

Chulalongkorn University

## Chula Digital Collections

---

Chulalongkorn University Theses and Dissertations (Chula ETD)

---

2021

### Depolymerization of kraft lignin to phenolic compounds by electrochemical advanced oxidation in microreactor

Chawakorn Rittirong  
*Faculty of Engineering*

Follow this and additional works at: <https://digital.car.chula.ac.th/chulaetd>



Part of the [Chemical Engineering Commons](#)

---

#### Recommended Citation

Rittirong, Chawakorn, "Depolymerization of kraft lignin to phenolic compounds by electrochemical advanced oxidation in microreactor" (2021). *Chulalongkorn University Theses and Dissertations (Chula ETD)*. 4577.

<https://digital.car.chula.ac.th/chulaetd/4577>

This Thesis is brought to you for free and open access by Chula Digital Collections. It has been accepted for inclusion in Chulalongkorn University Theses and Dissertations (Chula ETD) by an authorized administrator of Chula Digital Collections. For more information, please contact [ChulaDC@car.chula.ac.th](mailto:ChulaDC@car.chula.ac.th).

DEPOLYMERIZATION OF KRAFT LIGNIN TO PHENOLIC COMPOUNDS  
BY ELECTROCHEMICAL ADVANCED OXIDATION IN MICROREACTOR



Mr. Chawakorn Rittirong

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

Academic Year 2021

Copyright of Chulalongkorn University

การสลายตัวทางโพลิเมอร์ของกราฟท์ลิกนินให้เป็นสารประกอบฟีนอลิกด้วยการออกซิเดชันขั้นสูงเชิง  
ไฟฟ้าเคมีในเครื่องปฏิกรณ์ขนาดไมโคร



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต  
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี  
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย  
ปีการศึกษา 2564  
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

Thesis Title	DEPOLYMERIZATION OF KRAFT LIGNIN TO PHENOLIC COMPOUNDS BY ELECTROCHEMICAL ADVANCED OXIDATION IN MICROREACTOR
By	Mr. Chawakorn Rittirong
Field of Study	Chemical Engineering
Thesis Advisor	Professor VARONG PAVARAJARN, Ph.D.

---

Accepted by the FACULTY OF ENGINEERING, Chulalongkorn University in  
Partial Fulfillment of the Requirement for the Master of Engineering

..... Dean of the FACULTY OF  
ENGINEERING  
(Professor SUPOT TEACHAVORASINSKUN, D.Eng.)

THESIS COMMITTEE

..... Chairman  
(KRITCHART WONGWAILKHIT, Ph.D.)

..... Thesis Advisor  
(Professor VARONG PAVARAJARN, Ph.D.)

..... Examiner  
(Professor SUTTICHAJ ASSABUMRUNGRAT, Ph.D.)

..... External Examiner  
(Nawin Viriya-empikul, D.Eng.)

ชวกร ฤทธิ์รงค์ : การสลายตัวทางโพลีเมอร์ของคราฟท์ลิกนินให้เป็นสารประกอบฟีนอลิกด้วยการออกซิเดชันขั้นสูงเชิงไฟฟ้าเคมีในเครื่องปฏิกรณ์ขนาดไมโคร. (DEPOLYMERIZATION OF KRAFT LIGNIN TO PHENOLIC COMPOUNDS BY ELECTROCHEMICAL ADVANCED OXIDATION IN MICROREACTOR) อ.ที่ปรึกษาหลัก : ศ. ดร.วรงค์ ปวรจารย์

การวิจัยนี้มุ่งเน้นไปที่การสลายตัวทางโพลีเมอร์ของคราฟท์ลิกนินเป็น สารประกอบฟีนอลิกที่มีมูลค่า และ ใช้ประโยชน์ในอุตสาหกรรมต่างๆได้ การสลายตัวทางโพลีเมอร์นี้จะทำโดยใช้วิธีออกซิเดชันขั้นสูงเชิงไฟฟ้าเคมีด้วยอนุมูลไฮดรอกซิล ซึ่งในกระบวนการนี้จะใช้เครื่องปฏิกรณ์ขนาดไมโคร ซึ่งประกอบด้วยขั้วแอโนดแกรไฟต์ และ ขั้วแคโทดเป็นสแตนเลสสตีล ผลของตัวแปรที่ได้ทำการศึกษาได้แก่ ความหนาแน่นของกระแสไฟฟ้า (3.7 และ 5.5 แอมแปร์ต่อตารางเมตร), เวลาของสารที่คงอยู่ในเครื่องปฏิกรณ์ (100-400 วินาที), ความเป็นเบสที่ (9), ความแตกต่างกันของเบส (โซเดียมไฮดรอกไซด์ และ โพแทสเซียมไฮดรอกไซด์)จากการทดลองพบว่าผลิตภัณฑ์หลักออกตะเดคานาไมด์ และผลิตภัณฑ์รอง โพลีฟัลกัวคอล เพิ่มขึ้นจากการเพิ่มกระแส ในทางกลับกัน ผลิตภัณฑ์รองบางชนิดเพิ่มขึ้นจากการลดลงของกระแส เมื่อของระยะเวลาที่อยู่ในเครื่องปฏิกรณ์เพิ่มขึ้นจะส่งผลให้ทั้งผลิตภัณฑ์หลักและผลิตภัณฑ์รองลดลง แต่เมื่อปรับเป็นเบสที่ pH9 ส่งผลให้ออกตะเดคานาไมด์เพิ่มขึ้นจากการเพิ่มกระแส และระยะเวลาในเครื่องปฏิกรณ์ โดยที่ได้สารผลิตภัณฑ์หลัก คือ 1,3 ไดออกเซน และพบผลิตภัณฑ์รองตัวใหม่เพิ่มขึ้น กล่าวได้ว่าการเพิ่มความหนาแน่นของกระแสไฟฟ้าและ ระยะเวลาที่นานในเครื่องปฏิกรณ์ ช่วยเพิ่มการก่อตัวของอนุมูลไฮดรอกซิลส่งผลให้สารประกอบฟีนอลิกลดลง ในทางกลับกันเมื่อมีความเป็นเบสส่งผลให้อนุมูลไฮดรอกซิลลดลง โดยเฉพาะโพแทสเซียมไฮดรอกไซด์ นอกจากนี้ได้ศึกษาผลิตภัณฑ์ประเภทไดเมอร์ เพื่ออธิบายกลไกการเกิดปฏิกิริยาที่ได้ซึ่งสารประกอบฟีนอลิก ในเครื่องปฏิกรณ์ขนาดไมโคร

สาขาวิชา วิศวกรรมเคมี  
ปีการศึกษา 2564

ลายมือชื่อนิสิต .....  
ลายมือชื่อ อ.ที่ปรึกษาหลัก .....

# # 6270058321 : MAJOR CHEMICAL ENGINEERING

KEYWORD: LIGNIN / ELECTROCHEMICAL ADVANCED OXIDATION PROCESS /  
DEPOLYMERIZATION / MICROREACTOR

Chawakorn Rittirong : DEPOLYMERIZATION OF KRAFT LIGNIN TO PHENOLIC  
COMPOUNDS BY ELECTROCHEMICAL ADVANCED OXIDATION IN  
MICROREACTOR. Advisor: Prof. VARONG PAVARAJARN, Ph.D.

This research focuses on the depolymerization of kraft lignin to phenolic compounds that are valuable and useful in various industries. Depolymerization is performed using an electrochemical advanced oxidation process with the hydroxyl radicals. In this process, microreactors are used. It consists of a graphite anode and a stainless steel cathode. The results of the variables studied were current density (3.7 and 5.55 A/m<sup>2</sup>), residence time (100-400 s), base pH (9), the base difference (sodium hydroxide and potassium hydroxide). The experiment found that the major product is octadecamide and the minor product propyl guaiacol is increased when the current increases. On the other hand, some of the minor products increased when the decrease in current. However, residence time increases, both major and minor products decrease. In the base condition, The resulting octadecamide increased from increasing current and residence time. Give the major product is 1,3 dioxane and found the new minor products have been increased. In other words, increasing the current and residence time enhances the formation of hydroxyl radicals, resulting in a decrease of phenolic compounds. On the other hand, the base conditions can decrease the hydroxyl radicals, Especially potassium hydroxide. In addition, the study of dimer products for describing the pathway mechanism of phenolic compounds in microreactors.

Field of Study: Chemical Engineering

Student's Signature .....

Academic Year: 2021

Advisor's Signature .....

## ACKNOWLEDGEMENTS

I am very thankful to my advisor, Professor Dr. Varong Pavarajarn, Department of Chemical Engineering Chulalongkorn University, for introducing me to this research and their helpful and deep discussion during this research study. I am also grateful to Assistance Dr. Kritchart Wongwailikhit and Professor Dr. Suttichai Assabumrungrat and Dr. Nawin Viriya-empikul for serving as chairman and member of this thesis evaluating committee, consequently

Furthermore, I would like to thank all members of the Center of Excellence in Particle Technology for their help and suggestion.

Finally, I would like to thank my family for their encouragement and give good advice.

Chawakorn Rittirong



## TABLE OF CONTENTS

	Page
.....	iii
ABSTRACT (THAI) .....	iii
.....	iv
ABSTRACT (ENGLISH) .....	iv
ACKNOWLEDGEMENTS .....	v
TABLE OF CONTENTS .....	vi
LIST OF FIGURES .....	ix
CHAPTER 1 INTRODUCTION .....	1
objective .....	3
Scope of this research .....	3
CHAPTER 2 THEORY AND LITERATURE REVIEW .....	4
1. Lignin .....	4
1.1 Source of lignin.....	4
1.2 structure of lignin.....	5
2. Phenolic compounds.....	5
2.1 Processes to produces phenolic compound from lignin.....	6
2.1.1 Pyrolysis process.....	6
2.1.2 Gasification process.....	7
2.1.3 oxidation.....	8
2.1.4 Advanced oxidation process .....	8
2.2 Electrochemistry.....	8



2.2.1 Electrooxidation .....	9
2.3 reactor for usage in depolymerization of kraft lignin .....	10
2.4 literature review .....	10
CHAPTER 3 EXPERIMENTAL.....	13
3.1 Study design.....	13
3.2 Research Methodology .....	15
3.3 Analytical instruments.....	17
CHAPTER 4 RESULT AND DISCUSSION .....	20
4.1 The study occurrence of oxidizing agent from the relation between current density and residence times. ....	20
4.1.1 Effect of oxidizing agent on conversion of kraft lignin .....	22
4.2 The study effect of base condition on oxidizing agent and conversion .....	23
4.3 The study occurrence of phenolic compounds and other monomer from the relation between current density at 1.5 mA (5.55 A/m <sup>2</sup> ) and residence times more than 400 seconds.....	25
4.4 The study occurrence of phenolic compounds and other monomer from the relation between current density and residence times. ....	32
4.5 The study occurrence of phenolic compounds and other monomer from the relation between current density and residence times with base PH 9 of NaOH and KOH.....	39
4.6 The study pathway mechanism from the relation between current density 1.5 mA and residence times at 100, 200, and 400 seconds.....	56
CHAPTER 5 CONCLUSION .....	59
5.1 summary results.....	59
5.2 Conclusion .....	61
5.3 Recommendations .....	61

REFERENCES .....	74
------------------	----

VITA.....	76
-----------	----



## LIST OF FIGURES

	Page
Figure 1 lignin in plants. ....	4
Figure 2 Lignin structure with labeled subunits and linkages. ....	5
Figure 3 structure of phenolic compounds during lignin depolymerization. ....	6
Figure 4 product from pyrolysis and gasification process conversion of lignin. ....	7
Figure 5 Schematic diagram of experimental set up .....	14
Figure 6 Microreactor .....	15
Figure 7 UV-visible spectrophotometer .....	17
Figure 8 Gas Chromatograph-Mass Spectrometer.....	18
Figure 9 Liquid Chromatography-Triple Quadrupole Mass Spectrometry (LC-MS). ....	19
Figure 10 The effect of relation between current density and residence times on the occurrence of hydrogen peroxide.....	21
Figure11 The conversion between current density 1.0 mA ( $3.7\text{A/m}^2$ ) and 1.5mA ( $5.55\text{A/m}^2$ ) at residence times 100, 200 and 400 seconds.....	22
Figure12 The formation of hydroxyl radical in form of hydrogen peroxide of relation between current density and residence times adjusted with PH 9 of a) NaOH and b) KOH.....	23
Figure13 The formation of conversion with relation between current density and residence times when adjusted PH 9 of a) NaOH and b) KOH .....	24
Figure14 The conversion of kraft lignin at each of cycle .....	26
Figure 15 The component in kraft lignin analyzed by Gas chromatography with mass spectrometry (GC-MS/MS): a) initial kraft lignin, b) after the reaction of cycle1, c) cycle2, d) cycle3 and e) cycle 4.....	27

Figure16 Trends to increase of oxidation products a) (Z)-9-octadecenamide, b) acetoguaiacone, c) vinyl guaiacol, d) guaiacylacetone and e) eugenol. ....	30
Figure17 Trends to decrease of oxidation products a) Guaiacol ,b) 2-methyl(1,3-dioxane, c) vanillin, d) propyl guaiacol and e) Homovanillic acid. ....	31
Figure 18 The component in kraft lignin a) initial kraft lignin, b) 1.0 mA (3.7 A/m <sup>2</sup> ) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds. ....	33
Figure19 The component in kraft lignin a) initial kraft lignin, b) 1.5 mA (5.55 A/m <sup>2</sup> ) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds ....	36
Figure20 Trends of oxidation products to higher with 1.5 mA (5.55 A/m <sup>2</sup> ) at residence time 100,200- and 400-seconds a) (Z)-9-octadecenamide, and b) Propyl guaiacol. ....	37
Figure21 Trends of oxidation products to higher with 1.0 mA (5.55 A/m <sup>2</sup> ) at residence time 100,200- and 400-seconds a) phenol, b) guaiacol, c) vinylguaiacol, d) vanillin, e) acetoguaiacone, f) guaiacylacetone, and g) homovanillic acid.....	39
Figure 22 the component without the reaction a) initial kraft lignin, b) PH 9 with NaOH, and c) PH9 with KOH.....	40
Figure 23 the component in the condition at PH9 by NaOH a) initial kraft lignin, b) 1.0 mA (3.7 A/m <sup>2</sup> ) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds. ....	43
Figure 24 the component in the condition at PH9 by KOH a) initial kraft lignin, b) 1.0 mA (3.7 A/m <sup>2</sup> ) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds ....	45
Figure 25 Trends of oxidation product of a). catechol-guaiacol, b). propyl guaiacol and c) (Z)-9-octadecenamide.....	48
Figure 26 the component in the condition at PH9 by NaOH a) initial kraft lignin, b) 1.5 mA (5.55 A/m <sup>2</sup> ) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds.....	49

Figure 27 the component in the condition at PH9 by KOH a) initial kraft lignin, b) 1.5 mA (5.55 A/m <sup>2</sup> ) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds.....	52
Figure 28 Trends of oxidation product of a) Dioxane derivative, b) (Z)-9-octadecenamide, c). eugenol, d) catechol-guaiacol, and e) propyl guaiacol .....	55
Figure 29 The component in the condition at a) initial kraft lignin, b) 1.5 mA (5.55 A/m <sup>2</sup> ) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds. ....	57
Figure 30 structure of lignin depolymerization intermediates and proposed depolymerization pathway of lignin in microreactor. ....	58



## CHAPTER 1

### INTRODUCTION

At present the paper manufacturing industry and bio-refineries around the world. The manufacturing processes are constantly evolving. However, in various production processes there is waste that has no value. The main waste from the manufacturing processes is lignin. In the paper industry lignin is a waste product from the bleaching process of paper same as the bio-refining, lignin is waste product in produced methanol from cellulose. These abundant of lignin incinerated to only generate heat energy for boiler. Some of these wastes released into the water causing a lot of environmental pollution, especially water pollution. Therefore, the recycling waste of lignin to create value and reduce production costs are interested [1].

Lignin is a polymer present in plants and has a very high carbon content in complex structures with aromatic rings that tend to be transformed or developed to higher value. The structure of lignin consists of three phenolic monomer types: p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S). Connected by chemical bonds[2]. Usually, to convert lignin to higher value through depolymerization. The depolymerization with various reactions such as pyrolysis, gasification, hydrogenolysis, liquefaction, and oxidation. These methods can break down lignin molecular structure to a certain extent but these methods are often used in conjunction with metal catalysts. To achieve depolymerization more efficient Including the increase yield percentage of product. The reactions of pyrolysis, gasification, hydrogenolysis, liquefaction and oxidation is a reaction that requires heat and pressure to depolymerization. The main disadvantage is generated char during the reaction, which affects the quality of the product. In the use of metal catalyst make the operating condition more expensive is another disadvantage[3].

Recently, lignin conversion energy has been studied in a form of electrochemistry instead of using heat to avoid the limitations mentioned above. This is because electrochemistry has the advantage of being able to control the conversion better than the thermal reaction due to the electrode potential, for this reason the control of the reaction energy can be controlled[4]. The purpose of finding a substance that could replace the metal catalyst, the objective is to reduce costs of operating conditions. The use of base (cation) has been studied in place of an expensive catalyst for example, NaOH and KOH are combined with oxidation reaction in lignin depolymerization. Conclude of NaOH and KOH were cleavage ether bonds as well as increase the Hydroxyl group to aromatic ring and increase the yield percentage of the product such as phenolic compounds. In lignin structure, it consists of monolignols bonded to C-C bonds and ether  $\beta$ -O-4 bonds, which ether bonds are most abundant in lignin structures and are more weakness to C-C bonds, which are most easy to cleavage[5]. Most of the methods mentioned above are mostly batch reactors which have limitations on heat transfer and mass transfer and takes a long time to react. Therefore, making the products are not of the quality or performance as expected. Choosing of reactor is another significant factor. Previous studies have applied microreactor to the reaction. The advantage of microreactor is high surface area to volume ratio and short reaction time compared to other reactors [6].

The depolymerization of the structure of lignin to obtain high valuable substances, such as, phenolic compounds. In general, extreme reaction conditions are used at high temperatures and expensive catalysts. Makes the operating condition high costs and the reaction time is longer result of choosing a suitable reactor. This research is interested to depolymerization of lignin structures using mild reaction conditions. By using electrochemical methods instead of high temperatures. NaOH and KOH are used instead of high costs catalysts to obtain a greater yield percentage of products such as phenolic compounds. Compare the effects of

different NaOH and KOH with microreactor use to determine optimal conditions for obtaining products such as phenolic compounds. All of these can help reduce the operating conditions of reaction including cost in operation and reaction time.

### **objective**

The objectives of this research are to study depolymerization of kraft lignin dissolved in deionized water 1000 ppm to obtain phenolic compounds and added different based (cation) are NaOH and KOH via advanced oxidation in microreactor with electrochemical.

### **Scope of this research**

1. Study occurrence of phenolic compounds without NaOH and KOH via advanced oxidation in microreactor with electrochemical.
  - 1.1 Study the effect of current density to generate phenolic compounds from kraft lignin dissolved in deionized water which various condition such as 3.7 and 5.55 A/m<sup>2</sup>.
  - 1.2 Study the effect of residence time to generate phenolic compounds from kraft lignin dissolved in deionized water which various condition such as 100, 200 and 400 seconds
2. Study occurrence of phenolic compounds with NaOH and KOH via advanced oxidation in microreactor with electrochemical.
  - 2.1 study the different based are NaOH and KOH to generate phenolic compounds from kraft lignin dissolved in deionized water which adjusted at PH 9.



## CHAPTER 2

### THEORY AND LITERATURE REVIEW

#### 1. Lignin

Lignin was introduced in 1819 by de Candolle and comes from the Latin lignum. It is one of the most abundant organic polymers on the planet. Lignin is a polymer in plants and is the second most abundant after cellulose. The lignin structure has many linkages of aromatic rings. That is resistant to degradation and depolymerization. Making it a waste of no value.

##### 1.1 Source of lignin

Lignin is an important constituent in plant tissues and is found in cell walls. In plant tissues are composed of cellulose, hemicellulose and lignin (shown in figure 1). Lignin's important function is to keep plants strong. The presence of lignin in each plant is different but it has the second quantity after cellulose in all plants[7].



