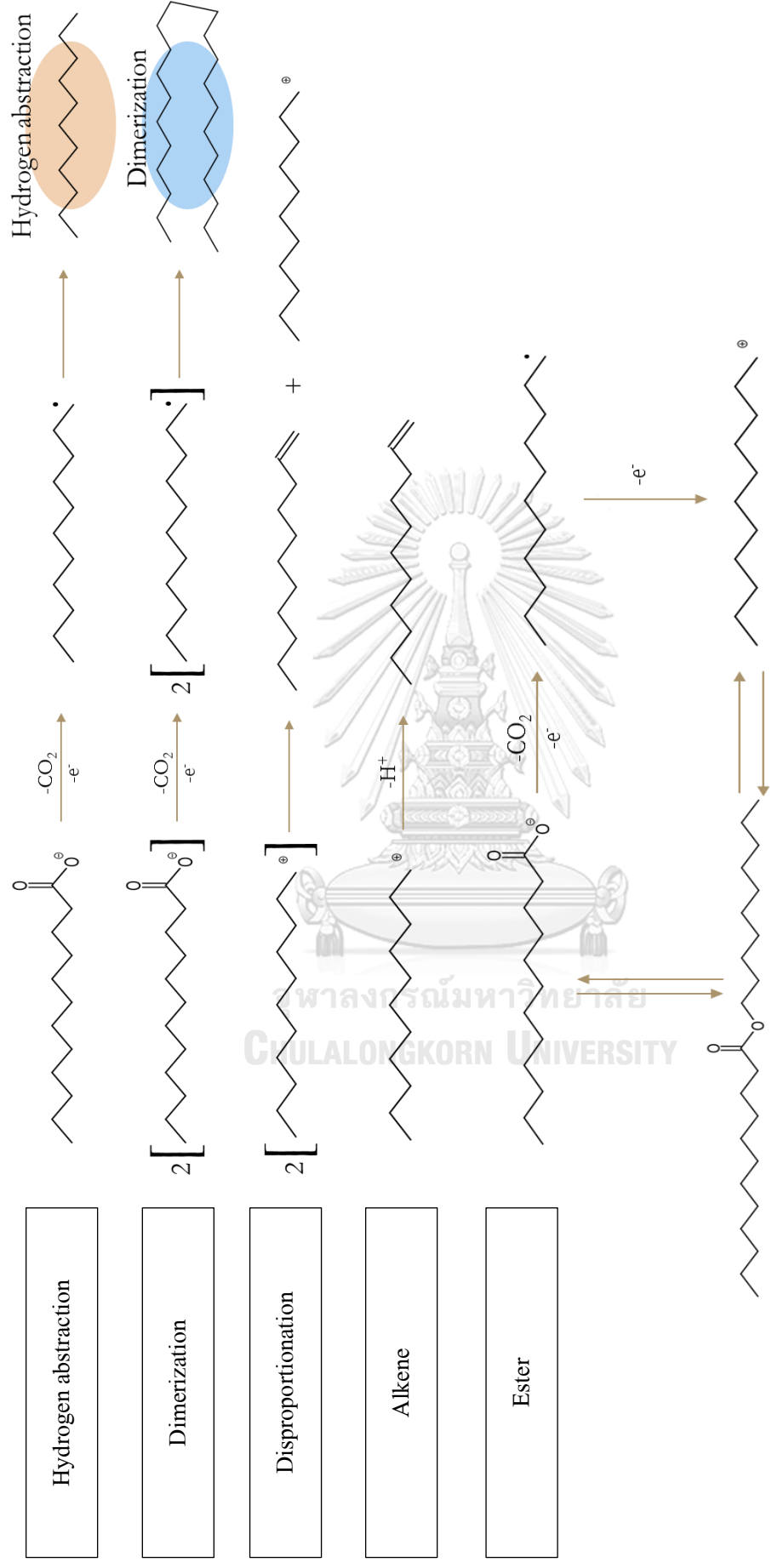


Figure 16 The reaction pathway for the Kolbe synthesis of undecane

4.4 Effect of addition ion in lauric acid on conversion of lauric acid and yield of product

From the previous experiment, the hydrogen is very important for occurrence of undecane. The desired product or undecane can produce from combination of hydrogen and alkyl. For the assumption, when the hydrogen in reaction was increase, the desired product ratio per alkene was increase.

So, the experiment used 0.1 M HCl as additive acid in initial reactant to compare the product distribution with common experiment at the condition; concentration of lauric acid is 50 mM, applied potential is 6V, current density is 7.40 A/m² and residence time is 405s.

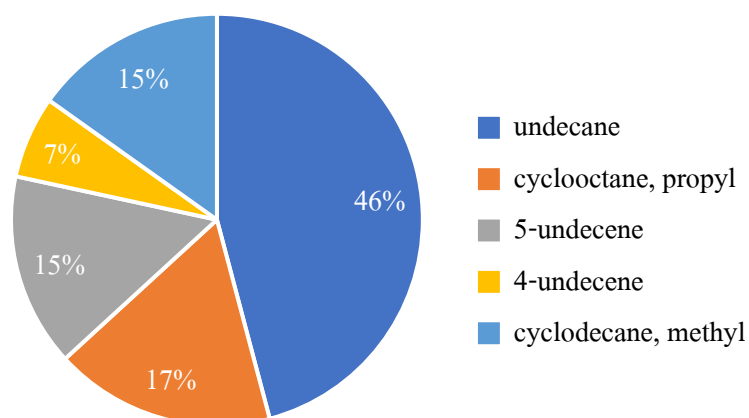


Figure 17 The product distribution of iso-C11 in the reaction with no adding acid

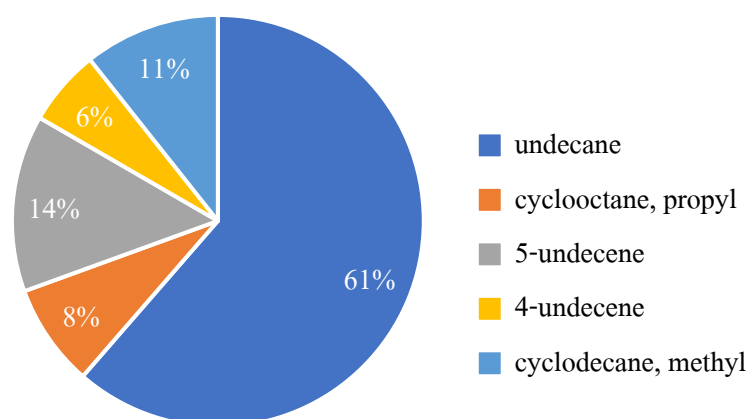
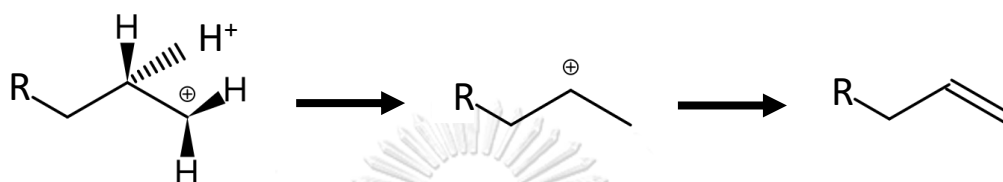


Figure 18 The product distribution of iso-C11 in the reaction with adding acid

For the result in Figure 21 and Figure 22, the experiment that added acid in initial reactant can produce more of undecane from 46% to 61%. So, the additive hydrogen in solvent is effect to the pathway of the reaction. It's increase alkane but decrease propyl cyclooctane, and methyl cyclodecane. The added acid maybe supports to convert the cyclo-alkane to be alkane. Besides, the research work of Kurihara and colleagues [7] said when high amount of alkene can force the molecule into more stable form which is cycloalkane.