Figure 1 lignin in plants.

At present, lignin can still be found in industries such as Paper industry and bio-refinery in the form of waste. In the paper industry is found in the bleaching process. In the bio-refinery is found to produce ethanol from cellulose.

## 1.2 structure of lignin

lignin is an organic substance having a large molecular structure. the average of molecular weight from 1000-20000 g.mol<sup>-1</sup>. The structure is composed of three aromatic phenolic units: p-coumaryl (H), guaiacyl (G) and syringyl (S), linked by ether bonds and carbon-carbon covalent bonds (shown in figure 2)[8].

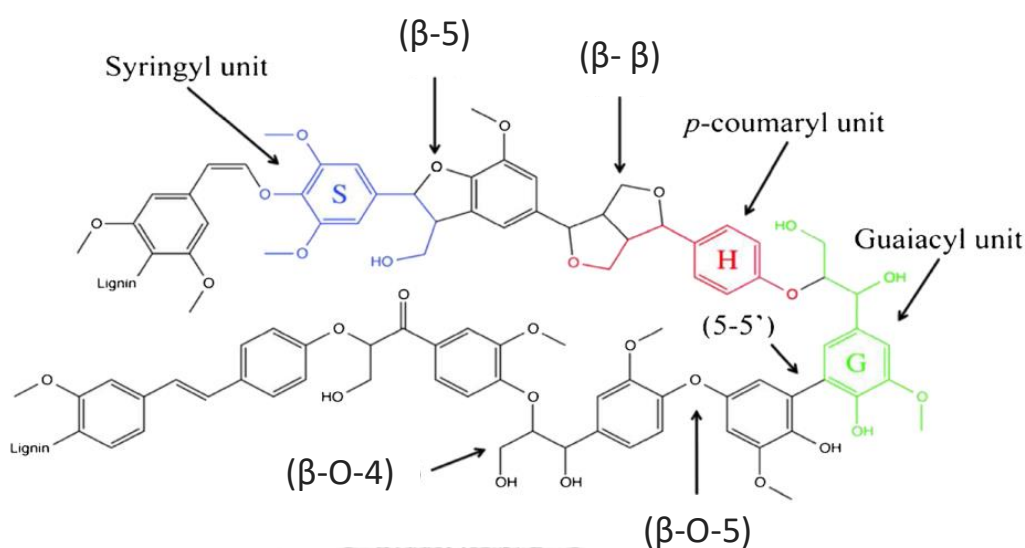


Figure 2 Lignin structure with labeled subunits and linkages.

## 2. Phenolic compounds

Phenolic compounds are substance with a benzene-derivative ring structure formula and at least one hydroxyl group. Make the basic structure of Phenolic compounds, including phenol. Phenolic compounds are formed by depolymerization of lignin by breaking the bonds in the lignin structure with chemical reactions. This produces Phenolic compounds in the form of functional groups such as phenolic aldehydes and phenolic ketones (shown in figure 3). Phenolic compounds are useful substances in various fields such as used for extraction some types of medicine, food flavoring additive and antioxidant[9].

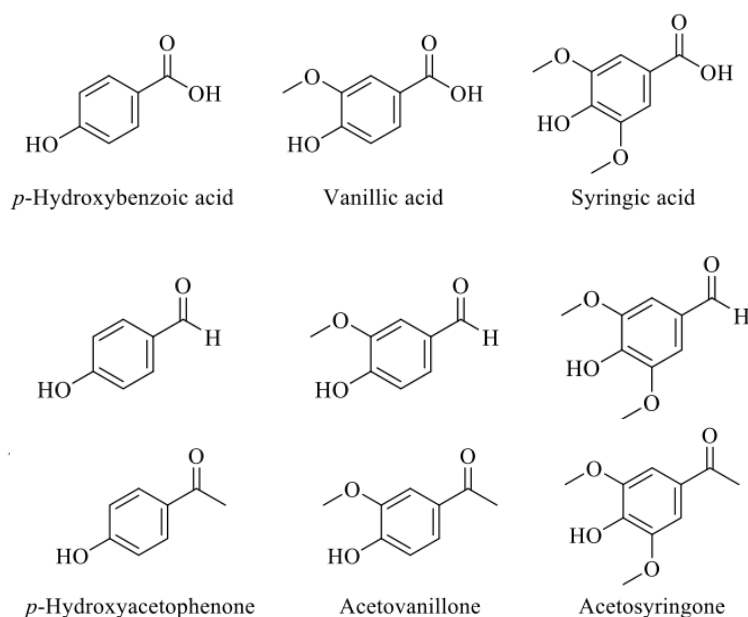


Figure 3 structure of phenolic compounds during lignin depolymerization.

## 2.1 Processes to produces phenolic compound from lignin

### 2.1.1 Pyrolysis process

Pyrolysis process is the process of biomass thermal decomposition in anaerobic conditions cause most of the chemical break bonds. It is commonly used to break bonds with large molecules into smaller molecules. The volatile carbon component is converted into a fuel gas, and the other is condensed by distillation to liquid fuel. pyrolysis lignin in depolymerization range of temperature is 280-500 °C to cleavage ether bonds and carbon-carbon covalent bonds in lignin structure. Pyrolysis can be divided into two types 1) slow pyrolysis and 2) fast pyrolysis. In the process of slow pyrolysis, lignin is heated to 500 °C with a slower heating rate compared to fast pyrolysis. Fast of heating rate has the advantage of increasing the yield percentage of a liquid product but there are also limitations on char that produced by heat from pyrolysis process.

### 2.1.2 Gasification process

Gasification process is the process to convert biomass under the high conditions of temperature and pressure. Lignin gasification process is the conversion of solids lignin into gas by heating with oxygen and steam, using the range of temperature is 400-750 °C. catalytic gasification is the use of a catalyst in the reaction can reduce the reaction temperature with the reaction temperature range of 350-500 °C. The method of gasification and catalytic gasification processes will limit the air entering the reaction. As a result, process of the reaction there is an incomplete combustion. The products obtained from this process to be in form of combustible gas but limitations on char that produced by heat and low yield percentage of the liquid products. When comparing the quantity of products made from pyrolysis process and gasification process (shown in figure 7) [7].

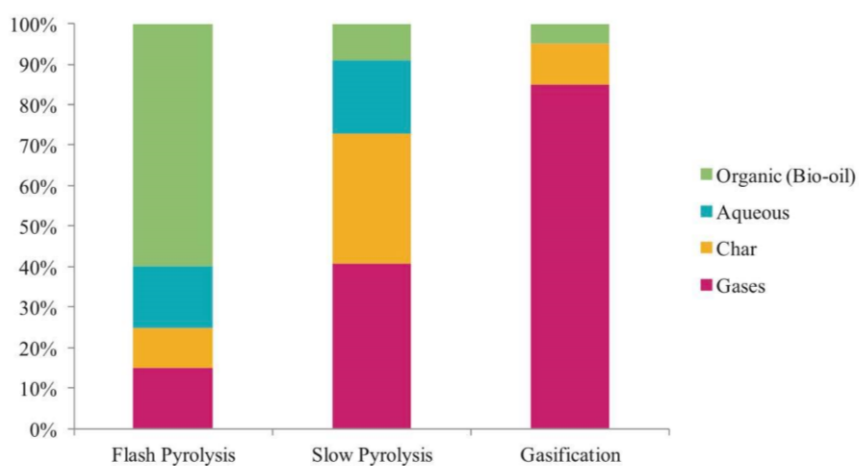


Figure 4 product from pyrolysis and gasification process conversion of lignin.

### 2.1.3 oxidation

Oxidations process to depolymerization liquid solution using air and oxygen as oxidizing agents in the reaction with high temperature and pressure. The range of reaction temperature is 100-320 °C and vapor pressure is higher than the vapor pressure of solution for inhibit the phase transition.

### 2.1.4 Advanced oxidation process

Advanced oxidation process (AOPS) generated highly oxidizing hydroxyl radical. It is a highly oxidized process for depolymerization of lignin to obtain a value substance for various industry. Uses OH radical derived from water disintegration as an oxidized agent because it is a strong oxidizing agent. Advanced oxidation process can be applied with various method to depolymerization of lignin such as ozone oxidation, photo oxidation and electrochemical[10].

## 2.2 Electrochemistry

Electrochemistry is use of electrical energy to generate chemical reaction. occurs through the motion of an electron, called an electrolyte, by introducing an external voltage to the system. Reactions are performed in the reactor such as batch reactor, in which there is agitation all the time to keep the ions of the sample closer to the surface of the electrode for reaction on the surface of electrode. As a result of this reaction generated solid particles are placed on the electrode, increasing the weight of the electrode. Usually, the electrode inside reactor is used as two electrodes, is anode and a cathode in the system, called positive is anode and negative is a cathode.

The solution inside the reactor is an electrolyte that carries current through ions dissolved in the solution. These ions carry current to both of electrodes, but the ability to transmit current may depend on the properties of the electrolyte such as acidity-base.

Potential difference produced from electromotive force between the two electrodes This is called the standard voltage measurement of a half cells relative to the hydrogen and the electrode required to know the voltage. The standard voltage of hydrogen is zero.

### 2.2.1 Electrooxidation

Electrooxidation reaction can be used to degrade pollutant from wastewater and depolymerization coupled with the degradation. It is oxidized by OH radical as strong oxidizing agent. there are three types of electrooxidation: direct, indirect and electrical-chemical combination reactions. In this process called direct anodic process. Depolymerization and electrolysis occur simultaneously on the surface of the anode electrode to obtain a phenolic compound. The equations of reactions used in this process to depolymerization are as follows [4].



When

Anode ( ) is surface area of anode.

Anode (OH<sup>•</sup>) is hydroxyl radical adsorb on anode.

R is lignin biopolymer

RO is product from oxidizing lignin biopolymer

### 2.3 reactor for usage in depolymerization of kraft lignin

The reactor to use in this research is microreactor with continuous flow commonly used in lab scales but they can also be developed into pilot scales in the form of scale-up or increased reactors for larger industries. micro channel sizes in the range of microns (1-1000  $\mu\text{m}$ ) for generated reaction. The main advantages of microreactor are short residence time, easy to control system and high surface to volume ratio. Compared with the batch reactor, the microreactor has a better reaction efficiency because the micron-sized reaction gap can control mass transfer and thermodynamics[11].

### 2.4 literature review

obtained the phenolic compounds from depolymerization of Lignin is great interest as it is a material obtained through processes such as bleaching in paper industry and ethanol production from cellulose in biorefinery. Causing lignin to be abundant but not utilized in addition to being used only as a combustion fuel to generated heat for boiler. Researchers have studied the feasibility and tendency of converting lignin to be more useful and valuable. lignin is an aromatic polymer linked by ether bonds and carbon-carbon covalent bonds [2]. In this research, study the formation of phenolic compounds from the depolymerization of lignin. The formations of phenolic compounds obtained from the Gas Chromatograph-Mass Spectrometer (GC-MS).

Process for depolymerization of lignin can be achieved from various processes such as pyrolysis, gasification, hydrothermal and oxidation. fast co-pyrolysis process between soda lignin and phenolic-derivative polymers for quantitative study of the product of phenolic compounds in the form of bio-oil. The temperature for used in this process was 500 °C and adjusted the heating rate up 10 °C.min<sup>-1</sup> found to increase the amount of bio-oil, including phenol(23%), isopropylphenol (10.5%),

isopropenylphenol (7%) and bisphenol (13%). It was concluded that the unit of guaiacol (G) retained the methyl- and ethyl- groups as the main components[12]. Next, hydrothermal process for depolymerization of lignin to phenolic compounds. Have studied the temperature of reactions 200-350 °C in 2 hour found The content of phenolic compounds such as phenol, guaiacol and vanillin are 8.9%, 16.67%, and 1.66%, which is relatively low, and generated coke is formed during the reaction with hydrothermal, affecting the yield percentage[13].

The process of advanced oxidation to depolymerization of lignin found this process was suitable for the lignin conversion by used the hydroxyl radical. Hydroxyl radical is a strong oxidizing agent to cleavage aromatic ring in structure of lignin called depolymerization. Its makes lignin as a small chemical that can replace existing products on the market such as phenolic compounds along with processes such as electrochemistry. The used of electrochemistry is suitable for the reactions than the hydrothermal reaction because electrochemistry is no effect of char. However, electricity for oxidation or electrooxidation reaction with oxidizing agent. It is concluded that used of electrochemistry is suitable for depolymerization to cleavage the ether bonds between C-O and C-C bonds generates phenolic compounds[14]. study of the effects of oxidizing agents such as  $H_2O_2$  on the cleavage of lignin aromatic dissociation. Found the concentrations of oxidizing agents have effect to degradation and amounts of phenolic compounds[15]. The efficiency of oxidation reactions can be increased with based catalyst found based catalyst can be deprotonation intermediate to cleavage of ether bonds[16].

Based used of NaOH have concluded in the reaction, occurs split of NaOH in form cationic sodium and the negative hydroxyl group. Sodium can cleavage the ether bonds of lignin and adds hydroxyl group into aromatic rings in lignin structure [5].



Microreactor have high surface area to volume ratio that effect to potential of products. Used microchannel gap between surface of anode and cathode to generated reaction for used in this research. Studied microreactor catalyst for the hydrodeoxygenation reaction of lignin found a good result to elimination of aromatic, prevent of repolymerization and increase the yield percentage of the products[17].

In additions the microreactor can also be used in emulsions as a reaction between liginosulfonate and isopropanol. Emulsion microreactor using Raney Ni as catalyst and isopropanol as hydrogen donor which shows a depolymerization of liginosulfonate to generated phenolic compounds under mild condition. Indicates the suitability of microreactor with emulsions due to its high efficiency, mild reaction conditions and reduces cost of catalyst[18]. Microreactor is good efficiency to depolymerization lignin because the high surface area to volume ratio get the good reaction and product distribution. This research used advanced oxidation process with electrochemical in microreactor for depolymerization of lignin to phenolic compounds.

## CHAPTER 3

### EXPERIMENTAL

#### 3.1 Study design

This research is experimental research in laboratory. To find the optimum conditions and compare the different cation effects of NaOH and KOH to obtain more valuable substances such as phenolic compounds. This research has tools and methods as detailed below. The schematic diagram of experimental set up (shown in figure 5)

##### 3.1.1 Chemicals

1. Kraft lignin
2. Deionized water
3. Hydrogen peroxide
4. Sodium Hydroxide 0.1M
5. Potassium Hydroxide 0.1M

จุฬาลงกรณ์มหาวิทยาลัย  
CHULALONGKORN UNIVERSITY

##### 3.1.2 Tools and equipment in this research

1. Microreactor
2. Syringe pump
3. Dc power supply

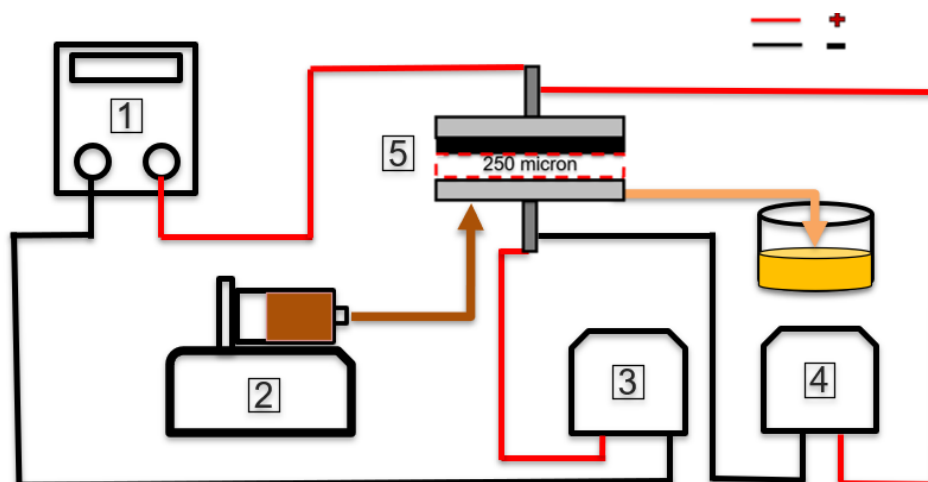


Figure 5 Schematic diagram of experimental set up

(1) Dc-power supply, (2) Syringe pump, (3) Ammeter, (4) Voltmeter, (5) Reactor

### 3.1.3 Reactor

Reactor in this research is microreactor. The volume of reactor up to size of teflon and electrode of this reactor is that anode is graphite and cathode is stainless steel. Cathode plate has holes for compound in-out. The reactor will be mass transfer on single channel. The surface area of this reactor is 10x27 millimeter and Teflon's thickness is 250 micrometers (show in figure 6)

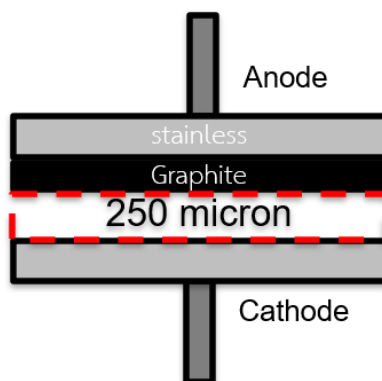


Figure 6 Microreactor

### 3.1.4 Sample

Lignin solution that used in this research is Kraft lignin dissolved in deionized water 1000 ppm.

## 3.2 Research Methodology

### 3.2.1 Analysis of kraft lignin dissolved in deionized water

Sampling of kraft lignin dissolved in deionized water from the initial sample preparation at a concentration of 1000 ppm. Before the experiment, the sample must be filtered before entering the reactor to avoid blockage problems in the reactor.

The parameters were used in analysis of physical and chemical properties from kraft lignin dissolved in deionized water

1. color
2. Lignin concentration
3. Different base
4. pH

### **3.2.2 The formation of Phenolic compounds from kraft lignin dissolved in deionized water 1000 ppm.**

This research studies to find substances that have value with depolymerization of lignin in order to obtained phenolic compounds by analyzes the variables affecting the formation of substances such as phenolic compounds. As indicated by modifying factors affecting to generated of the substance such as phenolic compounds.

1. Study the occurrence of phenolic compounds without NaOH and KOH via advanced oxidation in microreactor with electrochemical.
  - 1.1 Current density is adjusted values are 3.7 and 5.55 A/m<sup>2</sup>
  - 1.2 Residence time is adjusted values 3 are 100, 200 and 400 seconds.
2. Study the occurrence of phenolic compounds with NaOH and KOH via advanced oxidation in microreactor with electrochemical.
  - 2.1 Study the different based are NaOH and KOH to generates phenolic compounds from kraft lignin dissolved in deionized water by adjusted at PH 9.

### 3.3 Analytical instruments

In this research, various analytical tools were used to identify the most explicit experiments, both physically and chemically, of lignin dissolved in deionized water such as conductivity, PH, color, concentration and structure of lignin. The details and requirements of the analytical tools are shown below.

#### 3.3.1 Uv-vis spectrophotometer

The concentration of lignin products was analyzed by UV-Vis spectrophotometer and using quartz as cuvette. The scanning was commenced at wavenumber ranging from 200 - 800 nanometers. The UV-Vis spectrophotometer (UV-2600, Shimadzu) was analyzed at Excellence in Particle and Technology Engineering laboratory. A photo of UV-Vis spectrophotometer is shown in figure 7



Figure 7 UV-visible spectrophotometer

#### The analysis of product by using UV-Visible spectrophotometer

##### 3.3.1.1 Lignin

Lignin concentration was detected at 280 nanometers. To find the percentage of degradation by using equation 3 as shown in below

$$\text{Percentage of degradation of lignin} = (\text{initial lignin} - \text{final lignin}) / \text{initial lignin} \times 100 \quad (3)$$

### 3.3.1.2 Hydrogen peroxide

The concentration of hydrogen peroxide was analyzed by mixing solution A (Solution A consists of 0.1 g sodium hydroxide, 3.3 g of potassium iodide, 0.01 g of ammonium molybdate. There is diluted with deionized water to 50 mL.) 1 mL and solution B (Solution B that is 1 g of potassium hydrogenphthalate is diluted with deionized water to 50 mL.) 1 mL and product 1 mL. Then use UV-Visible spectrophotometer detect at 350 nanometers.

### 3.3.2 Gas Chromatograph-Mass Spectrometer (GC-MS)

Lignin after the reaction is oxidation products which has water as the main constituent. Therefore, it is not possible to analyze with GC-MS. So must use the solvent exchange method. By mixing between products and solvent N,N-dimethylformamide in a ratio of 1 to 1. The water was then evaporated at 80 °C for 3 hours. Oxidation samples were injected into the GC-MS with the following protocol: 1:75 split, hold at 100 °C for 3 min, ramp at 6°C per minute to 300 °C, hold for 10 min [4],[19]. Instrument name: Triple Quadrupole GC-MS/MS (GC-QQQ) Agilent Technologies. With HP-5 column for analytical products. A photo of Gas Chromatograph-Mass Spectrometer is show in figure 8.



Figure 8 Gas Chromatograph-Mass Spectrometer.

### 3.3.3 Liquid Chromatography-Triple Quadrupole Mass Spectrometry (LC-MS)

The depolymerization products of lignin were analyzed by LC-MS with a ultra-high performance tandem mass spectrometry (maxis impact, Bruker Co., USA) and a LC system (1290 Infinity, Agilent Co., USA) equipped with a capillary column (Agilent RRHD SB-C18, 2.1×150 mm, 1.8  $\mu\text{m}$ ). The mobile phase was composed of eluent A (formic acid, 0.1%) and eluent B (methanol in acetonitrile, 10%). The gradient elution was programmed as 10% B for 1 min, 20% B for 5 min, and then 20% B for 16 min. The column was held at 30°C and the detector was set at a wavelength of 280 nm. The flow rate and injection volume were 0.2 mL/min and 5  $\mu\text{L}$ , respectively[20]. A photo of Liquid Chromatography-Triple Quadrupole Mass Spectrometry is show in figure 9.



Figure 9 Liquid Chromatography-Triple Quadrupole Mass Spectrometry (LC-MS).



## CHAPTER 4

### RESULT AND DISCUSSION

This research is focused on the depolymerization of kraft lignin to phenolic compounds by using the electrochemical advanced oxidation process with a microreactor. This research is to study first, relations between current density and residence times for depolymerization kraft lignin to phenolic compounds second, the study of depolymerization kraft lignin to phenolic compounds under the base conditions with the difference of 2 types of bases are NaOH and KOH. The kraft lignin concentration is used in the process at 1000 milligram per liter.

The experimental procedure variables studied in this research are current density, residence times, pH, and difference of 2 type base are 0.1 M of NaOH and KOH for depolymerized kraft lignin dissolved in deionized water that has 1000 milligram per liter of kraft lignin concentration. In the first part will discuss the results of these four variables on the depolymerization of kraft lignin on the occurrence of phenolic compounds.

#### **4.1 The study occurrence of oxidizing agent from the relation between current density and residence times.**

The effect of current density on occurrence of oxidant agent for depolymerization of kraft lignin was studied by varied the current between 1.0 and 1.5 mA (3.7 and 5.55 A/m<sup>2</sup>) at residence time 100, 200, and 400 seconds. The depolymerization of kraft lignin has occurred by oxidation reaction between kraft lignin and oxidizing agent, which is formed by split of water to hydroxyl radical at anode electrode. The applied current and residence times are a major key of occurrence oxidizing agent to depolymerization kraft lignin in this system. However, the measurement of hydroxyl radical cannot be done. So, the formation of hydroxyl

radical was analyzed by using the hydrogen peroxide concentration with colorimetric method. Because in this research, there is water in the process for dissolved kraft lignin at low concentrations, it can analyze the Hydrogen Peroxide by UV-vis spectroscopy. The formation of hydrogen peroxide was combined from both of hydroxyl radical on anode side and this reaction followed by **Eq. 3**. The formation occurrence of hydrogen peroxide with relation between current density and residence times as shown in **figure10**. In this figure shows the formation of hydrogen peroxide has increased when applied the current density from 1.0 to 1.5 mA or (3.7 to 5.55 A/m<sup>2</sup>) that gives a significant difference of up to 40 percentages. While the trend of residence times of both current as the same tendency to increase. Suggest that the applied current density is major key to generated hydroxyl radical more than residence times in this system, which is oxidizing agent to depolymerization of kraft lignin to phenolic compounds.

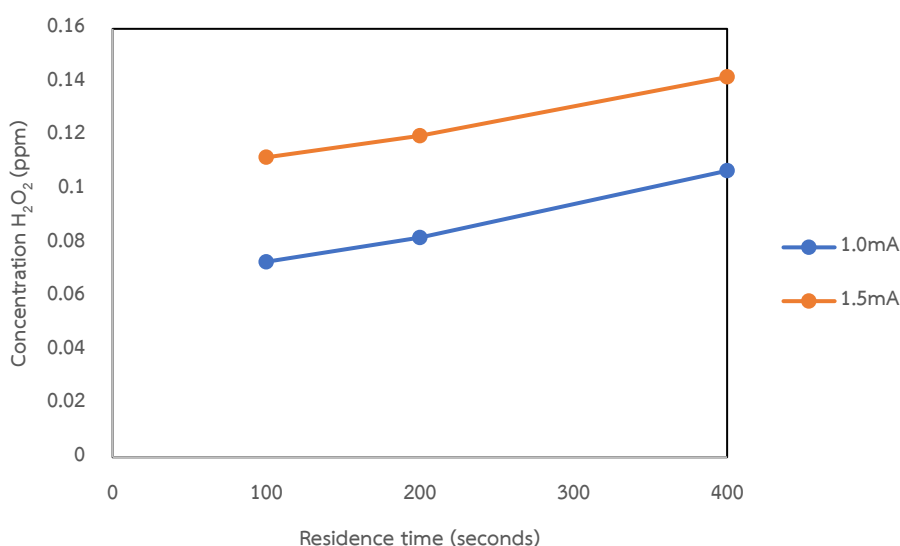
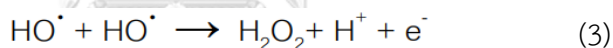


Figure 10 The effect of relation between current density and residence times on the occurrence of hydrogen peroxide.

In this process found that when increasing applied current more than 1.5 mA, cannot be done because when the system was applied more current than 1.5 mA the bubble was a lot appear on the outlet of reactor from splitting of water.

#### 4.1.1 Effect of oxidizing agent on conversion of kraft lignin

It is well known that when the system has oxidizing agent, that can depolymerize kraft lignin to phenolic compounds. If there is a large amount of hydrogen peroxide, it may result in a noticeable change in color with the variable of current density and residence time that can be analytical by UV-vis spectroscopy. The formation of conversion with relation between current density and residence times as shown in **figure 11**. This figure shows that, the formation of conversion between current density 1.0 and 1.5 mA ( $3.7$  and  $5.55 \text{ A/m}^2$ ) at residence times 100, 200 and 400 seconds. The result show conversion are 29 and 35.5 percentages respectively. which has very little conversion and contradicts the amount of hydroxyl radicals produced from **figure10**. that is the result of the hydrogen peroxide can reduce to hydroxyl radical but it difficult to generate hydroxyl radical from hydrogen peroxide by using this method because rate of reaction is low value.

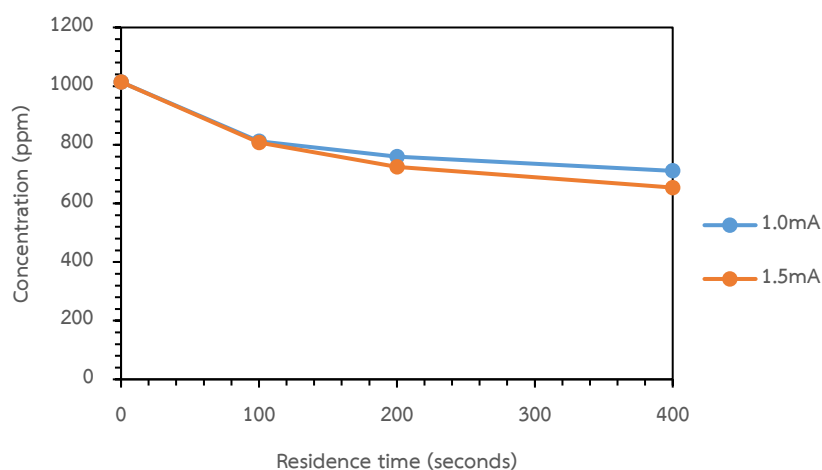


Figure11 The conversion between current density 1.0 mA ( $3.7 \text{ A/m}^2$ ) and 1.5mA ( $5.55 \text{ A/m}^2$ ) at residence times 100, 200 and 400 seconds.

#### 4.2 The study effect of base condition on oxidizing agent and conversion

Base solution of both NaOH and KOH has effect on the oxidizing agents in kraft lignin depolymerization. In this research, the study was done by adjusting at PH 9 of both NaOH and KOH. Including the study of the different bases of NaOH and KOH on oxidizing agents and a comparison of the normal conditions. **Figure 12** show formation of hydroxyl radical in form of hydrogen peroxide of the relation between current density and residence times adjusted with PH 9 of a) NaOH and b) KOH respectively.

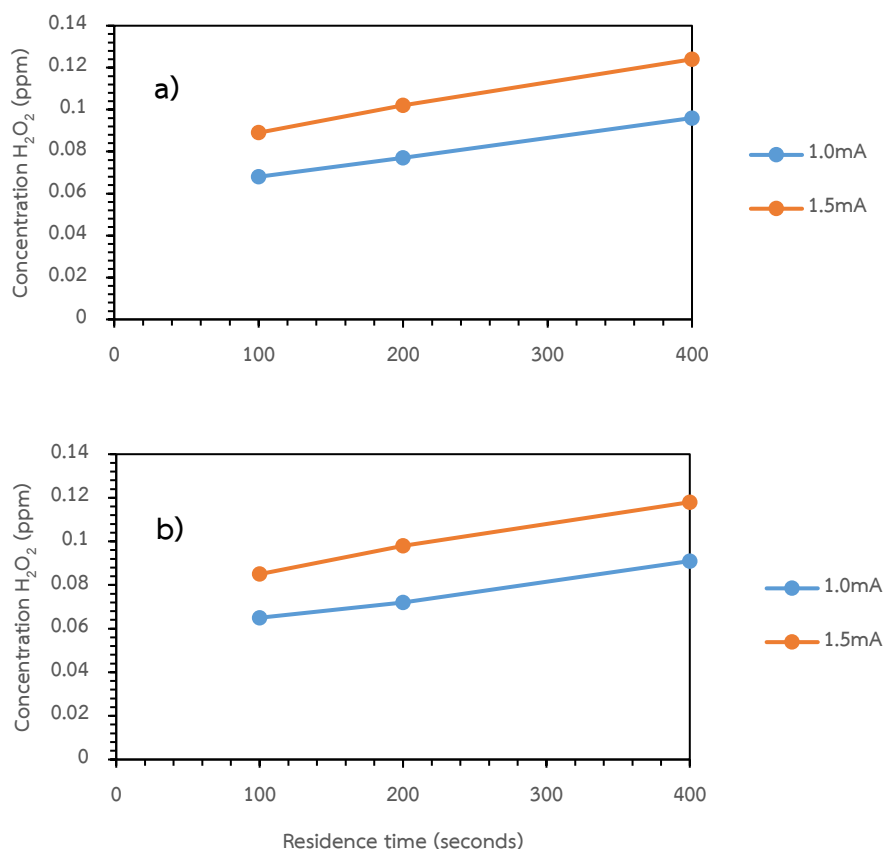


Figure12 The formation of hydroxyl radical in form of hydrogen peroxide of relation between current density and residence times adjusted with PH 9 of a) NaOH and b) KOH

From the figure 12 when adjusted PH 9 of NaOH and KOH gives a quantity of hydrogen peroxide of the same quantity but a lower quantity than normal conditions. However, when studying from the theory, it was found that the reaction at PH 9 will generating perhydroxyl radical from superoxide anion as show in **eq 4**. which affects the quantity of occurrence of hydrogen peroxide. Perhydroxyl radical will usurp hydroxyl radical for the oxidation reaction. This will result in a value trend of conversion decreased. **Figure13** show the formation of conversion with relation between current density and residence times when adjusted PH 9 of NaOH and KOH

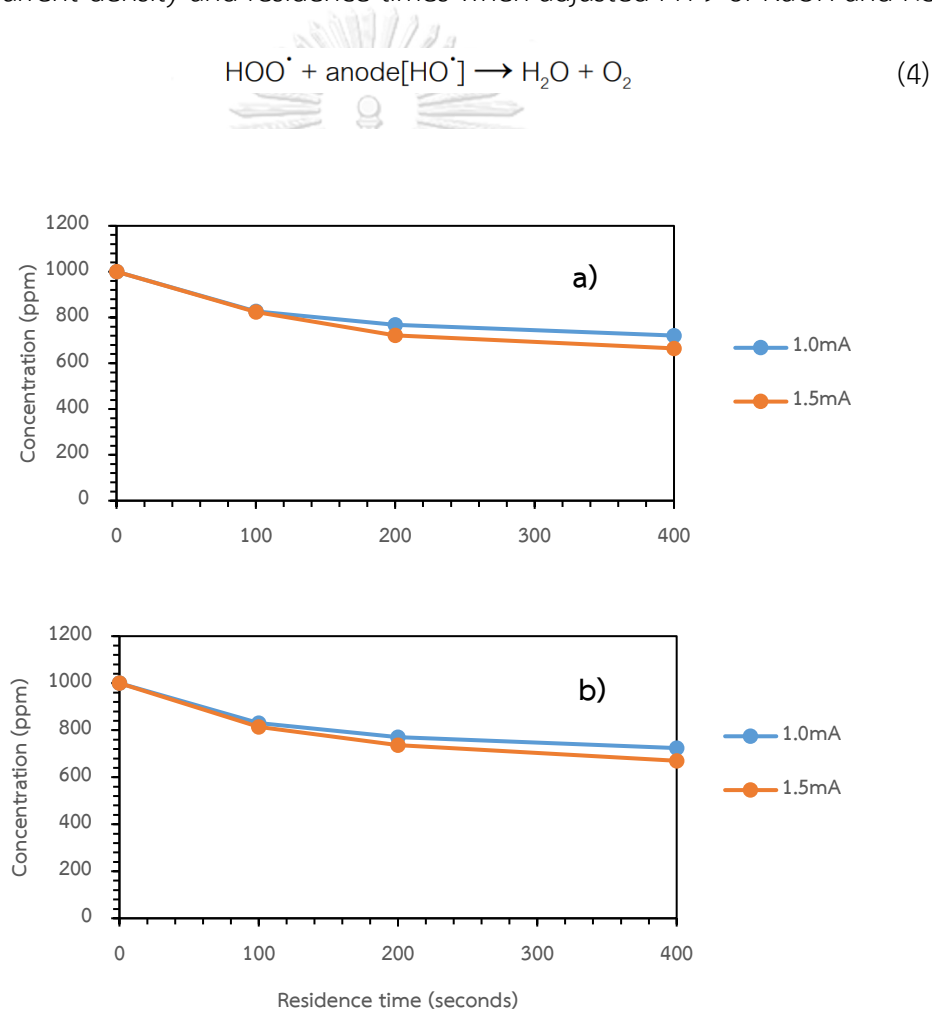


Figure13 The formation of conversion with relation between current density and residence times when adjusted PH 9 of a) NaOH and b) KOH

The result was found that the value of conversion decreased when adjusted PH 9 of NaOH and KOH. Which corresponds to a decrease in the quantity of hydrogen peroxide. The percentage of conversion is 27.6 and 33 percent of NaOH with current density 1.0 and 1.5 mA ( $3.7$  and  $5.55 \text{ A/m}^2$ ) at residence times 100, 200 and 400 respectively. whose value of the conversion is close to that of KOH is 27.9 and 33.5 percent respectively. That can be proved the base conditioning decreases the quantity of Hydrogen peroxide and thus decreases the conversion accordingly. But lower quantities of both may be suitable conditions for occurrence oxidation product such as phenolic compounds and other monomers. which still need to be analyzed further into the internal components of kraft lignin.

#### **4.3 The study occurrence of phenolic compounds and other monomer from the relation between current density at 1.5 mA ( $5.55 \text{ A/m}^2$ ) and residence times more than 400 seconds.**

In this part is the study of oxidation products from the reaction more than 400 seconds in form of cycle 1 to cycle 4 where each of cycle takes residence times at 200 seconds with current density 1.5 mA ( $5.55 \text{ A/m}^2$ ). That means that the at cycle 4 has doubled the residence time as 800 seconds. To observe the emergence or disappearance of oxidation products such as phenolic compounds or others monomer.

From the result when increasing the residence time in the form of cycle make increased the lignin conversion to 60 percent as shown in **Figure14**. Which the result 2 time of the percentage conversion is caused by a more quantity of hydroxyl radical, which maybe also be same double. this may be beneficial from the point of view of degradation, but from the point of view of depolymerization of kraft lignin will be analyzed by Gas chromatography with mass spectrometry (GC-MS/MS).