Alkanes can produce in pathway of carbocation occurrence. It's loss one electron and one of proton from alkyl radical. Then the positive charge in molecule can move the position and pull another carbon in same chain to form cycloalkane. So, the increasing of proton in system can reduce alkene and cycloalkane forming in products.



Additionally, the alkane in products is also increase. F. M'Halla and colleagues research work [16] are explained about the hydrogen abstraction of halo acid(X-H) to produce haloaromatics. They found aromatics (Ar-H) has produced as co-products with haloaromatics (Ar-X) because the radical which occurred by electroactive can attack the near molecule and pull halogen or hydrogen in form of radical.

For this experiment, it is possible that the hydrochloric acid can breakdown and donor proton which can inhibit the product of carbocation and some of them can occur the hydrogen abstraction with alkyl radical to be alkane formation.

4.5 Deuterium experiment

Aforementioned in chapter 2, the hydrogen in undecane or desired product are received from solvent by hydrogen abstraction reaction. It's can confirm by deuterium experiment, the deuterium solvent was used as solvent in the reaction instead common solvents. For the example;

this works used acetonitrile-3d or acetonitrile which deuterium replace the hydrogen with 3 positions. The result of the experiment was observed in Figure 19.

The mass spectrum of undecane from the reaction was analyzed by GC-MS. The Figure 20 and Figure 21 is mass spectrum of undecane in common acetonitrile and acetonitrile-3d as solvent, respectively. A breakthrough platform shows the deuterium is transfer into undecane molecule or hydrogen abstraction was occurred in the reaction. The molecular weight at 157.1 m/z was increase and 191, 281 m/z was evinced.

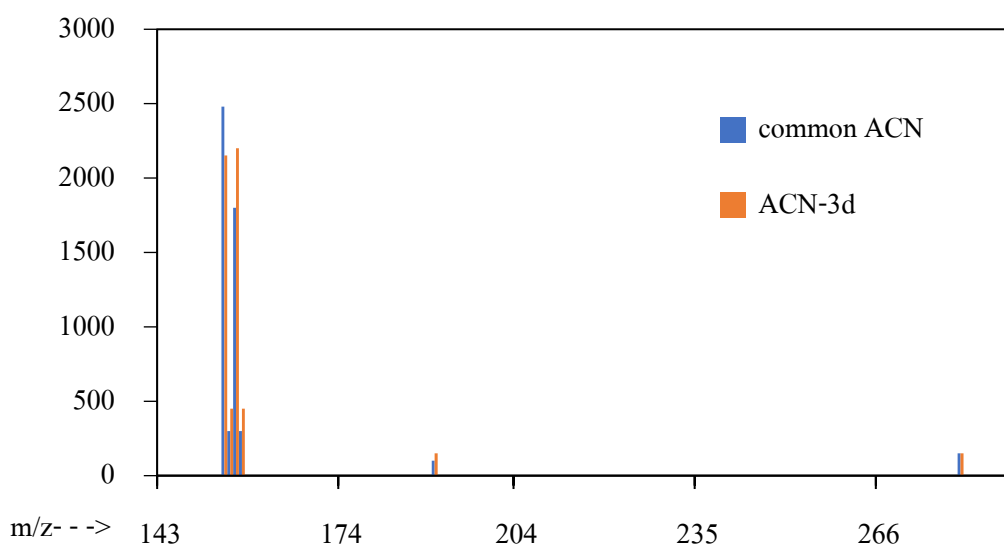


Figure 19 The mass spectrum of undecane in acetonitrile and acetonitrile-3d

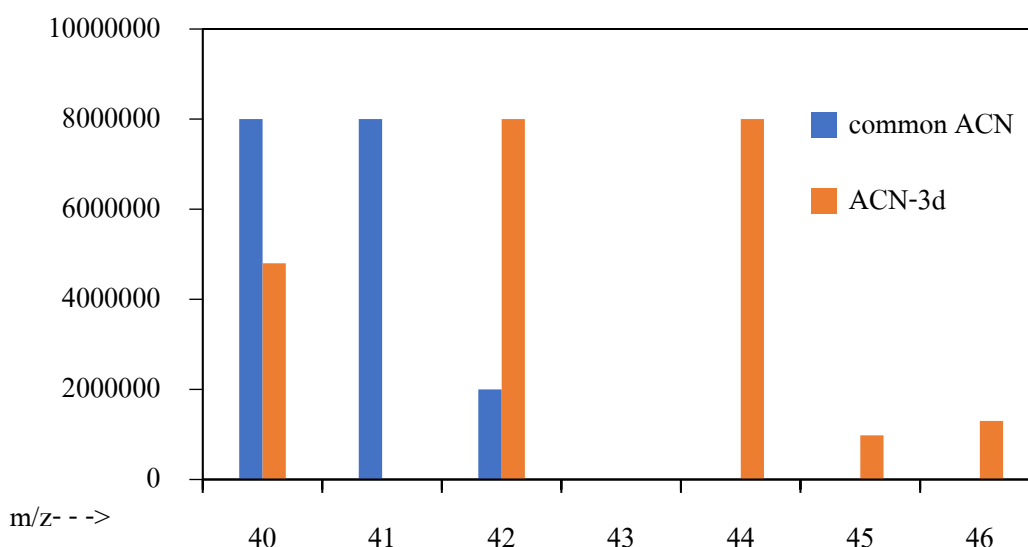


Figure 20 The mass spectrum of acetonitrile compares with acetonitrile-3d in the reaction

The mass spectrum of common acetonitrile has molecular weight at 40, 41, 42, and 43 m/z. The adding deuterium acetonitrile-3d must be 42, 44, and 46 for 1st, 2nd, and 3rd deuterium. However, the mass spectrum has a trend and ratio similar acetonitrile-3d but the molecular weight 45 was found that can assume deuterium in solvent can be replaced by hydrogen in solution.

The presence of the undecane was indicated by ^{13}C -NMR spectrum at around δ 14, 23, 25, 30, and 33 ppm. The type carbon atoms are depending on force of any atoms around them. For undecane have 6 types as shown in Figure 21 and Figure 22.