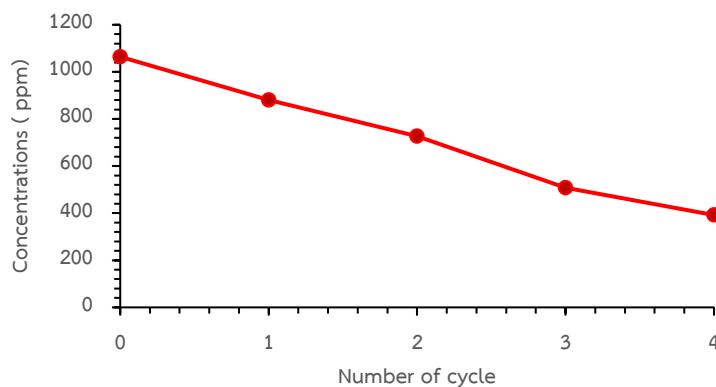
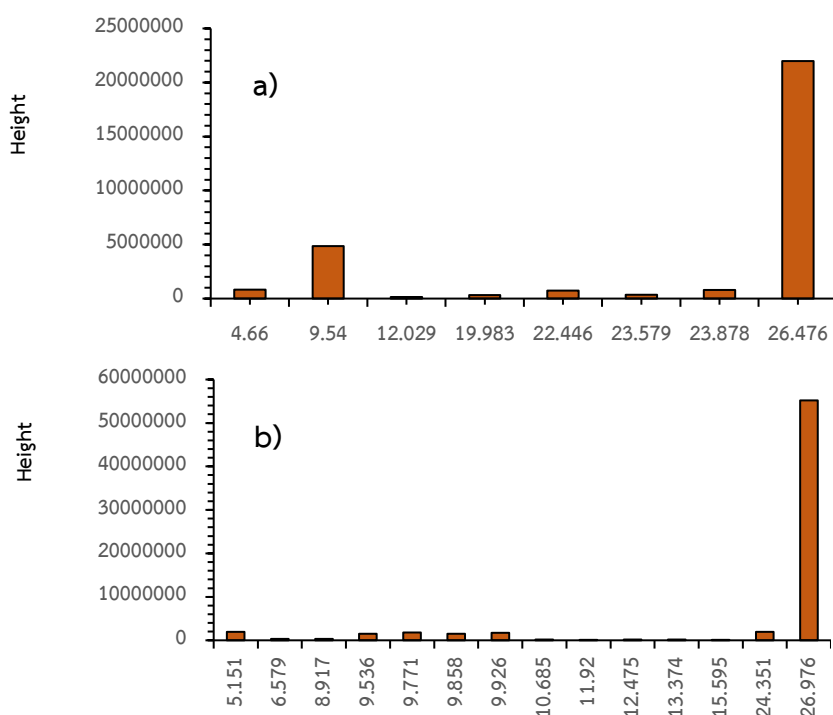


Figure14 The conversion of kraft lignin at each of cycle

The component of phenolic compounds or other monomers in kraft lignin will be analyzed by Gas chromatography with mass spectrometry (GC-MS/MS) as shown in **Figure 15**. However, the initial kraft lignin was performed as a baseline and compared with the occurrence of oxidation products after the reaction. which will be divided according to the figure 6 (a-e) are initial kraft lignin, cycle1, cycle2, cycle3, and cycle 4 respectively



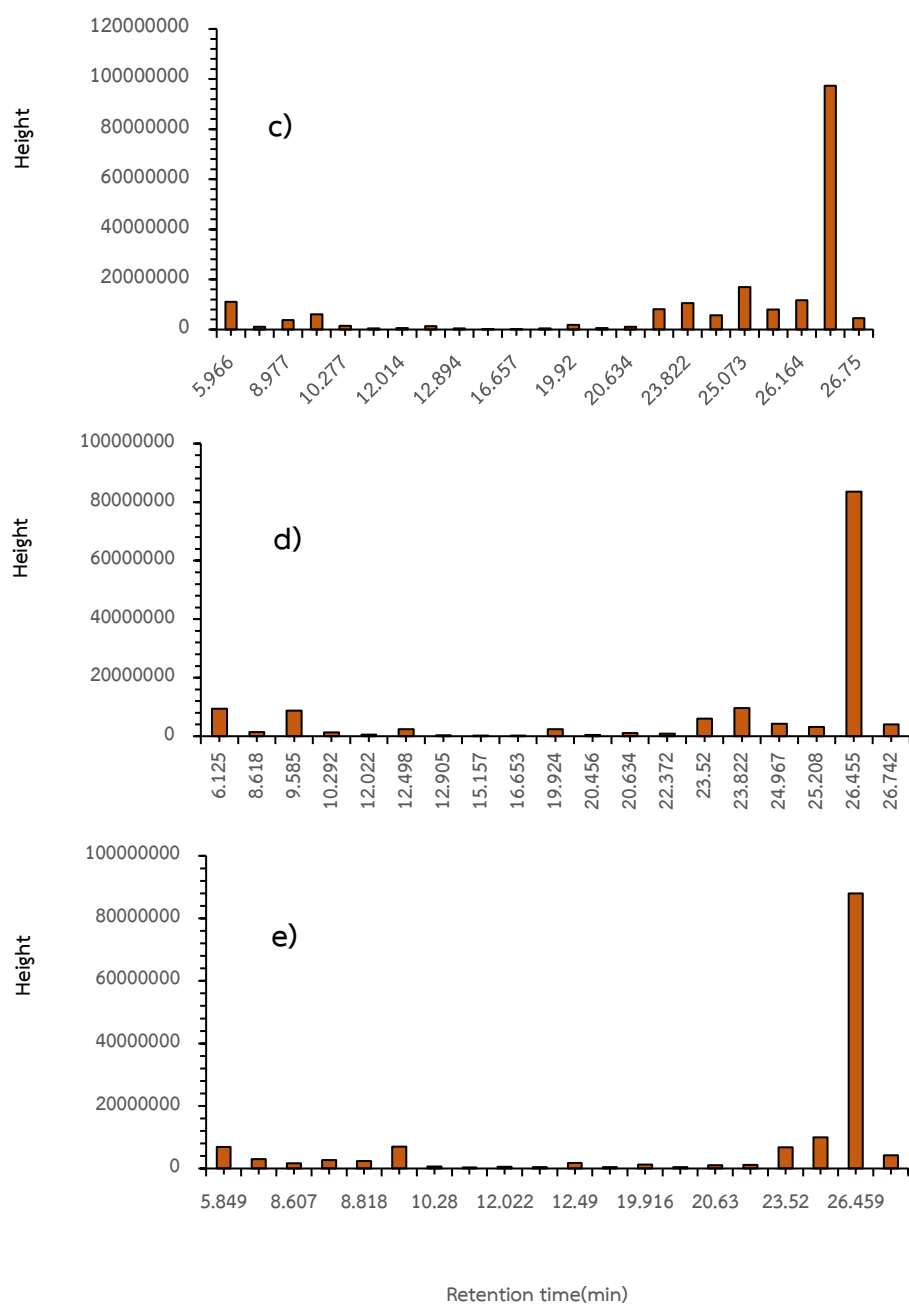
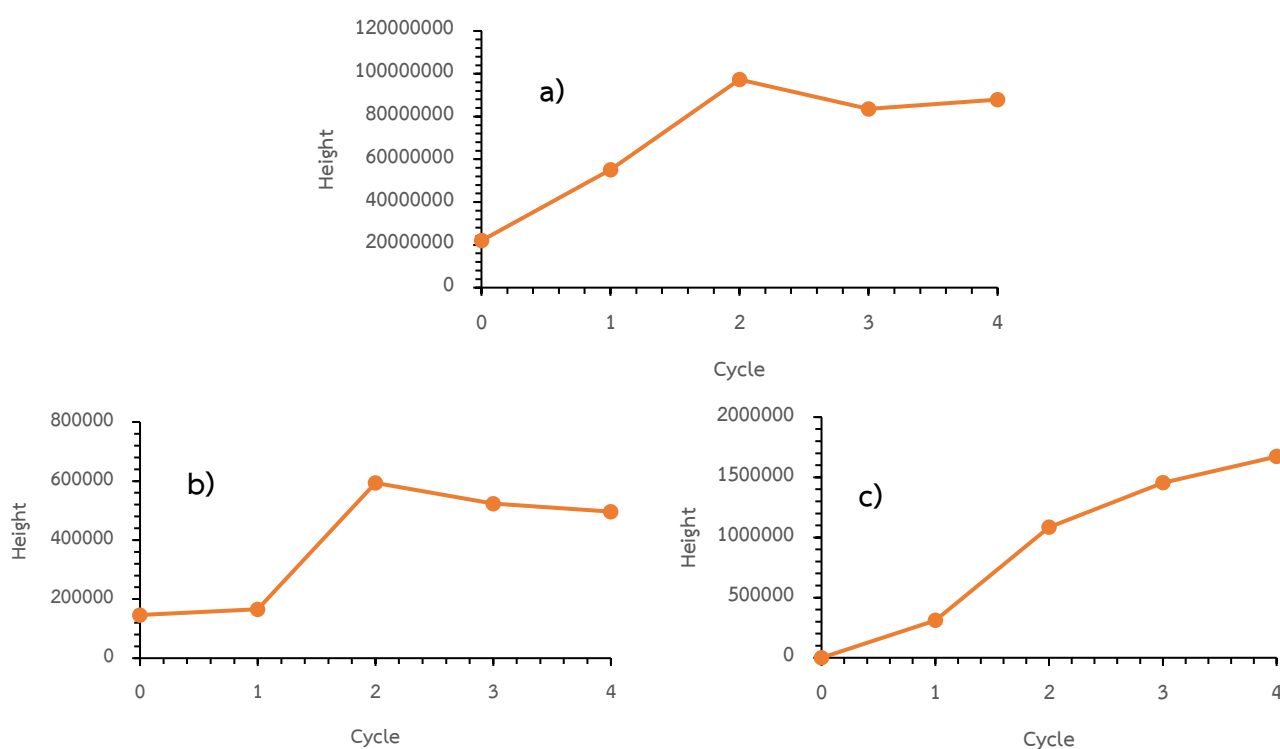


Figure 15 The component in kraft lignin analyzed by Gas chromatography with mass spectrometry (GC-MS/MS): a) initial kraft lignin, b) after the reaction of cycle1, c) cycle2, d) cycle3 and e) cycle 4.



In **figure 15a).** The major product is (Z)-9-octadecenamide in initial kraft lignin were found at retention time 26.4 which is thought to be a substance with a large structure of type Dimer molecule. Including some phenolic compounds were found in the Initial kraft lignin at retention time 4.66, 9.54, and 12.029 min These are Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone respectively. The presence of minor products may be caused by the dissolution of products in deionized water. Therefore, it is detected when analyzing by Gas chromatography with mass spectrometry (GC-MS/MS). In **figure 15b.)** (Z)-9-octadecenamide and minor products that are expected to be obtained by dissolving in deionized water such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same which was detected in retention time at 26.9, 5.15, 9.53 and 12.47 min respectively. However, after the reaction in cycle 1, a new minor product was found in retention time at 8.91, 10.68, 11.92, 13.37 and 15.59 min. These are vinylguaiacol, vanillin, propyl guaiacol, guaiacylacetone and homovanillic acid respectively. In **figure 15c.)** (Z)-9-octadecenamide and minor products as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same which was detected in retention time at 26.47, 5.95, 9.55 and 12.01 min respectively. But in cycle 2 was found new minor product in retention time at 16.65 is coniferyl aldehyde and found the missing of propyl guaiacol, which happened to occur in cycle 1. In **figure 15d.)** (Z)-9-octadecenamide and minor products as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same which was detected in retention time at 26.45, 5.84, 9.58 and 12.02 min respectively. In which, in this condition, there is not found a new minor product or missing product when compared to cycle2. And In **figure 15e.)** (Z)-9-octadecenamide and minor products as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same which was detected in retention time at 26.45, 5.84, 9.58 and 12.02 min respectively. But in cycle 4 was found new minor product in retention time at 11.30 is eugenol and found the missing of coniferyl aldehyde and homovanillic acid, which happened to occur in cycle 3.

From the result of cycle for depolymerization kraft lignin found (Z)-9-octadecenamide remains the same in range of retention time at 26 min and found all the new minor products compared to the initial kraft lignin are vinylguaiacol, vanillin, propyl guaiacol, guaiacylacetone, homovanillic acid, coniferyl aldehyde and eugenol. However, when the reaction is from cycle2 or more, there will be a disappearance of minor products due to decomposition over time such as propyl guaiacol in cycle 2, coniferyl aldehyde and homovanillic acid in cycle 4. On the other hand, a longer time is suitable for the formation of some compounds such as eugenol in cycle4 in form of cycle. All these studies in reaction times of more than 400 seconds can be adapted to obtain the desired product in a suitable of cycle for the formation of the substance. For the trend of occurrence of each oxidation products divided according to the criteria of products that tend to increase and decrease in each cycle. **Figure 16** show trends to increase of oxidation products. There are 5 types of products such as (Z)-9-octadecenamide, acetoguaiacone, vinyl guaiacol, guaiacylacetone, and eugenol respectively.



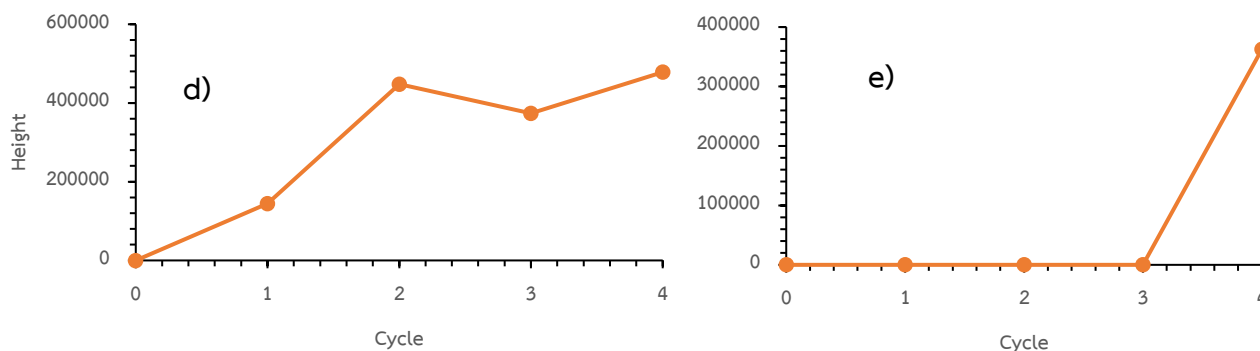


Figure16 Trends to increase of oxidation products a) (Z)-9-octadecenamide, b) acetoguaiacone, c) vinyl guaiacol, d) guaiacylacetone and e) eugenol.

Due to the structure of lignin that cannot tell the true structure. The results of this experiment can indicate an increase in the structure of the reaction, especially (Z)-9-octadecenamide. Which found before the reaction and after the reaction increased. This proved that the kraft lignin used in this research contained the (Z)-9-octadecenamide linked with ether and carbon-carbon covalent bonds with monolignol of kraft lignin such as G unit or Guaiacol unit. Because the results of the experiment revealed that the derivative of the minor product is G units or Guaiacol. Due to its smaller content than the major product and its aromatic functional group, it is difficult to depolymerization. Causes one point maximum value for a cycle and decreases over a longer cycle. **figure 17** shown trends to decrease of oxidation products. There are 5 types of products such as Guaiacol, 2methyl-1,3-dioxane, vanillin, propyl guaiacol, and homovanillic acid respectively.

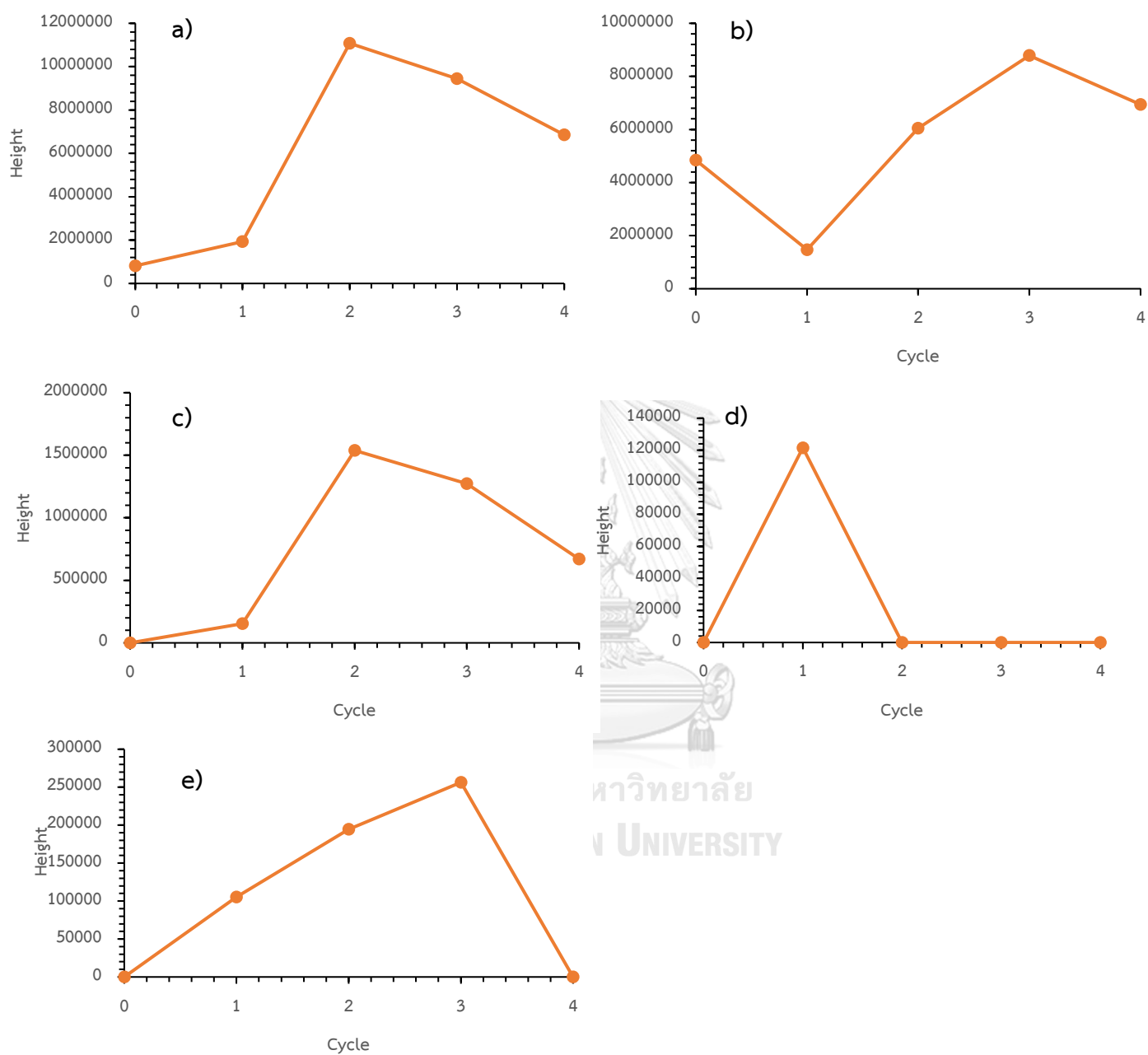


Figure17 Trends to decrease of oxidation products a) Guaiacol ,b) 2-methyl(1,3-dioxane, c) vanillin, d) propyl guaiacol and e) Homovanillic acid.

From the **figure 17** The resulting some oxidation products tends to react with an increase in the range of cycle 1 to cycle 2 and a decrease in cycle 3 such as guaiacol and vanillin follow by **figure 17a, b**. That's means that if the product is desired, it should not react more than 3 cycles. However, there are also some products that occur the most at cycle 3, such as 1,3-dioxane and homovanillic acid follow by **figure 17b, e**. while guaiacol and vanillin began to decrease. And there is the emergence of another product, propyl guaiacol. which occurs by reacting only one cycle follow by **figure 17 d**. In the future, if there is a need for various products for use in industries, Conditions should be adjusted or the cycle appropriate for the occurrence of oxidation products should be adjusted.

#### 4.4 The study occurrence of phenolic compounds and other monomer from the relation between current density and residence times.

In this part is the study of oxidation products from the relation between current density 1.0 and 1.5 mA ( $3.7$  and  $5.55 \text{ A/m}^2$ ) at residence times 100, 200 and 400 seconds respectively. To compare the oxidation products or conditions suitable for oxidation product formation. due to different quantities of oxidizing agents or hydroxyl radical that are expected to affect the occurrence or disappearance of the oxidation products. First, the occurrence of phenolic compounds or other monomers after the reaction at 1.0 mA ( $3.7 \text{ A/m}^2$ ) and residence time 100, 200, and 400 seconds respectively. Which will be analyzed by Gas chromatography with mass spectrometry (GC-MS/MS) as shown in **figure 18**.

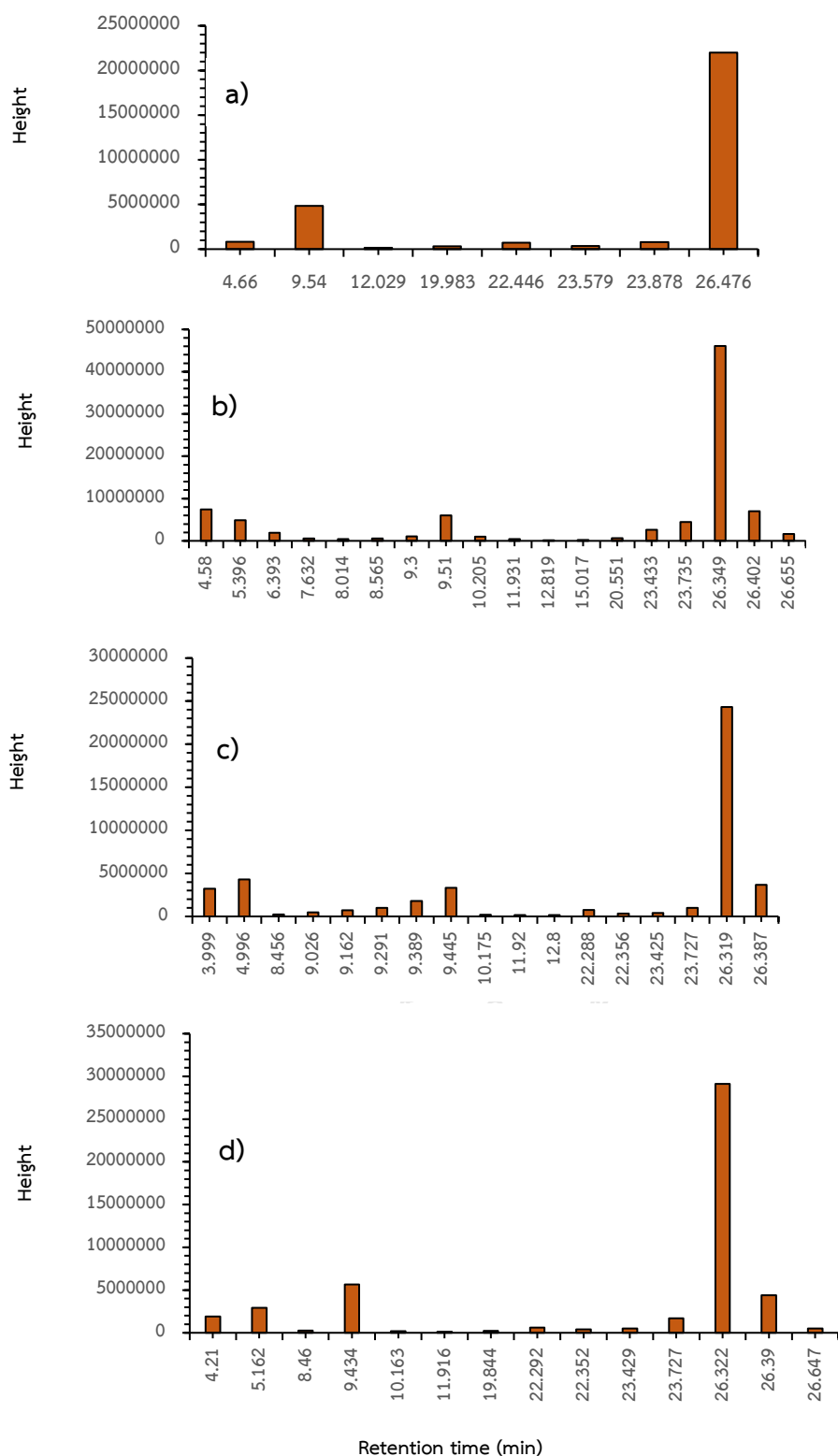
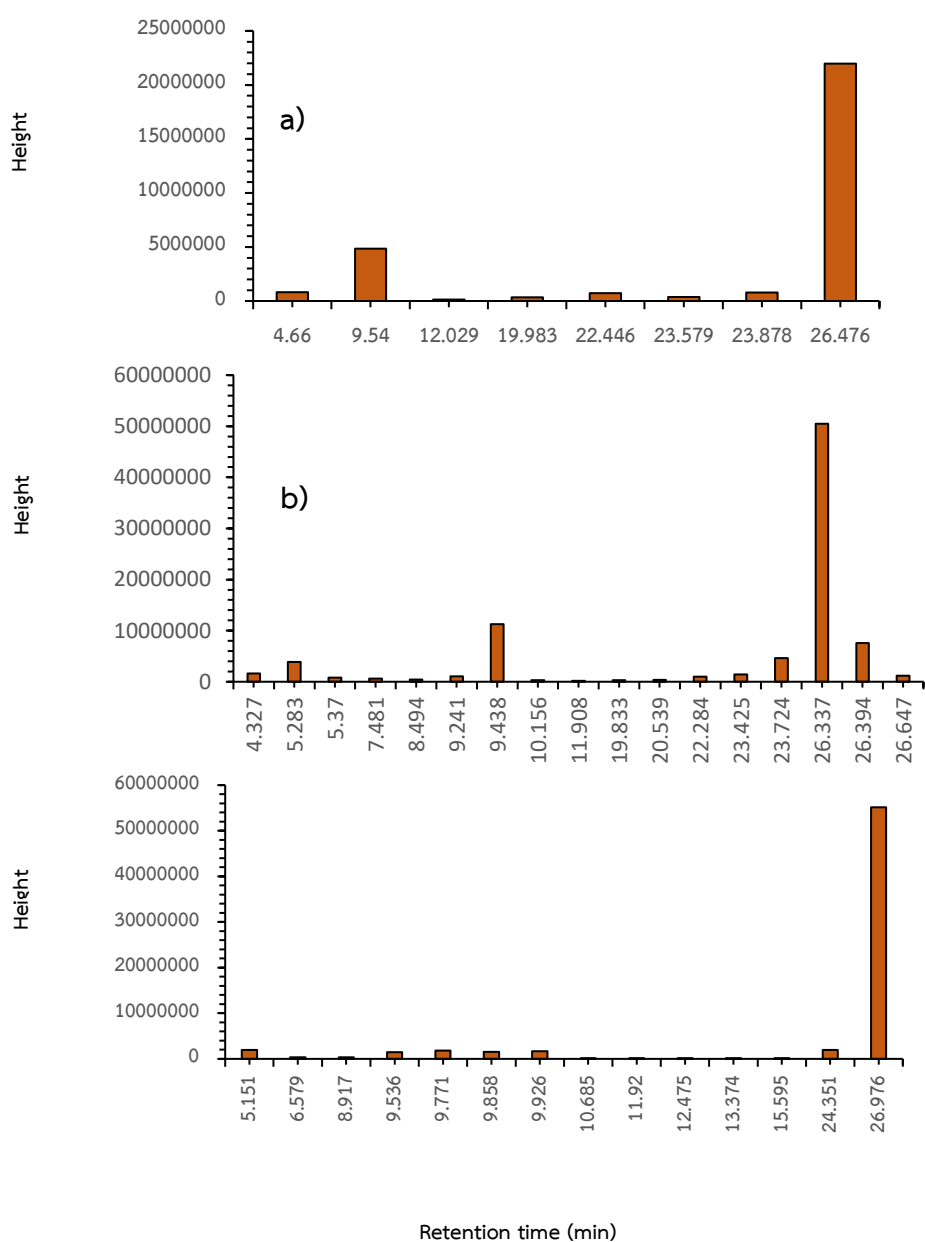


Figure 18 The component in kraft lignin a) initial kraft lignin, b) 1.0 mA (3.7 A/m<sup>2</sup>) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds.

From **figure 18a).** (Z)-9-octadecenamide in initial kraft lignin were found at retention time 26.4 which is thought to be a substance with a large structure of type Dimer molecule. Including some phenolic compounds were found in the Initial kraft lignin at retention time 4.66, 9.54, and 12.029 min These are Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone respectively. The presence of minor products may be caused by the dissolution of products in deionized water. Therefore, it is detected when analyzing by Gas chromatography with mass spectrometry (GC-MS/MS). In **figure 18b.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.35, 5.39, 9.51 and 11.93 min respectively. And a new minor product was found in retention time at 4.58, 8.56, 10.20, 12.80, and 15.01 min. These are phenol, vinyl guauaiacol, vanillin, guaiacylacetone and homovanillic acid respectively. In **figure 18c.)** The major product and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.31, 4.99, 9.44 and 11.92 min respectively. And a new minor product was found in retention time at 3.99, 8.45, 10.17, and 12.80 min. These are phenol, vinyl guauaiacol, vanillin, and guaiacylacetone and found the missing of homovanillic acid, which happened to occur at residence times 100 seconds. And In **figure 18d.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.32, 5.16, 9.43 and 11.91 min respectively. And a new minor product was found in retention time at 4.21, and 8.46 min. These are phenol, and vinyl guauaiacol. and more product disappearances such as vanillin and guaiacylacetone which happened to occur at residence times 200 seconds. including homovanillic acid, which happened to occur at residence times 100 seconds.

So, can be concluded that the use of current density 1.0 mA ( $3.7 \text{ A/m}^2$ ) gives an unprecedented oxidation product compared to previous experiments of the cycle with the constant current value at 1.5mA ( $5.55 \text{ A/m}^2$ ) that is phenol. However,

the consistent effect is that the longer the residence time, the more product disappears. To study and compare and suitable conditions for oxidation product formation to be more clear, between the reaction with 1.0 mA ( $3.7 \text{ A/m}^2$ ) and second, the reaction with current density 1.5mA ( $5.55 \text{ A/m}^2$ ) at residence time 100, 200, and 400 seconds. Which will be analyzed by Gas chromatography with mass spectrometry (GC-MS/MS) as shown in **figure 19**.





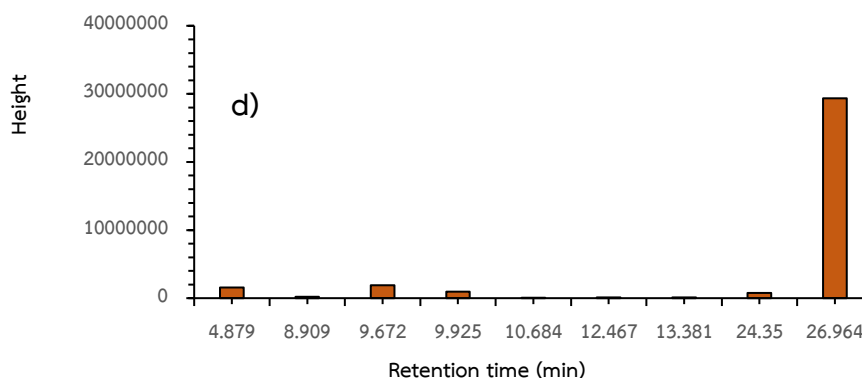


Figure 19 The component in kraft lignin a) initial kraft lignin, b) 1.5 mA ( $5.55 \text{ A/m}^2$ ) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds

From figure 19a). (Z)-9-octadecenamide in initial kraft lignin were found at retention time 26.4 which is thought to be a substance with a large structure of type Dimer molecule. Including some phenolic compounds were found in the Initial kraft lignin at retention time 4.66, 9.54, and 12.029 min These are Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone respectively. In figure 19b.) (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.33, 5.28, 9.43 and 11.90 min respectively. And a new minor product was found in retention time at 4.32, 8.49, and 10.15 min. These are phenol, vinyl guauaiacol, and vanillin respectively. In which this condition also found the occurrence of phenol as well as the current density at 1.0 mA ( $3.7 \text{ A/m}^2$ ). In figure 19c.) (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.97, 5.15, 9.77 and 12.475 min respectively. And a new minor product was found in retention time at 8.91, 10.68, 11.92, 13.37, and 15.59 min. These are vinyl guauaiacol, vanillin, propyl guaiacol, guaiacylacetone and homovanillic acid and found the missing of phenol, which happened to occur at residence times 100 seconds. And In figure 19d.) (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone

remains the same. which was detected in retention time at 26.96, 4.87, 9.67 and 12.46 min respectively. And a new minor product was found in retention time at 8.90, 10.68, and 13.38min. These are vinyl guaiacol, vanillin, and guaiacylacetone and found the missing of phenol, which happened to occur at residence times 100 seconds. And more product disappearances such as propyl guaiacol, and homovanillic acid which happened to occur at residence times 200 seconds. Including phenol, which happened to occur at residence times 100 seconds.

It can be concluded that the use of current density 1.5 mA ( $5.55 \text{ A/m}^2$ ) provide the same oxidation product with condition 1.0 mA ( $3.7 \text{ A/m}^2$ ) respectively. From previous experiments, it was found that the occurrence and disappearance of the oxidation product depended on the proper conditions. therefore, to compare the conditions between current density condition 1.0 mA ( $3.7 \text{ A/m}^2$ ) and 1.5 mA ( $5.55 \text{ A/m}^2$ ) as show the trend of oxidation products between those conditions. It divides the higher occurrence trend of oxidation products between condition 1.0 mA ( $3.7 \text{ A/m}^2$ ) and 1.5 mA ( $5.55 \text{ A/m}^2$ ). It will start with products that are high in 1.5 mA ( $5.55 \text{ A/m}^2$ ) as shown in **figure 20**.

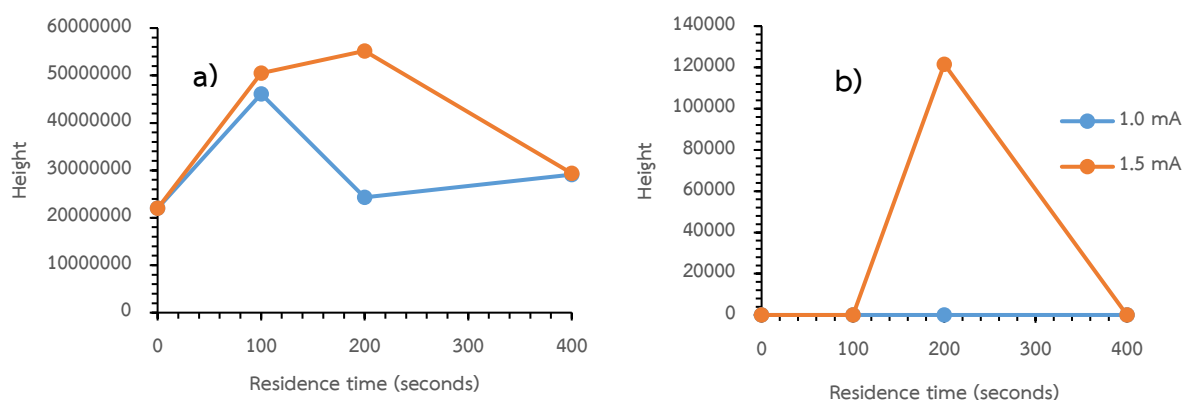
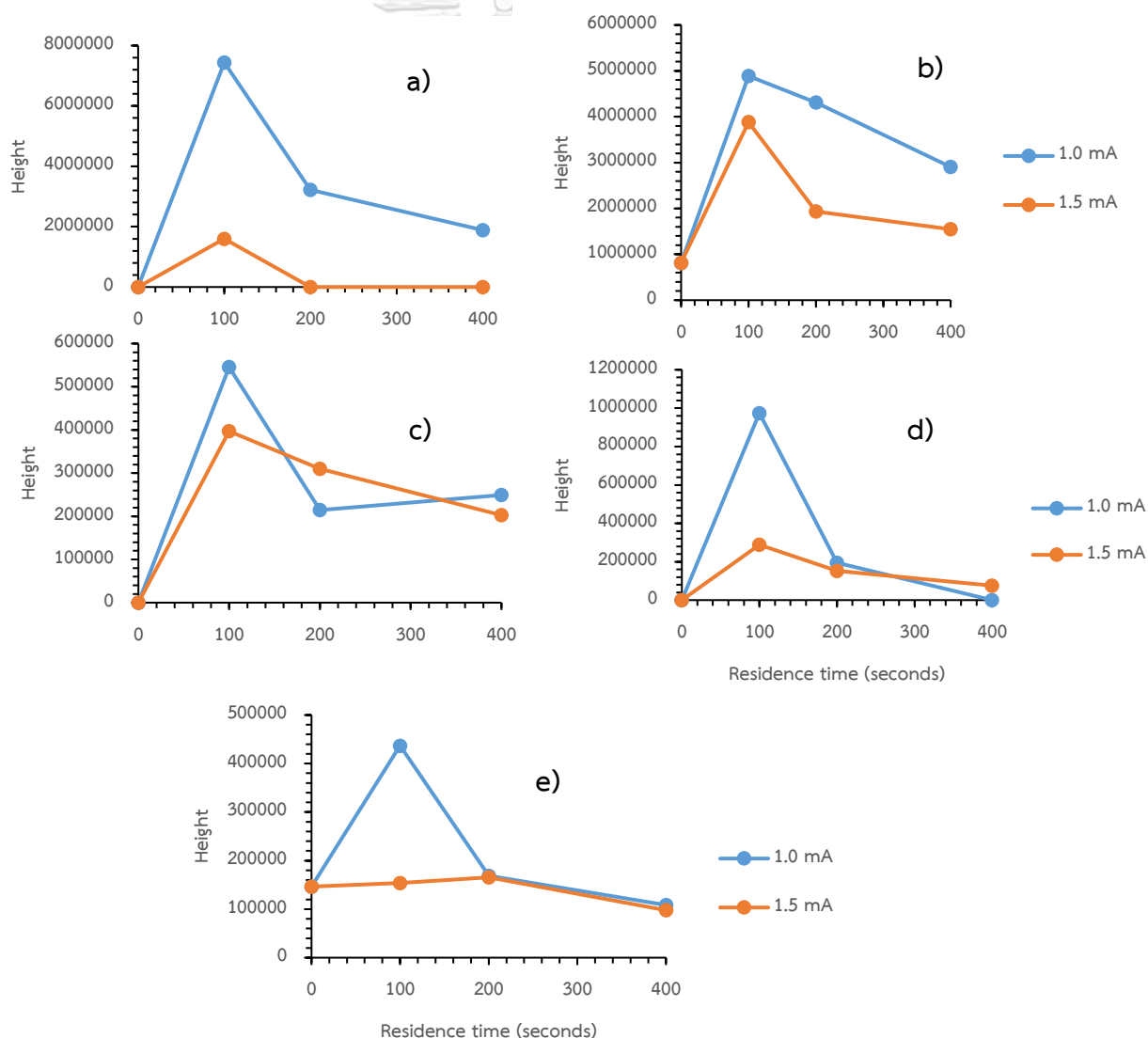


Figure 20 Trends of oxidation products to higher with 1.5 mA ( $5.55 \text{ A/m}^2$ ) at residence time 100, 200- and 400-seconds a) (Z)-9-octadecenamide, and b) Propyl guaiacol.

From figure 20a. (Z)-9-octadecenamide is highly formed at high current densities and the same greater amount of hydroxyl radicals. which that is the suitable quantity for depolymerization of major products. However, (Z)-9-octadecenamide provides the maximum value of residence time at 200 seconds and decreases over 200 seconds. In addition, minor product that occur only in this condition are found propyl guaiacol show in figure 20 b. This corresponds to the effect of cycle, found only in cycle1, and disappears in cycle2. On the other hand, most of the minor products are high at the condition of 1.0 mA ( $3.7 \text{ A/m}^2$ ). The trend of the remaining minor products is shown in the figure 21.



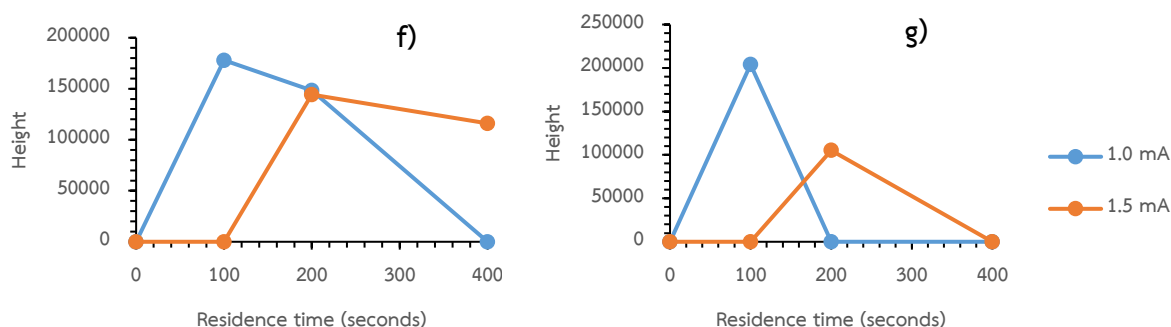


Figure 21 Trends of oxidation products to higher with 1.0 mA ( $5.55 \text{ A/m}^2$ ) at residence time 100, 200- and 400-seconds a) phenol, b) guaiacol, c) vinylguaiacol, d) vanillin, e) acetoguaiacone, f) guaiacylacetone, and g) homovanillic acid.

From **figure 21(a-g)** All minor products occur higher than 1.5 mA ( $5.55 \text{ A/m}^2$ ). This may be because the quantity of hydroxyl radical is not too much and is appropriate for the occurrence of oxidation products. All minor products give a maximum value at 200 seconds. When the residence time is over 200 seconds, the value is decreased. The result of depolymerization to obtain a high value of the minor products may require the proper use quantity of hydroxyl radical from current density 1.0 mA ( $3.7 \text{ A/m}^2$ ) only.

จุฬาลงกรณ์มหาวิทยาลัย  
CHULALONGKORN UNIVERSITY

#### 4.5 The study occurrence of phenolic compounds and other monomer from the relation between current density and residence times with base PH 9 of NaOH and KOH.