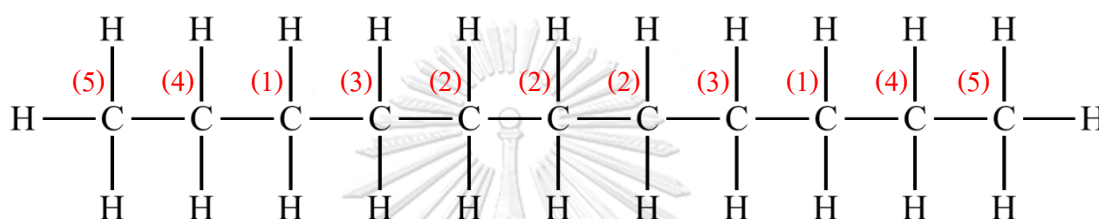


Figure 21 Position of 6 types of carbon atom in undecane molecule

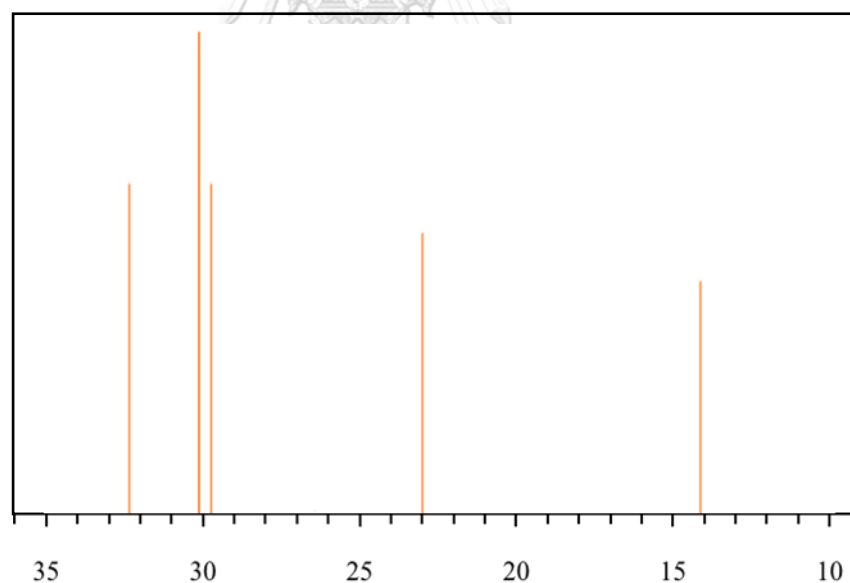


Figure 22 ^{13}C NMR spectrum of undecane

C(1) = 33.0203	C(2) = 30.7069
C(3) = 30.5877	C(4) = 23.7760
C(5) = 14.7727	

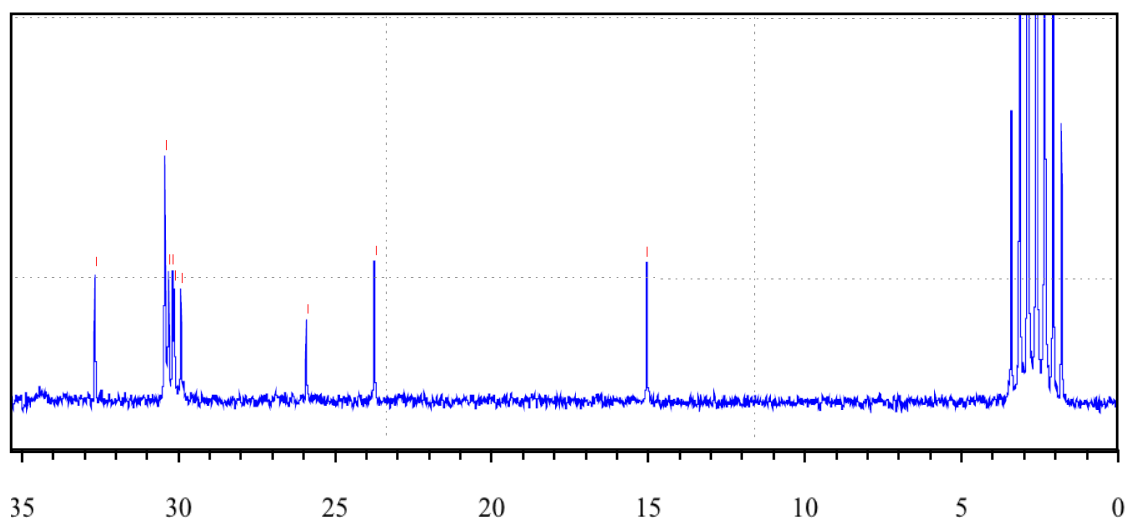


Figure 23 ^{13}C NMR spectrum of the reaction product of lauric acid in the condition (applied potential = 6V, current density = 7.40 A/m^2 , concentration = 50 mM, and resident time = 405s)

From the result, Figure 23, the undecane was found but at around δ 30 ppm have 4 addition peaks. Because hydrogen position is instead with deuterium atom that have effect to undecane molecule. Additionally, undecane (double bond) and dodecanoic acid, undecyl ester ($\text{C}=\text{O}$) was not detected. So, the result is only alkane structure.

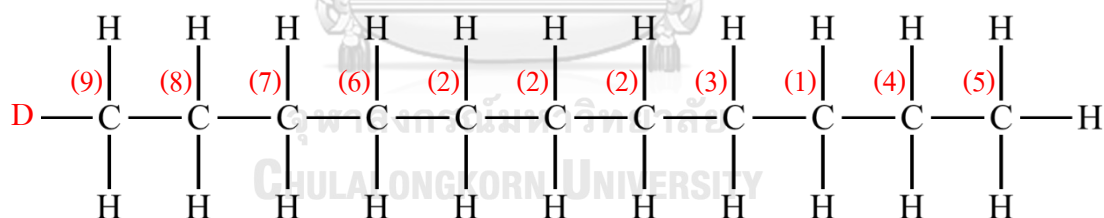


Figure 24 Position of 9 types of carbon atom in undecane molecule with 1 position of deuterium

The result support the assumption that the hydrogen which combine to alkyl radical from hydrogen abstraction with solvent. Besides, the main product in reaction was straight chain alkane.

4.6 Apparent rate of the reaction

4.6.1 Current density

The speed at which a chemical reaction proceeds. It is often expressed in terms of either the concentration (amount per unit volume) of a product that is formed in a unit of time or the concentration of a reactant that is consumed in a unit of time. The reaction kinetic of this reaction was study

1st order reaction is first assumption, the graph between $\ln(C_a/C_{a0})$ versus residence time was plotted and found correlation coefficients compare to the 2nd order reaction. Then, for the result that can conclude the reaction are 2nd order reaction. when C_{a0} is the initial concentration of lauric acid, C_a is the concentration of lauric acid at varies residence times.

The graph between $(1/C_a)-(1-C_{a0})$ versus residence time in varies current density as the data in table 9. The slope is reaction rate constant values that were obtained with correlation coefficients higher than 0.98 as shown in Figure 25.

Table 9 The calculation data from the experiment to find reaction rate constant

Residence time (s)	$1/C_A$	$1/C_{A0}$	$(1/C_A)-(1/C_{A0})$
1215	0.0976	0.02	0.0776
405	0.0456	0.02	0.0256
243	0.0364	0.02	0.0164

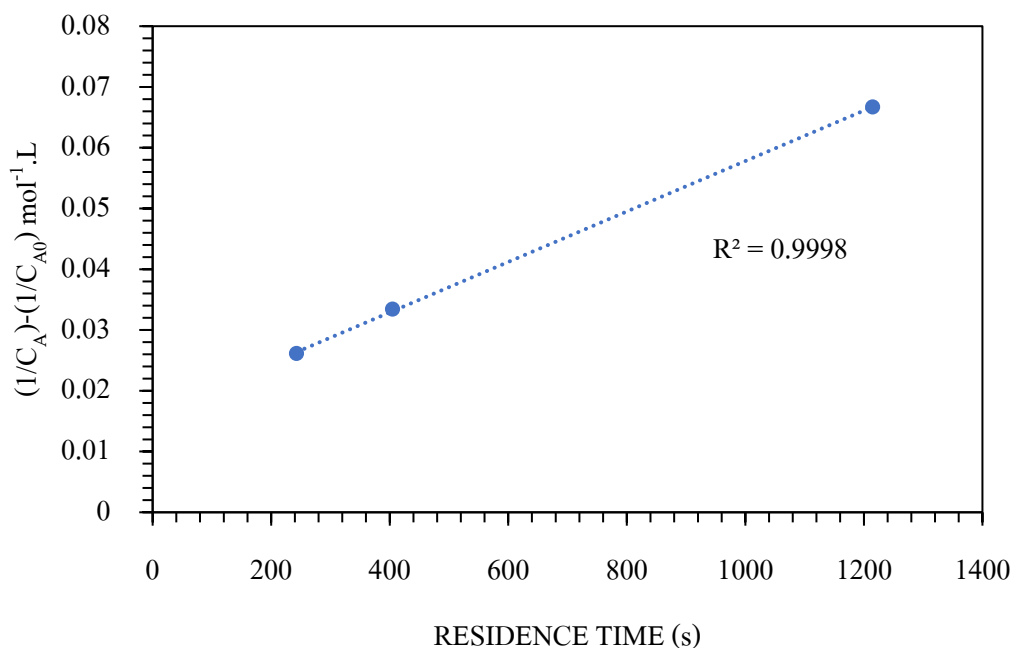


Figure 25 The reaction rate form plotting graph between $(1/C_A) - (1/C_{A0})$ versus residence time

Table 10 The reaction rate constant at varies current density

Current density (A/m^2)	k ($\text{mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$)
3.7	1.44×10^{-5}
7.4	4.15×10^{-5}
11.11	6.33×10^{-5}

From Table 10 and the corresponding Figure 26, the reaction rate of the reaction was increased by increase the current density. The more electron in reaction can support the reaction forward. Additionally, the trend of the reaction was linear regression that can conclude the reaction mechanism are depend on current density or electron in reaction. The slowest rate is the path to produce carbocation and this path are easiest in all of mechanism.

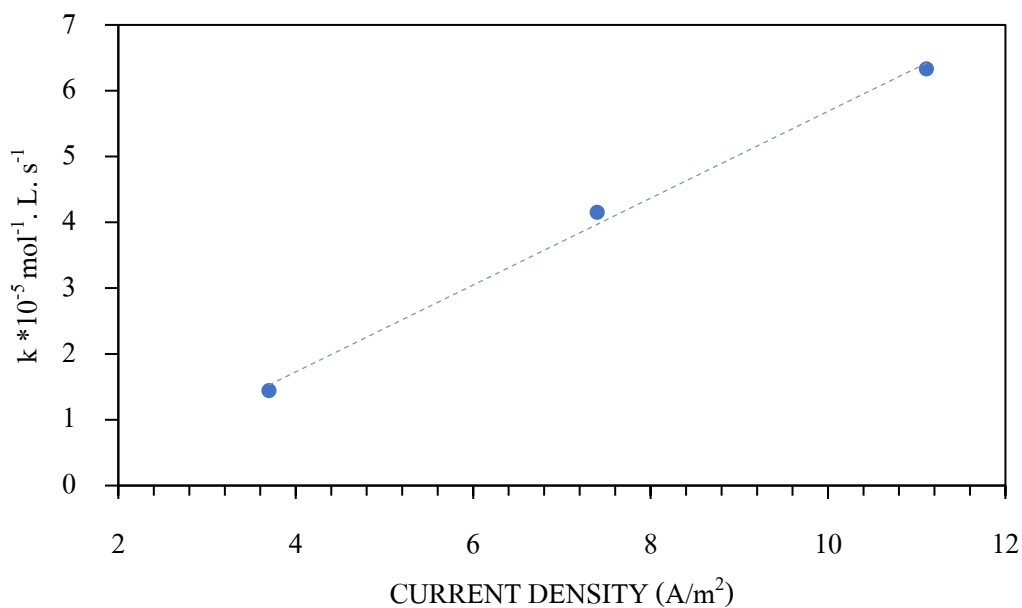


Figure 26 The reaction rate constant versus current density in the reaction

4.6.2 Concentration of lauric acid

The initial concentration was related to the density of lauric acid molecule in solvent. High concentration of substance can increase the chance of collision of molecule. To find k , the 2nd reaction solution for plug flow reactor were used as after mention. The result from the calculated as shown in Figure 27.

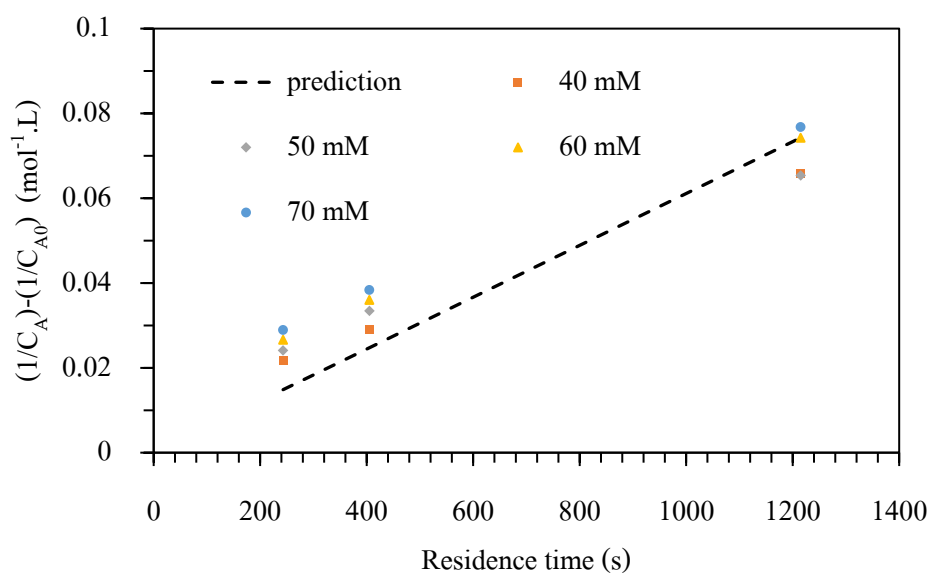


Figure 27 The reaction rate constant versus concentration of initial lauric acid

The reaction rate constants can calculate from the slope between concentration term ($1/C_A - 1/C_{A0}$) versus residence time. The slope in the range of 40-60 mM was linear trend. The reaction rate constant is $6.11 \times 10^{-05} \text{ mmol}^{-1}\text{L} \cdot \text{s}^{-1}$. So, the calculated reaction rate constant can be used to predict the concentration of lauric acid in the reaction.

4.7 Blended methanol

Methanol is protic solvent that have molecular weight and structure clos to acetonitrile. F.Joschka Holzhäuser and colleagues [18] studies the effect of system of solvent and explain the impact of protic solvent can increase the reaction rate of reaction. First, the experiment to studies the effect of methanol in solvent by varies ratio of methanol in solvent as 0/10, 1/9, 7/3, and 10/0 of methanol per acetonitrile.

As seen in Figure 28. The addition of methanol can increase the conversion. As the expect, the increasing of methanol in system of solvent maybe increase the rate of reaction. However, the high of conversion or rate of reaction but yield from the experiment are low. Then, to studies of the products. Methanol blended solvent was analyzed by GC-MS technique to identifies all of product. For the result, the by-products that different from used pure acetonitrile solvent are methyl undecyl ether, dodecanoic acid methyl ester, 2-undecanol methyl ether, 2-undecanol and dodecanoic acid methyl ester. Due to methanol are protic solvent that can donor proton and form to be nucleophile. Then, the nucleophile in negative charge will pull carbocation which a opposite charge to produce ether molecule.

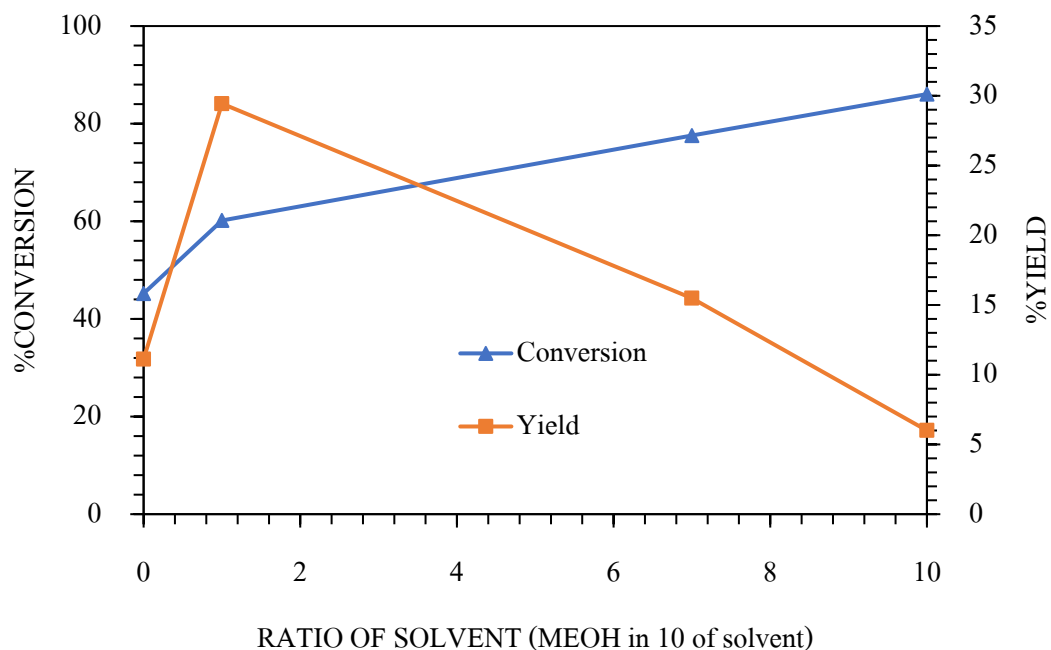


Figure 28 The lauric acid conversion versus blend ratio of methanol per solvent at applied potentials 6 V; resident time = 405s; concentration of lauric acid = 50mM in acetonitrile solvent