In this part is the study of oxidation products from the relation between current density 1.0 and 1.5 mA ( $3.7$  and  $5.55 \text{ A/m}^2$ ) at residence times 100, 200 and 400 seconds with PH9 of NaOH and KOH. To compare the oxidation products or conditions suitable for oxidation product formation. Most important in this part is the effect when adjusting the base conditions of NaOH and KOH. coupled with the relation between current density and residence time to the occurrence of oxidation

products. Since the previous results showed that the quantity of hydroxyl radical was decreased in the base condition. which, may be suitable for the occurrence of new oxidation products. **Figure 22** shows the component of unreacted initial kraft lignin and Compared to the initial kraft lignin with the adjusted condition at PH9 of both NaOH and KOH without the reaction. Which will be analyzed by Gas chromatography with mass spectrometry (GC-MS/MS).

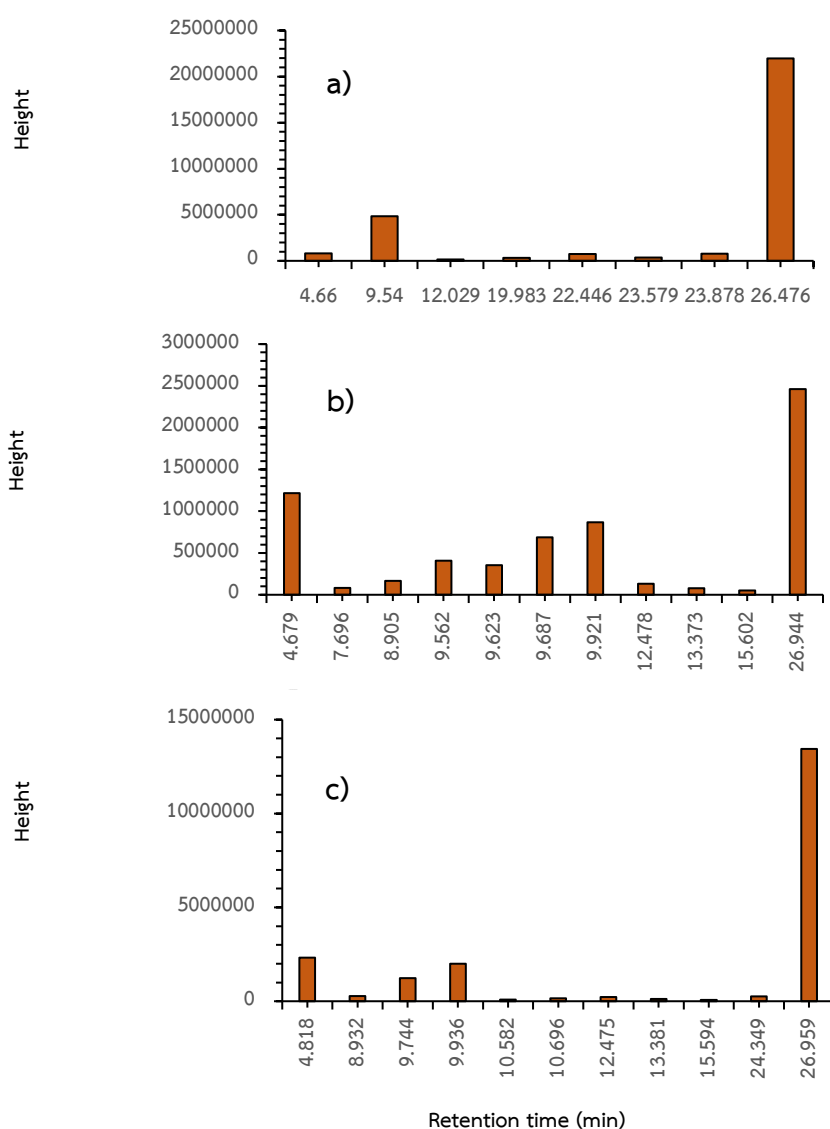


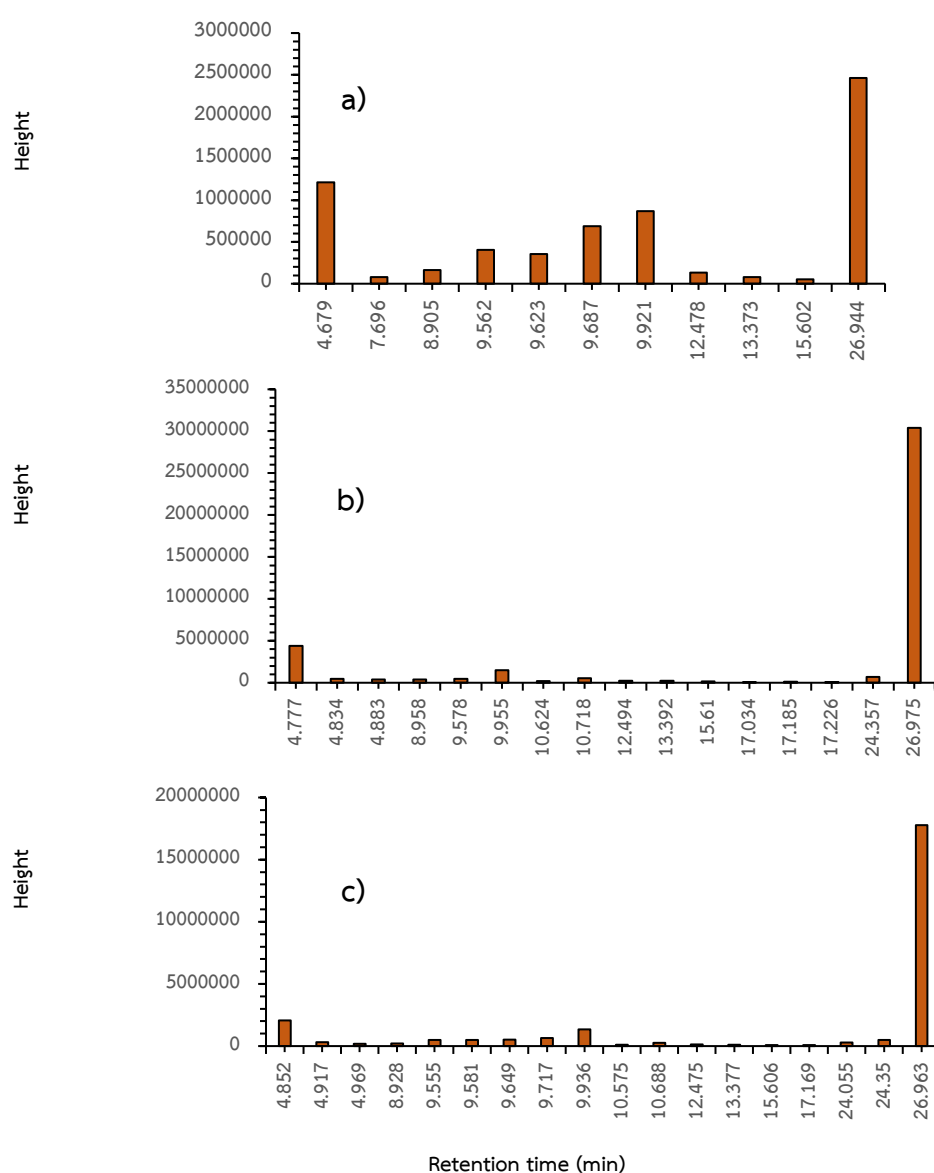
Figure 22 the component without the reaction a) initial kraft lignin, b) PH 9 with NaOH, and c) PH9 with KOH.

From **figure 22a.)** (Z)-9-octadecenamide in initial kraft lignin were found at retention time 26.4 which is thought to be a substance with a large structure of type Dimer molecule. Including some phenolic compounds were found in the Initial kraft lignin at retention time 4.66, 9.54, and 12.029 min These are Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone respectively. In **figure 22b.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.94, 4.67, 9.56 and 12.47 min respectively. And a new minor product was found in retention time at 8.90, 13.37, and 15.60 min. These are vinyl guauaiacol, guaiacylacetone and homovanillic acid respectively. And in **figure 22c.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.95, 4.81, 9.74 and 12.47 min respectively. And a new minor product was found in retention time at 8.93, 10.58, 10.69, 13.38 and 15.59 min. These are vinyl guauaiacol, catechol-guaiacol, vanillin, guaiacylacetone and homovanillic acid respectively. In this condition, the amount of oxidation product was greater than NaOH and found a product that had never been found before from previous trials is catechol-guaiacol.

It will be noted that when adjusting the base condition of both NaOH and KOH, the oxidation products was found without any reaction. That's proven from the previous theory that lignin to base conditioning can allow the oxidation products without any reaction. due to the intensity of the base can cause depolymerization in structure of the kraft lignin. If the intensity of this base is combined with the electrical reaction conditions will be able to produce new oxidation products or how it affects the oxidation products. that is the reason must the study combined with current densities of 1.0 and 1.5 mA ( $3.7$  and  $5.55 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds. So, is divided into 4 steps as follow: 1<sup>st</sup>) and 2<sup>nd</sup>) condition 1.0 mA ( $3.7 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds with PH9 of NaOH, and PH9 of KOH respectively. And 3<sup>rd</sup>) and 4<sup>th</sup>) condition 1.5 mA ( $5.55 \text{ A/m}^2$ ) at

residence times of 100, 200, and 400 seconds with PH9 of NaOH, and PH9 of KOH respectively.

**The first step** will be to study the differences between NaOH and KOH with current densities of 1.0 mA ( $3.7 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds to the occurrence of oxidation products. **Figure 23** shows the component in the condition at PH9 by **NaOH** of initial kraft lignin and compared to after the reaction with current densities of 1.0 mA ( $3.7 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds respectively. Which will be analyzed by Gas chromatography with mass spectrometry (GC-MS/MS).



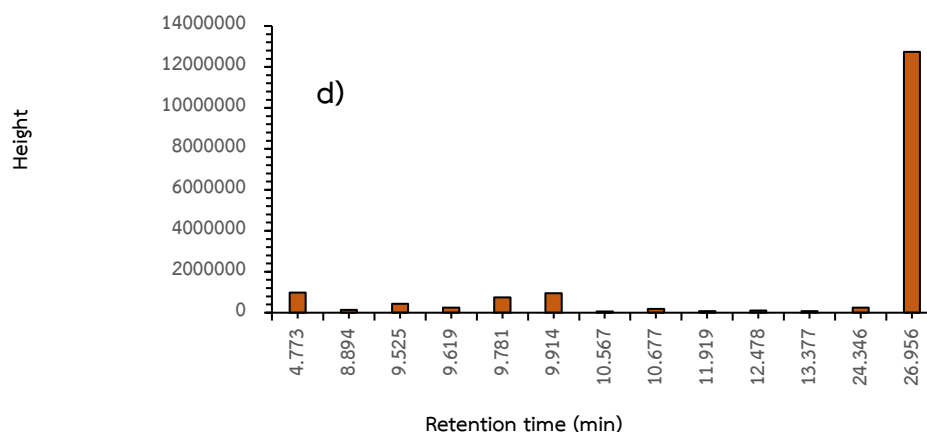


Figure 23 the component in the condition at PH9 by NaOH a) initial kraft lignin, b) 1.0 mA ( $3.7 \text{ A/m}^2$ ) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds.

From figure 23a.) (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.94, 4.67, 9.56 and 12.47 min respectively. And a new minor product was found in retention time at 8.90, 13.37, and 15.60 min. These are vinyl guauaiacol, guaiacylacetone and homovanillic acid respectively. **Figure 23b.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.97, 4.77, 9.57 and 12.49 min respectively. And a new minor product was found in retention time at 8.95, 10.62, 10.71, 13.92, and 15.61 min. These are vinyl guauaiacol, catechol-guaiacol, vanillin, guaiacylacetone and homovanillic acid respectively. For compared with normal conditions, some oxidation products appear and disappear. which from the previous experiments that normal conditions did not found catechol-guaiacol, but when adjusting the conditions make the occurrence of catechol-guaiacol. Meanwhile, found the disappearance of phenol from normal conditions. Thus, it was concluded that the base affects the occurrence of catechol-guaiacol and the disappearance of phenol. **Figure 23c.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.96, 4.85, 9.55 and 12.47 min respectively.



And a new minor product same as 100 seconds. which was found in retention time at 8.92, 10.57, 10.68, 13.37, and 15.60 min. For compared with normal conditions, some oxidation products appear and disappear. which from the previous experiments that normal conditions did not found catechol-guaiacol, and homovanillic acid but when adjusting the conditions make the occurrence of catechol-guaiacol and homovanillic acid. Meanwhile, found the disappearance of phenol from normal conditions as the same at 100 seconds. And **Figure 23d.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.95, 4.77, 9.61 and 12.47 min respectively. And a new minor product was found in retention time at 8.89, 10.56, 10.67, 11.91, and 13.92 min. These are vinyl guaiacol, catechol-guaiacol, vanillin, propylguaiacol, and guaiacylacetone respectively. For compared with normal conditions, some oxidation products appear and disappear. which from the previous experiments that normal conditions did not found catechol-guaiacol, vanillin, propyl guaiacol and guaiacylacetone. but when adjusting the conditions make the occurrence of catechol-guaiacol, vanillin, propyl guaiacol and guaiacylacetone respectively.

From the result when the adjusted base condition with NaOH into the reaction can maintain more oxidation products availability compared to normal conditions. This is believed to be the result of a decrease in the quantity of hydroxyl radical when adjusted to base conditions. And found the occurrence of catechol-guaiacol in every of residence time. On the other hand, this condition still affects the disappearance of phenol. So, that quantity of hydroxyl radical may not be enough or not suitable to depolymerization kraft lignin to phenol.

**The second step** will be to study the differences between NaOH and KOH with current densities of 1.0 mA ( $3.7 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds to the occurrence of oxidation products. **Figure 24** shows the component in the condition at PH9 by KOH of initial kraft lignin and compared to

after the reaction with current densities of 1.0 mA ( $3.7 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds respectively. Which will be analyzed by Gas chromatography with mass spectrometry (GC-MS/MS).

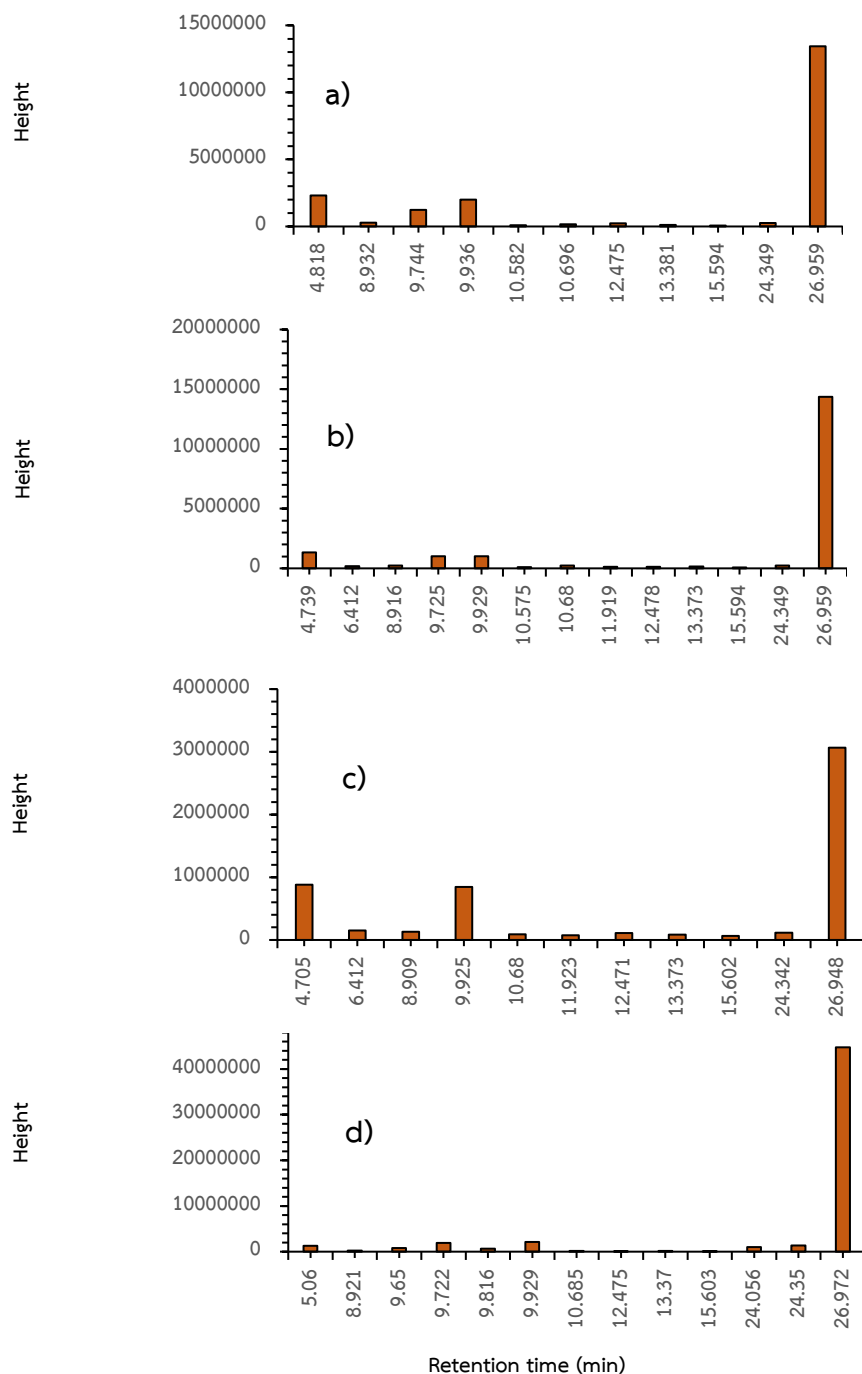


Figure 24 the component in the condition at PH9 by KOH a) initial kraft lignin, b) 1.0 mA ( $3.7 \text{ A/m}^2$ ) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds

In **figure 24a.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.95, 4.81, 9.74 and 12.47 min respectively. And a new minor product was found in retention time at 8.93, 10.58, 10.69, 13.38 and 15.59 min. These are vinyl guauaiacol, catechol-guaiacol, vanillin, guaiacylacetone and homovanillic acid respectively. **Figure 24b.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.95, 4.73, 9.72 and 12.47 min respectively. And a new minor product was found in retention time at 8.91, 10.57, 10.68, 11.91, 13.37, and 15.59 min. These are vinyl guauaiacol, catechol-guaiacol, vanillin, propyl guaiacol guaiacylacetone and homovanillic acid respectively. For compared with normal conditions and conditions of base NaOH PH9, some oxidation products appear and disappear. which from the previous experiments that normal conditions did not found catechol-guaiacol and in the base condition of NaOH at 100 seconds did not found propyl guaiacol but when adjusting the conditions make the occurrence of catechol-guaiacol and propyl guaiacol. **Figure 24c.)** (Z)-9-octadecenamide and minor products remain the same. which was detected in retention time at 26.94, 4.70, 9.92 and 12.47 min respectively. And a new minor product was found in retention time at 8.90, 10.68, 11.93, 13.37, and 15.60 min. These are vinyl guauaiacol, vanillin, propyl guaiacol guaiacylacetone and homovanillic acid respectively. And found the missing of catechol-guaiacol from 100 seconds. For compared with normal conditions and conditions of base NaOH PH9, some oxidation products appear and disappear. which from the previous experiments that normal conditions did not found propyl guaiacol, homovanillic acid and in the base condition of NaOH at 200 seconds did not found propyl guaiacol but when adjusting the conditions make the occurrence of and propyl guaiacol and homovanillic acid. **Figure 24d.)** (Z)-9-octadecenamide and minor products remain the same. which was detected in retention time at 26.97, 5.06, 9.65 and 12.47 min respectively. And a new minor product was found in retention time

At 8.92, 10.68, 13.37, and 15.60 min. These are vinyl guaiacol, vanillin, guaiacylacetone and homovanillic acid respectively. And found the missing of catechol-guaiacol from 100 seconds and propyl guaiacol from 200 seconds respectively. For compared with normal conditions and conditions of base NaOH PH9, some oxidation products appear and disappear. which from the previous experiments that normal conditions did not found vanillin, guaiacylacetone, homovanillic acid and in the base condition of NaOH at 400 seconds did not found homovanillic acid but when adjusting the conditions make the occurrence of vanillin, guaiacylacetone, and homovanillic acid.