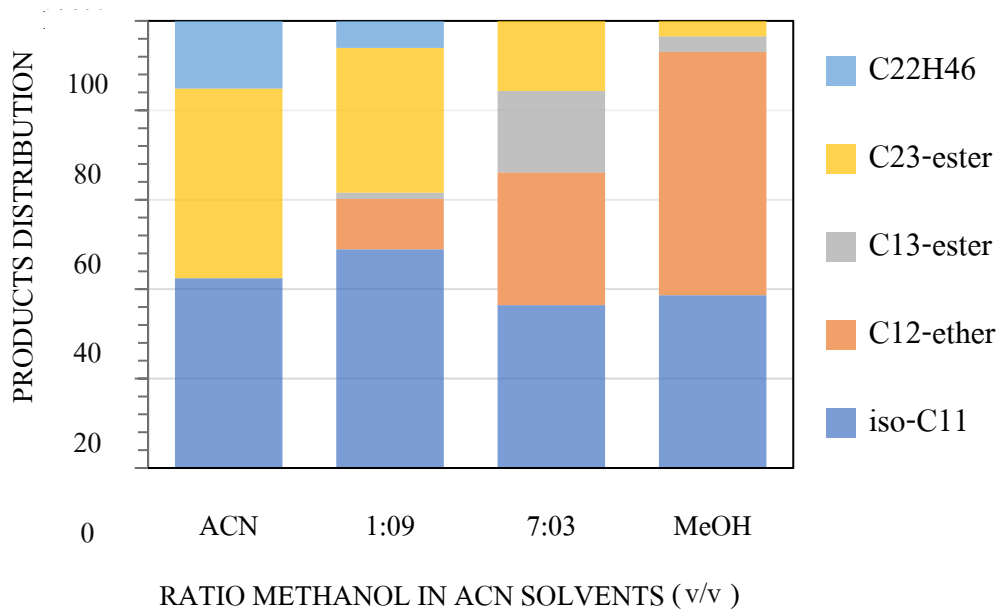


Figure 29 The product distribution versus applied ratio of methanol in solvent at resident time = 405s; current density = 7.04 A/m²; concentration of lauric acid = 50mM in acetonitrile solvent

Next, to studies the relation of methanol on product distribution, the compare amount of any products in varies of ratio of methanol in solvent as shown in Figure 29.

Holzhauser's research work [19], the non-Kolbe reaction can process by protic or aqueous solution. Solvent can donor proton and form to be nucleophile or negative charge and combined with carbocation. For this experiment; methanol can breakdown in to H^+ and MeO^- . So, MeO^- will attack the positive charge by nature and form to be ether. For the lauric acid that haven't enough of energy to breakdown ($R-COO^-$). It's also negative charge and pull MeO^- in system to be ester.

Then, from kinetics data, the reaction rate constant was increased by adding methanol in solvent as shown in Table 12. So, lauric acid can react more and breakdown in alkyl radical. The ester by-product will be decrease in high ratio of methanol in solvent or high reaction rate constant. In the same way, the experiment used pure methanol will have low of ester in products but high of ether because of nucleophile from methanol solvent.

Table 11 The reaction rate constant at varies ratio of methanol in solvent

ratio MeOH:ACN	k ($mol^{-1}.s^{-1}$)
ACN	3.44×10^{-5}
1:09	3.28×10^{-5}
7:03	6.85×10^{-5}
MeOH	7.78×10^{-5}

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary of results

5.1.1 The conversion and potential of the decarboxylation reaction of lauric acid in term of reaction kinetic can increased by increase current density, initial concentration of lauric acid, and the ratio of methanol in solvents. But the high of current density are support to produce by-product or docosane and ester-C23. However, ester-C23 was assumed as intermediate but take a long time in reaction. As expected, the ester-C22 will decreases when the acid is depleted. Additionally, the high of concentration can support to docosane. Because high of reaction rate and the density of molecule at surface of anode can force alkyl radical to occur dimerization reaction more than hydrogen abstraction with solvent.

5.1.2 Methanol can increase reaction rate but the dissociation of solvent is support to non-Kolbe products. When increase the ratio of methanol in mixed solvents, the by product or C12-ethers are increased. The suitable ratio of MeOH in mixed solvent are 1:9 to produce undecane.

5.1.3 The hydrogen transfer in reaction; first, alkyl radical can pull hydrogen around themselves to occur the hydrogen abstraction. The solvent inform radical can exchange hydrogen with others and solvent which close to cathode will received H-radical at surface.

5.2 Conclusions

The suitable condition to produce undecane in this research work is 8.2 A/m^2 , and long residence time (in this work maximum residence time is 1200 s). It's had conversion and yield equal to 79.51% and 57.10%, respectively.

The undecane in products are from the hydrogen abstraction reaction of alkyl radical with solvent. Then, the acetonitrile radical can receive hydrogen from proton in solution (from fatty acid).

5.3 Recommendations

The addition proton was effect to alkane formation. Besides, the high of proton can inhibit the occurrence of by-product. So, the adding acid compare between weak and strong will help to explain the reaction.

Used platinum as anode, Pt used as catalyst about hydrogenation or dehydrogenation of organic compound as well. Additionally, most of the research work that have alkane (not dimerization) as a co-product are used Pt at anode.



CALCULATION AND SOLUTIONS

Microreactor

$$\begin{aligned}
 \text{Width(W)} &= 0.01 \text{ m} \\
 \text{Length(L)} &= 0.027 \text{ m} \\
 \text{Thickness of Teflon(H)} &= 250 \times 10^{-6} \text{ m} \\
 \text{Surface are of electrode(A)} &= W \times L \\
 &= 0.01 \text{ m} \times 0.027 \text{ m} \\
 &= 2.7 \times 10^{-4} \text{ m}^2 \\
 \text{Volume of reactor(V)} &= A \times H \\
 &= (2.7 \times 10^{-4}) \text{ m}^2 \times (2.5 \times 10^{-4}) \text{ m} \\
 &= 6.75 \times 10^{-8} \text{ m}^3
 \end{aligned}$$

Current density

Current that observed from multimeter(I)

$$\text{For the example; I} = 1 \text{ mA}$$

$$\begin{aligned}
 \text{Current density} &= \frac{\text{current (I)}}{\text{cross section are (A)}} \\
 &= \frac{1 \times 10^{-3} \text{ A}}{2.7 \times 10^{-4} \text{ m}^2} \\
 &= 3.70 \text{ A/m}^2
 \end{aligned}$$

Residence time

$$\begin{aligned}
 \text{For the example ; flowrate(F)} &= 0.2 \text{ ml/hr} \\
 &= \frac{0.2 \times 10^{-6}}{3600} \text{ m}^3 \cdot \text{s}^{-1} \\
 &= 5.56 \times 10^{-11} \text{ m}^3 \cdot \text{s}^{-1} \\
 \text{Residence time(T)} &= \frac{\text{volume of the reactor(V)}}{\text{Flow rate(F)}} \\
 &= \frac{6.75 \times 10^{-8} \text{ m}^3}{5.56 \times 10^{-11} \text{ m}^3 \cdot \text{s}^{-1}} \\
 &= 1215 \text{ s}
 \end{aligned}$$

Solution to find reaction rate constant

$$r_1 = kC_A^n$$

For 2nd order reaction n=2

$$r_1 = kC_A^2$$

$$\frac{dC_A}{dt} = kC_A^2$$

$$\frac{1}{C_A^2} dC_A = k dt$$

$$\frac{1}{C_{A0}} - \frac{1}{C_A} = kt$$

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APPENDIX

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APPENDIX

Table 12 Calibration data of undecane, hexadecane, and lauric acid

Compound	Retention time (min)	Level	Amount(mmol.L ⁻¹)	Area
C11	5.288	1	5	23.0367
		2	10	102.4070
		3	15	126.0534
		4	20	196.3364
		5	25	253.8804
C16	10.742	1	5	20.9772
		2	10	35.3112
		3	15	54.7470
		4	20	80.4177
		5	25	99.5694
C12 acid	11.328	1	10	109.9800
		2	20	349.2201
		3	30	524.3422
		4	40	740.3302
		5	50	999.7275
		6	60	1216.0433