From the result when the adjusted base condition with KOH into the reaction can maintain more oxidation products availability compared to normal conditions as the same with NaOH. This is believed to be the result of a decrease in the quantity of hydroxyl radical when adjusted to base conditions with KOH. Found the occurrence of propyl guaiacol in residence time at 100 and 200 seconds. While the condition with base NaOH can be occurrence of propyl guaiacol in residence time at 400 seconds. On the other hand, this condition still affects the disappearance of phenol. So, that quantity of hydroxyl radical may not be enough or not suitable to depolymerization kraft lignin to phenol. However, when adjusted the base conditions of both NaOH and KOH with 1.0 mA ( $3.7 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds, it affects the formation of the oxidation product is catechol-guaiacol and propyl guaiacol. which does not found in normal conditions. Including (Z)-9-octadecenamide, it tends to increase and decrease at more than 200 seconds, but at the condition of KOH have effect to major products. it increases after more than 200 seconds. **Figure 25** show trends of oxidation product of a) catechol-guaiacol, propyl guaiacol and (Z)-9-octadecenamide.

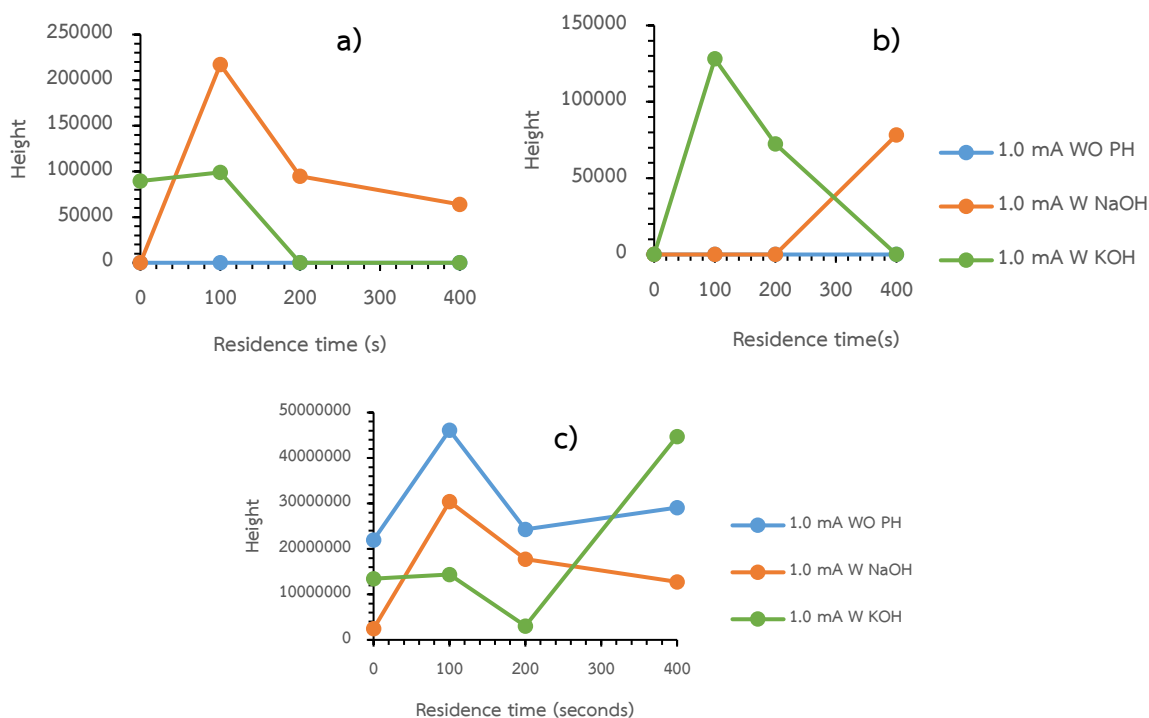


Figure 25 Trends of oxidation product of a). catechol-guaiacol, b). propyl guaiacol and c) (Z)-9-octadecenamide.

**The third step** will be to study the differences between NaOH and KOH with current densities of 1.5 mA ( $5.55 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds to the occurrence of oxidation products. **Figure 26** shows the component in the condition at PH9 by **NaOH** of initial kraft lignin and compared to after the reaction with current densities of 1.5 mA ( $5.55 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds respectively. Which will be analyzed by Gas chromatography with mass spectrometry (GC-MS/MS).

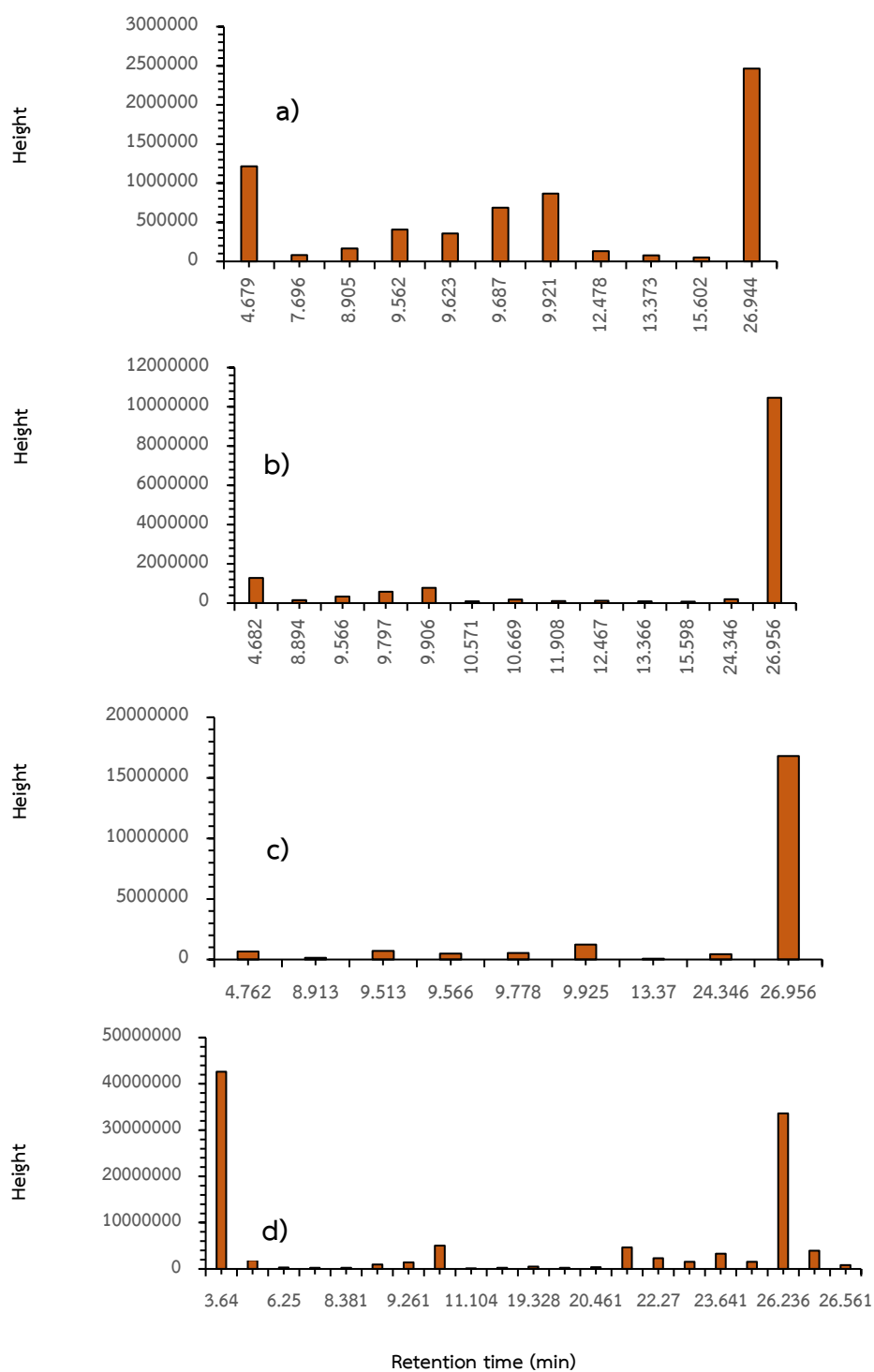


Figure 26 the component in the condition at PH9 by NaOH a) initial kraft lignin, b) 1.5 mA (5.55 A/m<sup>2</sup>) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds.

From figure 26a.) (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.94, 4.67, 9.56 and 12.47 min respectively. And a new minor product was found in retention time at 8.90, 13.37, and 15.60 min. These are vinyl guauaiacol, guaiacylacetone and homovanillic acid respectively. **Figure 26b.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.95, 4.68, 9.56 and 12.46 min respectively. And a new minor product was found in retention time at 8.89, 10.57, 10.66, 11.90, 13.36 and 15.61 min. These are vinyl guauaiacol, catechol-guaiacol, vanillin, propyl guaiacol, guaiacylacetone and homovanillic acid respectively. For compared with normal conditions, some oxidation products appear and disappear. which from the previous experiments that normal conditions did not found catechol-guaiacol, propyl guaiacol, guaiacylacetone, and homovanillic acid but when adjusting the conditions make the occurrence of those oxidation products. Meanwhile, found the disappearance of phenol from normal conditions at 100 seconds. **Figure 26c.)** (Z)-9-octadecenamide and minor products such as Guaiacol, and 2-methyl-1,3-Dioxane still remains the same. which was detected in retention time at 26.95, 4.76, and 9.51min respectively. But found the missing of Acetoguaiacone that had appeared in all previous conditions. And a new minor product was found in retention time at 8.91 and 13.37 min. These are vinyl guaiacol and guaiacylacetone. For compared with normal conditions, some oxidation products appear and disappear. At this condition, the oxidation product disappears more than in normal conditions. Vanillin, propyl guaiacol, acetoguaiacone, and homovanillic acid. **Figure 26d.)** (Z)-9-octadecenamide has changed from 9major to 1,3-dioxane that found in the retention time at 3.64 min. So, make the minor products are 9major, Guaiacol, and 2-methyl-1,3-Dioxane remains the same. which was detected in retention time at 26.23, 4.97, and 9.35 min respectively. And a new minor product was found in retention time at 6.25, and 11.1 min.

These are methyl guaiacol and eugenol respectively. Methyl guaiacol is a oxidation product that has just been found for the first time, but Eugenol has already been found in cycle 4 experiment. Therefore, it can be concluded that this condition can cause eugenol to occur for a shorter of residence time.

From the result found a decrease in the occurrence of oxidation products. which gives the opposite effect in 1.0 mA ( $3.7 \text{ A/m}^2$ ). which is caused by quantity of hydroxyl radical that is not suitable. However, significant changes were found in the condition 1.5 mA ( $5.55 \text{ A/m}^2$ ) at residence time 400 seconds. That is, obtaining which 1,3-dioxane is the new major product as well as the minor product that is methyl guaiacol, eugenol and (Z)-9-octadecenamide, which was the major product in all previous experiments, tends to increase steadily.

**The fourth step** will be to study the differences between NaOH and KOH with current densities of 1.5 mA ( $5.55 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds to the occurrence of oxidation products. **Figure 27** shows the component in the condition at PH9 with **KOH** of initial kraft lignin and compared to after the reaction with current densities of 1.5 mA ( $5.55 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds respectively. Which will be analyzed by Gas chromatography with mass spectrometry (GC-MS/MS).



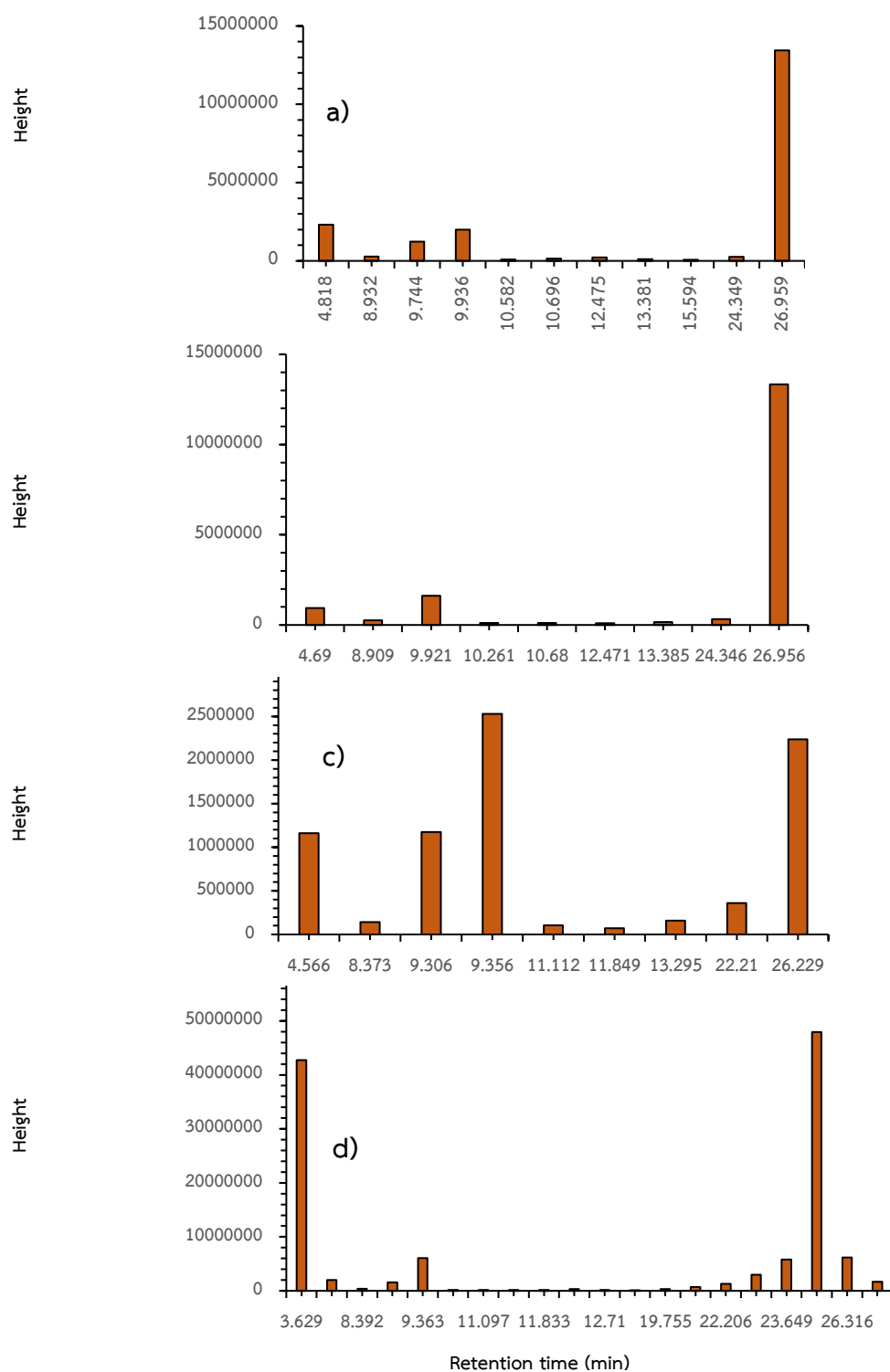


Figure 27 the component in the condition at PH9 by KOH a) initial kraft lignin, b) 1.5 mA (5.55 A/m<sup>2</sup>) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds.

From **figure 27a.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.95, 4.81, 9.74 and 12.47 min respectively. And a new minor product was found in retention time at 8.93, 10.58, 10.69, 13.38 and 15.59 min. These are vinyl guauaiacol, catechol-guaiacol, vanillin, guaiacylacetone and homovanillic acid respectively. **Figure 27b.)** (Z)-9-octadecenamide and minor products such as Guaiacol, 2-methyl-1,3-Dioxane, and Acetoguaiacone remains the same. which was detected in retention time at 26.95, 4.69, 9.92 and 12.47 min respectively. And a new minor product was found in retention time at 8.90, 10.68, and 13.36 min. These are vinyl guauaiacol, vanillin, and guaiacylacetone respectively. And found the missing of homovanillic acid from initial kraft lignin. Including to compared with normal conditions and conditions of base NaOH PH9, some oxidation products appear and disappear. which from the previous experiments that normal conditions did not found phenol and guaiacylacetone but in the base condition of NaOH at 100 seconds more products were found at this condition. **Figure 27c.)** (Z)-9-octadecenamide has changed from 9major to 2-methyl-1,3-dioxane that found in the retention time at 9.356 min. So, make the minor products are 9major, Guaiacol, and 2-methyl-1,3-Dioxane remains the same. which was detected in retention time at 26.22, 4.56, and 11.849 min respectively. And a new minor product was found in retention time at 8.37, 11.11, and 13.29 min. These are vinyl guaiacol, eugenol and guaiacylacetone respectively. where the oxidation product is not missing from 100 seconds, but the product is found increased by eugenol. which had been found in previous experiments but in this condition can be found at 200 seconds. And **Figure 27d.)** (Z)-9-octadecenamide has changed from 2-methyl-1,3-dioxane to Dioxane derivative that found in the retention time at 3.62 min. So, make the minor products are 9major, Guaiacol, and 2-methyl-1,3-Dioxane. which was detected in retention time at 26.25, 5.03 and 9.36 min respectively. And a new minor product was found in retention time at 8.39, 10.07, 11.09, 11.28, and 12.71 min. These are vinyl guaiacol,

vanillin, propylguaiacol, eugenol and guaiacyl acetone respectively. Which has oxidation products that are added from 200 seconds are propylguaiacol. Including to compared with normal conditions and conditions of base NaOH PH9, some oxidation products appear and disappear. which from the previous experiments that normal conditions did not found eugenol and in the base condition of NaOH at 400 seconds did not find guaiacylacetone. but when adjusting the conditions make the occurrence of eugenol and guaiacylacetone.

From the result found a decrease in the occurrence of oxidation products as the same with NaOH. which gives the opposite effect in 1.0 mA ( $3.7 \text{ A/m}^2$ ). which is caused by quantity of hydroxyl radical that is not suitable. However, significant changes were found in the condition 1.5 mA ( $5.55 \text{ A/m}^2$ ) at residence time 200 and 400 seconds. There are major product changes in both conditions are 2-methyl-1,3-Dioxane and 1,3-Dioxane. Including the minor product such as eugenol. that occurs in a shorter time than the condition of the base with NaOH and cycle. Including (Z)-9-octadecenamide, it was found that the increase of current density and residence time influence to increase in this product. However, when adjusted the base conditions of both NaOH and KOH with 1.5 mA ( $5.55 \text{ A/m}^2$ ) at residence times of 100, 200, and 400 seconds, it affects the formation of the minor product is eugenol, catechol-guaiacol, propyl guaiacol, respectively. which does not found in normal conditions. **Figure 28** show trend of oxidation products of dioxane derivative, (Z)-9-octadecenamide, eugenol, catechol-guaiacol, and propyl guaiacol respectively.