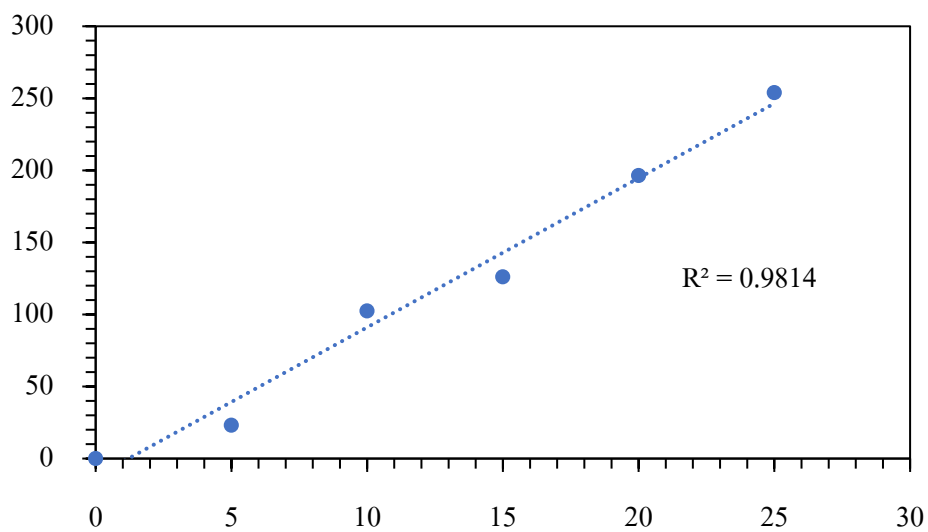


Figure 30 Calibration curve of undecane

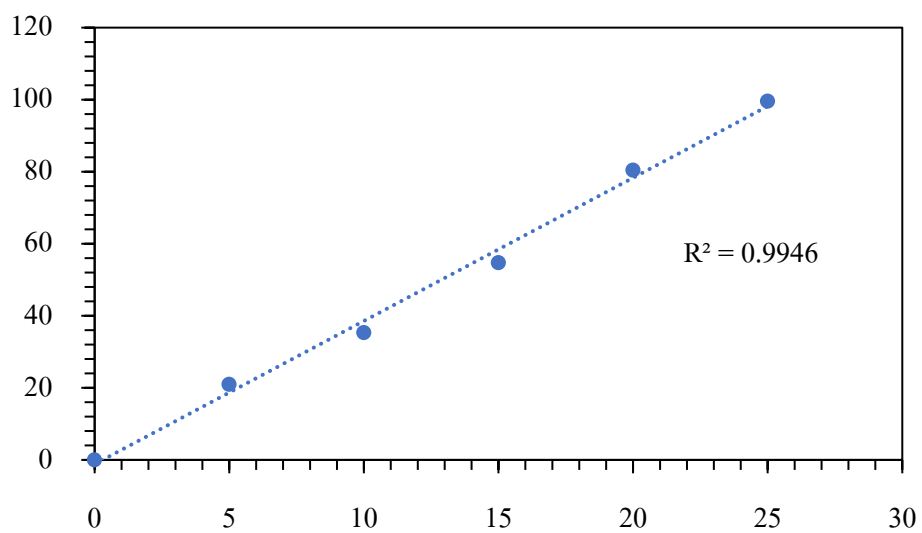


Figure 31 Calibration curve of hexadecane

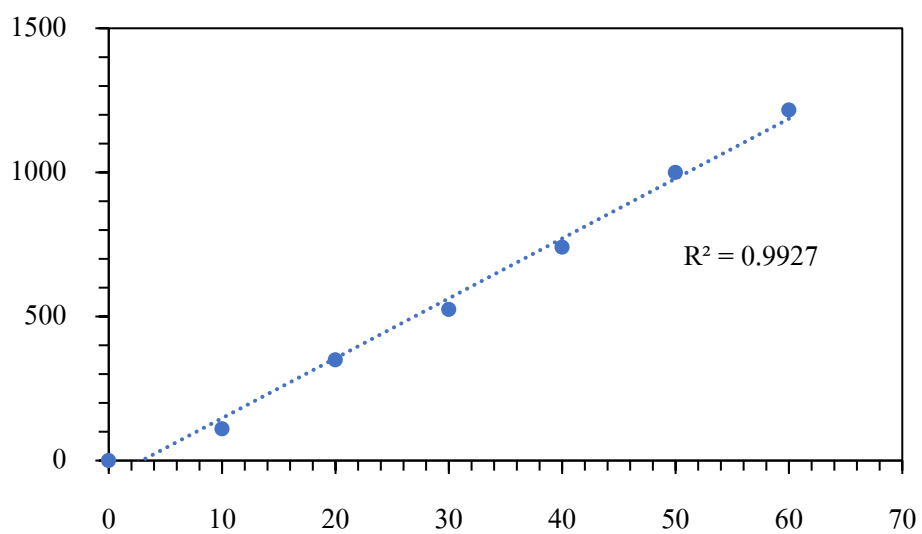


Figure 32 Calibration curve of lauric acid



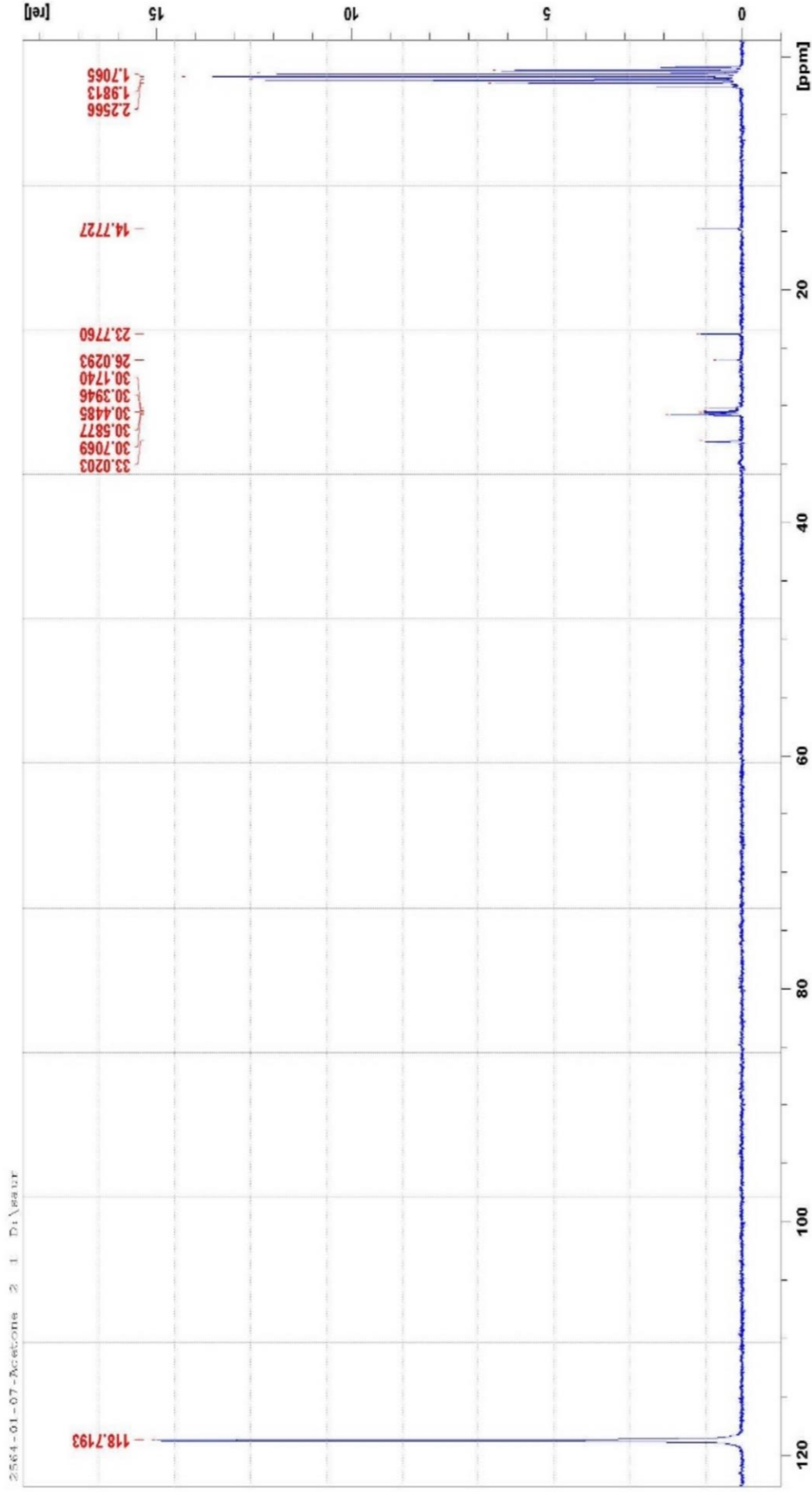


Figure 33 ^{13}C NMR spectrum in range 20-120 ppm of the reaction product of lauric acid in the condition

(current density = 8.2 A/m^2 , concentration = 50 mM, and resident time = 405s)

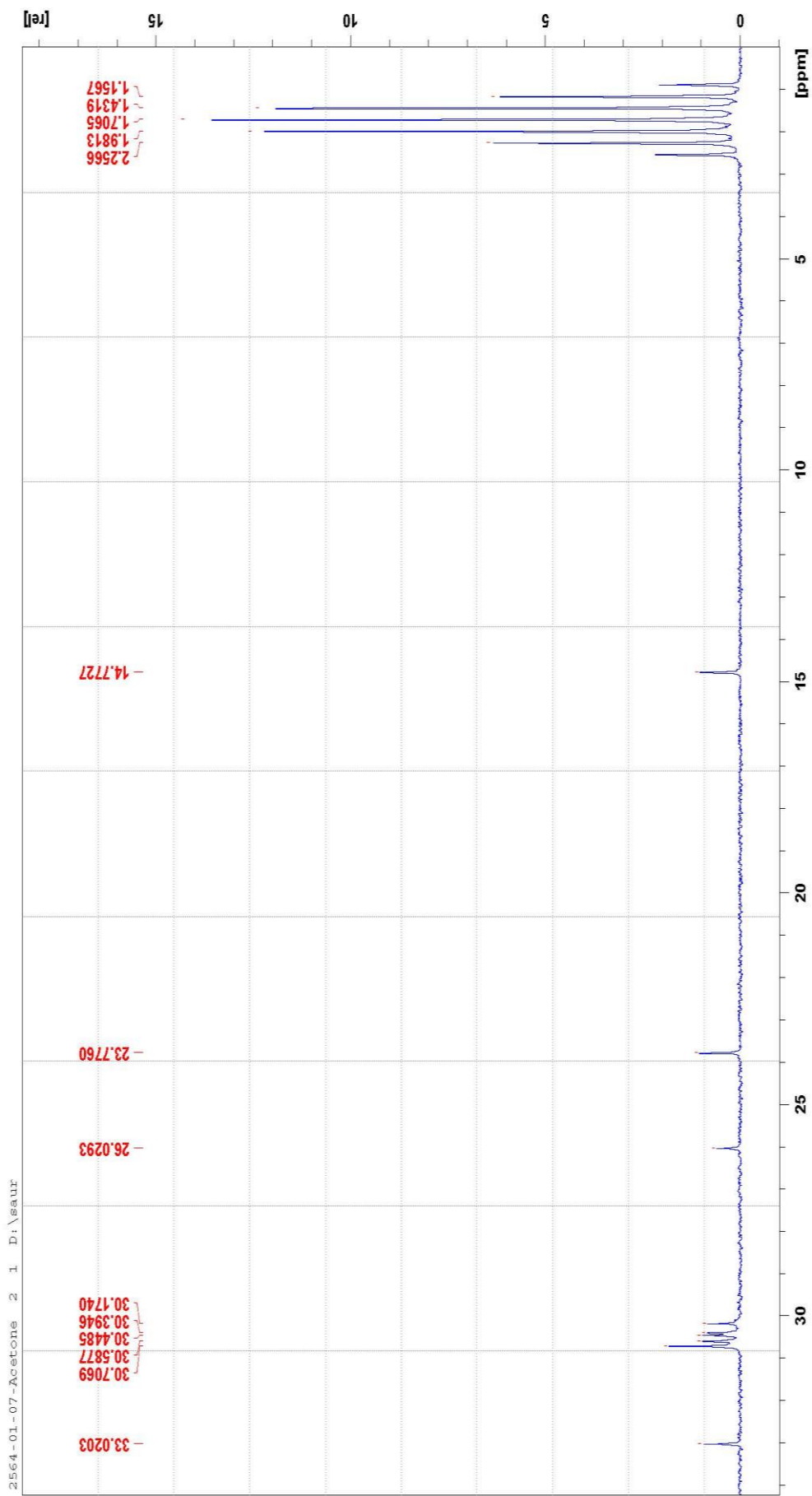


Figure 34 ^{13}C NMR spectrum in range 0-35 ppm of the reaction product of lauric acid in the condition (current density = 8.2 A/m^2 , concentration = 50 mM , and resident time = 405 s)

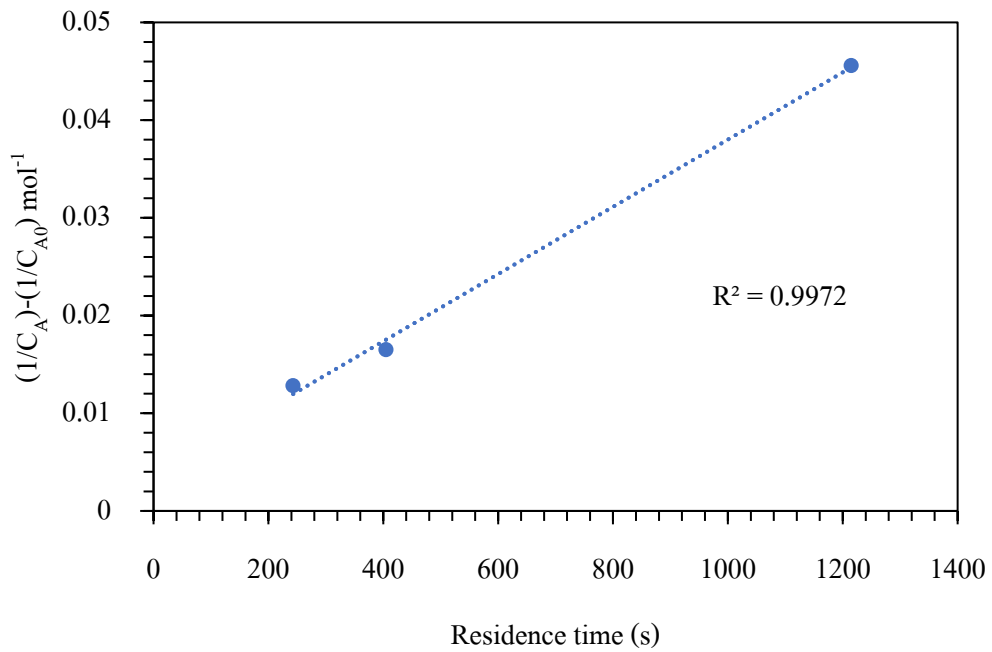


Figure 35 The reaction rate form plotting graph between $(1/C_A) - (1/C_{A0})$ versus residence time at pure acetonitrile solvent, and current density = 3.70 A/m^2

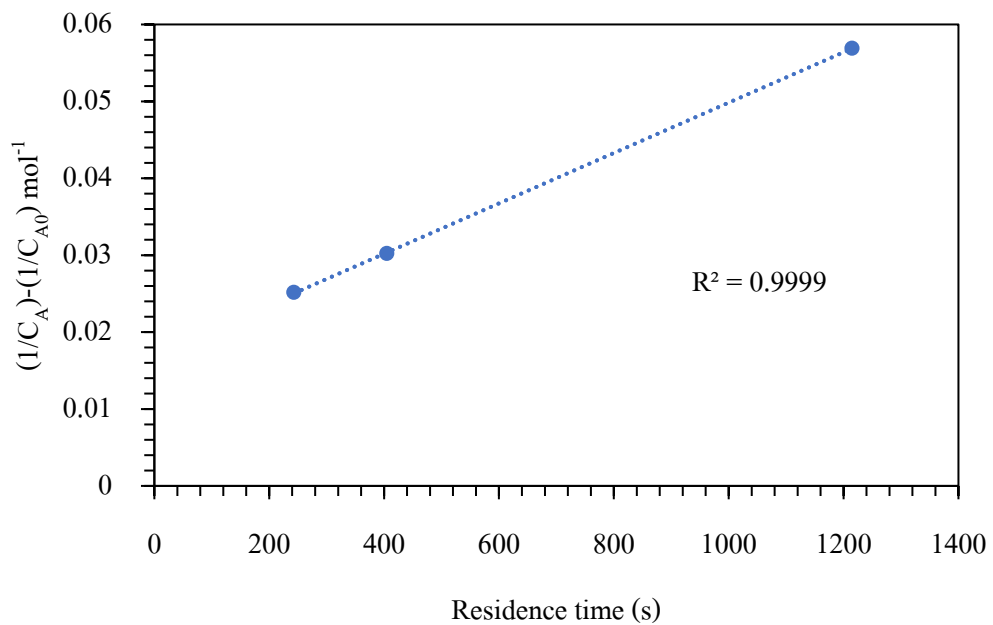


Figure 36 The reaction rate form plotting graph between $(1/C_A) - (1/C_{A0})$ versus residence time at pure 1:9 of MeOH:ACN solvent, and current density = 3.70 A/m^2

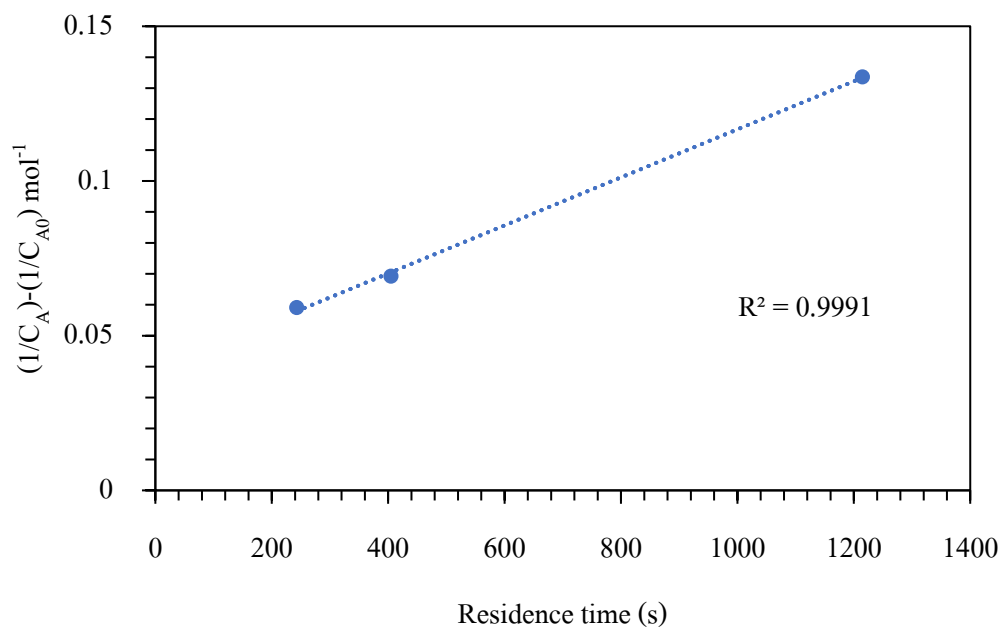


Figure 37 The reaction rate form plotting graph between $(1/C_A) - (1/C_{A0})$ versus residence time at 7:3 of MeOH:ACN solvent, applied potential = 6V, and current density = 3.70 A/m^2

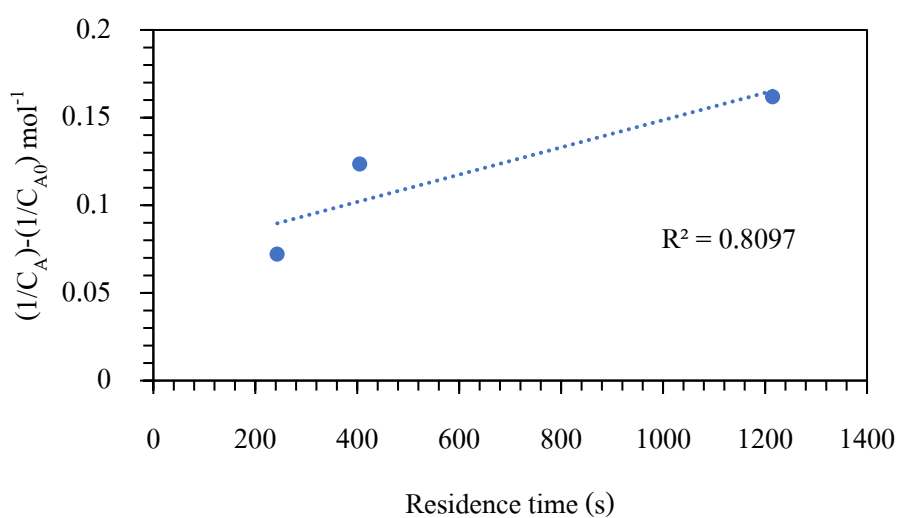


Figure 38 The reaction rate form plotting graph between $(1/C_A) - (1/C_{A0})$ versus residence time at 7:3 of pure methanol solvent, and current density = 3.70 A/m^2

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