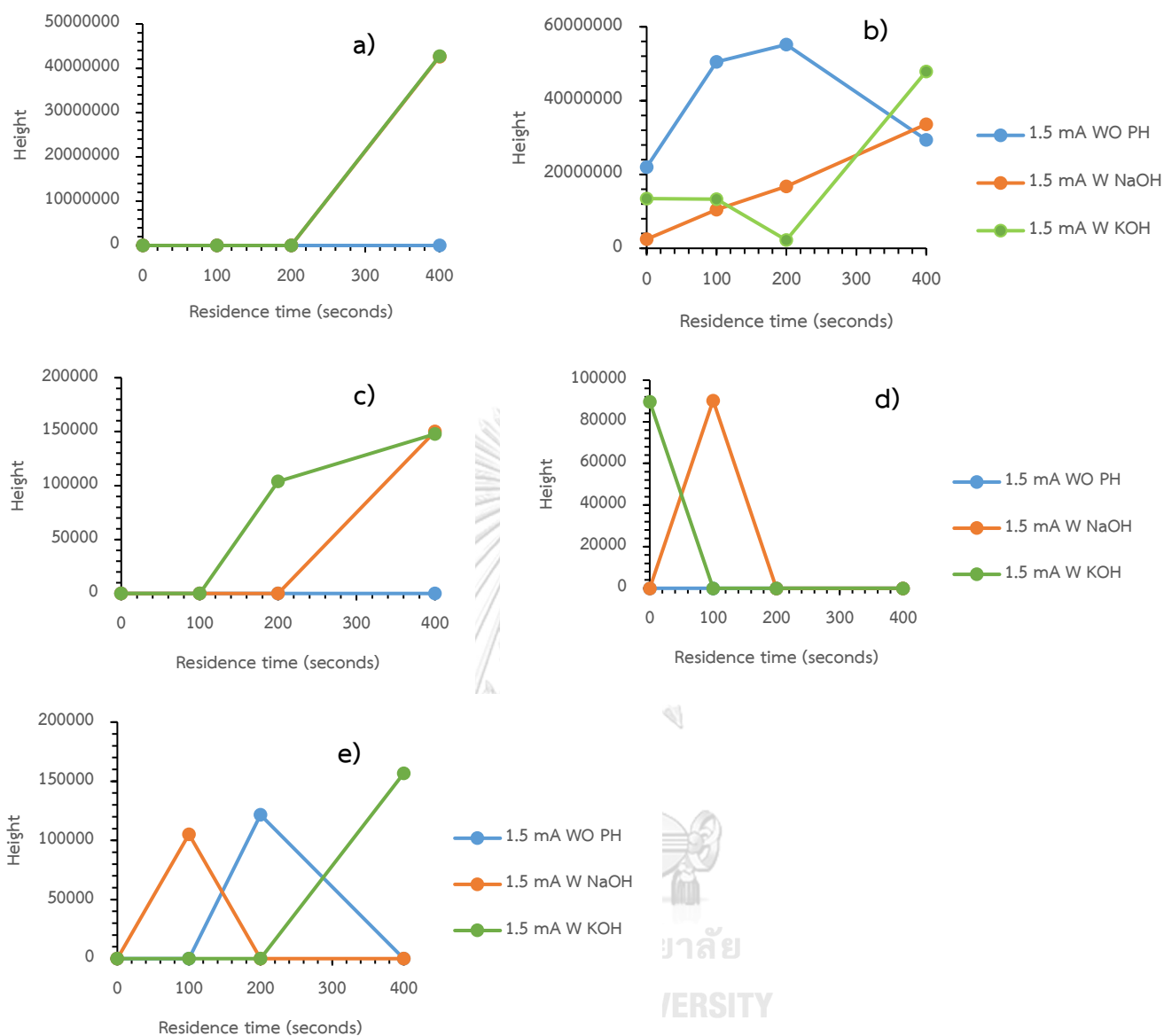


Figure 28 Trends of oxidation product of a) Dioxane derivative, b) (Z)-9-octadecenamide, c). eugenol, d) catechol-guaiacol, and e) propyl guaiacol

#### 4.6 The study pathway mechanism from the relation between current density 1.5 mA and residence times at 100, 200, and 400 seconds.

The results of previous experiments found the compounds of only monomers such as phenolic compounds. but the complex structure after the reaction of lignin not only produces the monomer products but is also expected to have larger structural characteristics that are the type of dimer structure. Due to the limitations of the analysis by Gas Chromatography with Mass Spectrometry (GC-MS) unable to analyze the dimer structure. Therefore, the large structure of products after the reaction was analyzed by Liquid Chromatography with Mass Spectrometry (LC-MS). which the analysis is divided into Products detected in negative mode and positive mode. However, the data from the positive mode could not be identified due to insufficient data. On the other hand, most of the detections are found in negative mode, so the analysis results shown are in negative mode. Which was the experiment using initial kraft lignin in **figure 29(a)** and compared to after the reaction with the conditions of current density 1.5 mA ( $5.55 \text{ A/m}^2$ ) and residence time 100, 200, 400 seconds followed by **figure 29(b-d)**. To study the occurrence of products and be able to describe the source of monomer products. which found from the Gas Chromatography with Mass Spectrometry (GC-MS) analysis.

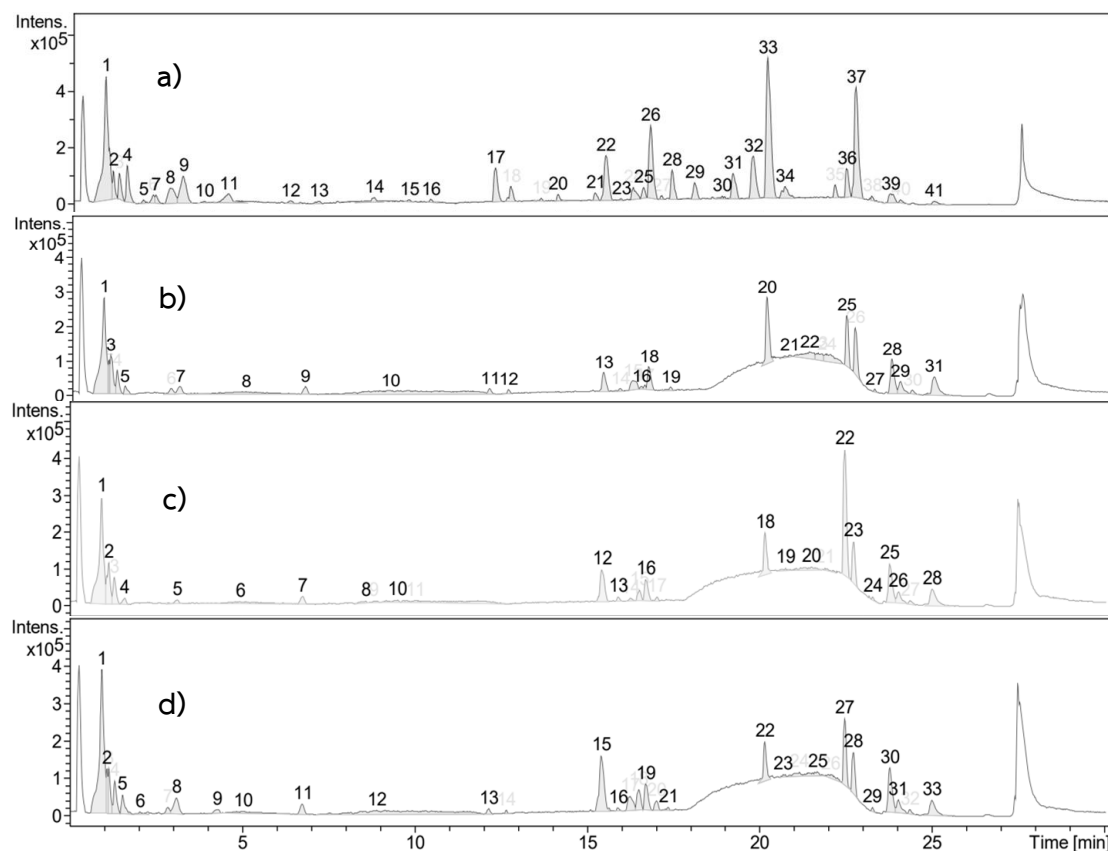


Figure 29 The component in the condition at a) initial kraft lignin, b) 1.5 mA (5.55 A/m<sup>2</sup>) and residence times 100 seconds, c) 200 seconds, and d) 400 seconds.

In **figure 29** the major product was detected at number 1 of all four trials, at retention time 1.0 min. In **figure 29 a)** Before reaction, the major product with 402 m/z and found other products are types of dimer products with 225 m/z, 268 m/z, 360 m/z, 209 m/z, and 334 m/z at 2.3, 2.4, 2.8, 3.2, and 8.7min. In **figure 29 (b-d)** After the reaction, the major product with 257 m/z at retention time 1.0 min and found some of the minor product with 235 m/z. the major product estimated that after the reaction depolymerization occurs because of the disappearance of one of the aromatic phenyl groups at approximately 150 m/z from 402 m/z.

However, this analysis also contained products that could not be identified in the range at retention time more than 10 minutes, is believed to be a type of trimer product or more because more than 450 m/z. So, this research can explain the pathway mechanism of monomers from dimer products inside the microreactor. which combining the results of the analysis with Gas chromatography with Mass Spectrometry (GC-MS) and Liquid chromatography with Mass Spectrometry (LC-MS) as shown in **figure 30**.

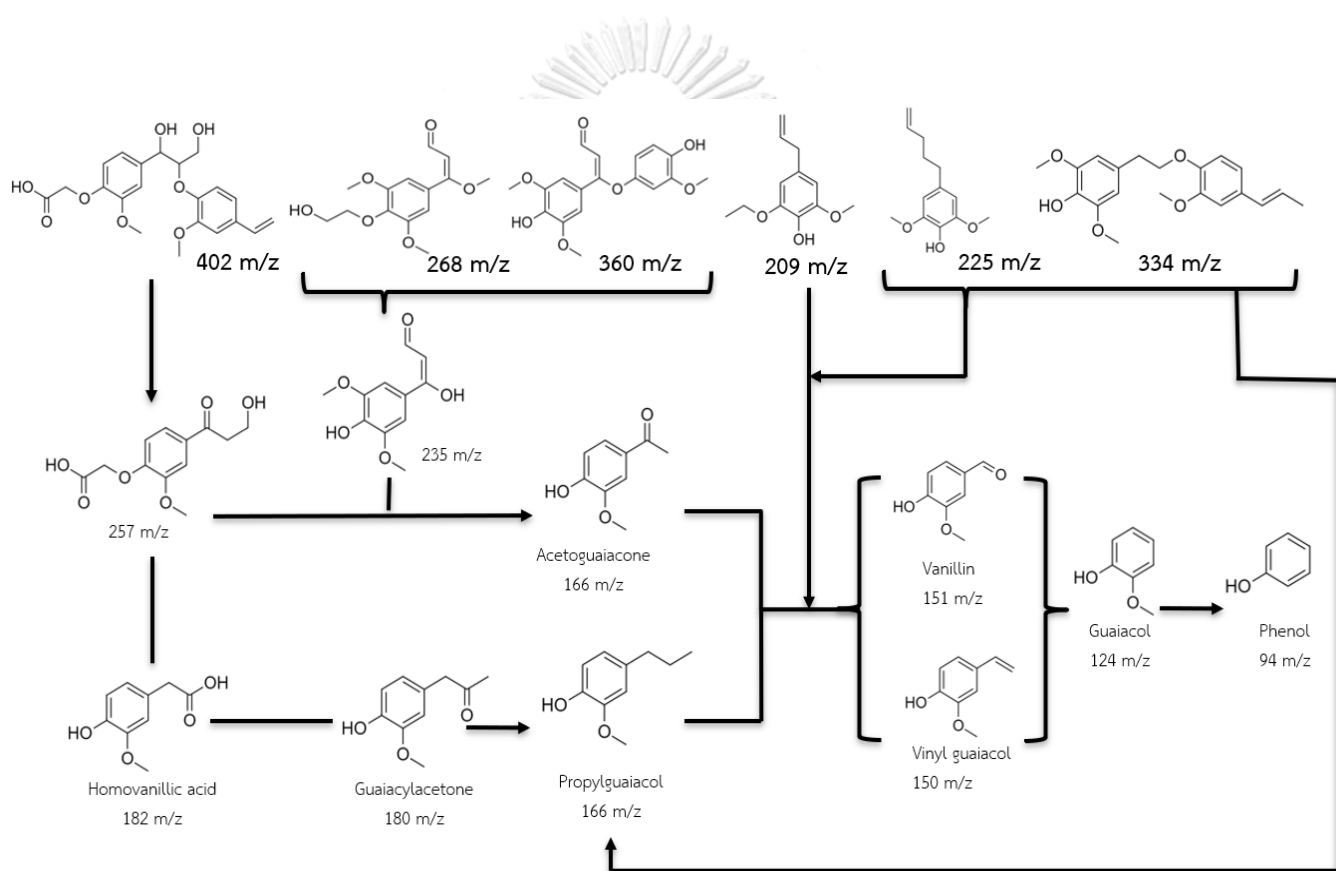


Figure 30 structure of lignin depolymerization intermediates and proposed depolymerization pathway of lignin in microreactor.

## CHAPTER 5

### CONCLUSION

#### 5.1 summary results

● The studied of current or current density. It was found that when the value increased it influenced the quantity of hydroxyl radical increased. Due to splitting of water with electrical, by check in the form of hydrogen peroxide in the outlet of products. The hydroxyl radical is strong oxidizing agent used to depolymerization of lignin. Found the oxidation products are (Z)-9-octadecenamide and propyl guaiacol, there is a tendency to increase as the current increases. On the other hand, at lower current and with quantity hydroxyl radical decreases, causing found the oxidation products are phenol, vanillin, vinyl guaiacol and homovanillic acid tend to increase. In other words, the increase and decrease of current is only suitable for certain products.

● The study of residence time is a time of solution is in the reactor that affects to depolymerization of lignin. By comparing the increase in residence time both of higher and lower current density. Found that when it reached 400 seconds, all oxidation products tended to decrease. Due to the longer time in the reactor, the solution can react with hydroxyl radical more than a few times, and hydroxyl radical can occur more than the low residence time.

● The factor of base condition. Found that the quantity of hydroxyl radical was decreased when compare the normal conditions. The product that occurs well in the base condition are (Z)-9-octadecenamide, propyl guaiacol, and guaiacylacetone. Including found new products are 1,3-dioxane, eugenol and catechol guaiacol, which tends to increase.



● The factor of different base sodium hydroxide and potassium hydroxide. found that the quantity of hydroxyl radical was decreased. which potassium hydroxide is less than sodium hydroxide. Depending on the current density and residence time. In the condition of sodium hydroxide as the current density and residence time increase, found the product occurs well of (Z)-9-octadecenamide as a major product and propyl guaiacol. On the other hand, when the current density and residence time decreases, found the product occur well of guaiacol, vinyl guaiacol, vanillin, acetoguaiacone, guaiacylacetone, homovanillic acid, and catechol guaiacol. In addition, the condition of potassium hydroxide as the current density and residence time increase, found the product occur well of (Z)-9-octadecenamide, vinyl guaiacol, propyl guaiacol, and guaiacylacetone. On the other hand, when the current density and residence time decreases, found the product occurs well of guaiacol, vanillin, acetoguaiacone, homovanillic, and catechol guaiacol. Except where both base conditions were current density and long residence time, found 1,3-Dioxane as the major product. In summary, both bases decreased the quantity of hydroxyl radical. But in the condition of potassium hydroxide gives a better product occurrence tendency than sodium hydroxide.

● The major of dimer product before the reaction with 402 m/z, and after the reaction the major product with 257 m/z. Other dimer products were also found, which made it possible to describe the pathway mechanism of the monomer from the dimer products. However, there are still larger structural products than dimers that cannot be identified. These products are expected to affect conversions.

## 5.2 Conclusion

The suitable condition to occurrence of phenolic compounds from depolymerization kraft lignin. As a result of smallest quantity of hydroxyl radicals. In this work is 9.7V of applied potential,  $3.7 \text{ A/m}^2$  and short residence time (in this work minimum residence time is 100s) in base condition of KOH.

Found 6 types of phenolic compounds such as Catechol guaiacol, Vinyl guaiacol, Vanillin, Propyl guaiacol, Guaiacylacetone, and Homovanilic acid. Which can be applied in many industries. Including (Z)-9-Octadecanamide still found, which can be another option for utilization in pharmaceutical industry.

## 5.3 Recommendations

The products utilization may require additional separation steps. Because different industries will take advantage of the product individually. which is usually in form of a solution.



## APPENDIX

## Calculation of surface area of electrode

Width (W)	=	0.01	m
Length (L)	=	0.027	m
Thickness of (H)	=	250	$\mu\text{m}$
Surface area of electrode (A)	=	$(W \times L)$	
	=	$(0.027 \times 0.01)$	
	=	$2.7 \times 10^{-4}$	$\text{m}^2$

## Calculation of flow rate and current density

Volume of the reactor (V)	=	$W \times L \times H$
	=	$0.027 \times 0.01 \times 250 \times 10^{-6}$
	=	$6.75 \times 10^{-8}$

Flow rate (F)	=	1	$\text{ml/h}$
	=	$2.77 \times 10^{-10}$	$\text{m}^3/\text{s}$

Residence time	=	$V/F$
	=	$6.75 \times 10^{-8} / 2.77 \times 10^{-10}$
	=	243.7 s

Current(I)	=	1.0	mA
Current density	=	$I/A$	
	=	$1.0 / 2.7 \times 10^{-4}$	
	=	3.70	$\text{A/m}^2$

$$\begin{aligned}
 \text{Current(I)} &= 1.5 \text{ mA} \\
 \text{Current density} &= I/A \\
 &= 1.5/2.7 \times 10^{-4} \\
 &= 5.55 \text{ A/m}^2
 \end{aligned}$$

Calculation 0.1 M of sodium hydroxide and potassium hydroxide.

sodium hydroxide (NaOH)

$$\begin{aligned}
 \text{Mol} &= (C \times V)/1000 \\
 \text{g/m} &= (C \times V)/1000 \\
 \text{g/40} &= [(0.1\text{M}) \times (50 \text{ mL})]/1000 \\
 \text{g} &= 0.2 \text{ gram} \\
 \text{but concentration 98 \%} \\
 \text{g} &= 0.2/0.98 \\
 \text{g} &= 0.204 \text{ gram in deionized water 50 mL}
 \end{aligned}$$

potassium hydroxide (KOH)

$$\begin{aligned}
 \text{Mol} &= (C \times V)/1000 \\
 \text{g/m} &= (C \times V)/1000 \\
 \text{g/56} &= [(0.1\text{M}) \times (50 \text{ mL})]/1000 \\
 \text{g} &= 0.28 \text{ gram}
 \end{aligned}$$

but concentration 86 %

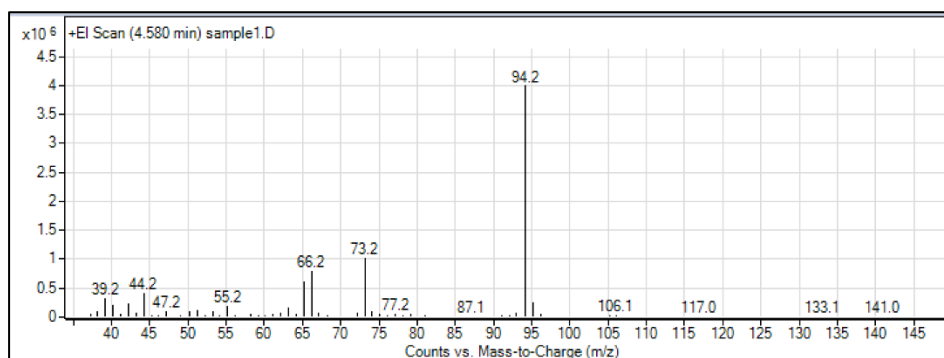
$$\text{g} = 0.28/0.86$$

$$\text{g} = 0.325 \text{ gram in deionized water 50 mL}$$

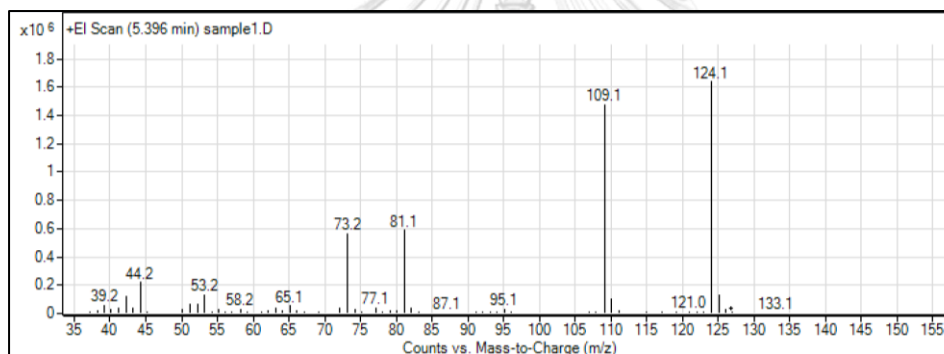
Data of mass spectrum for identified products.

Monomer products analytical by Gas chromatography with mass spectrometry.

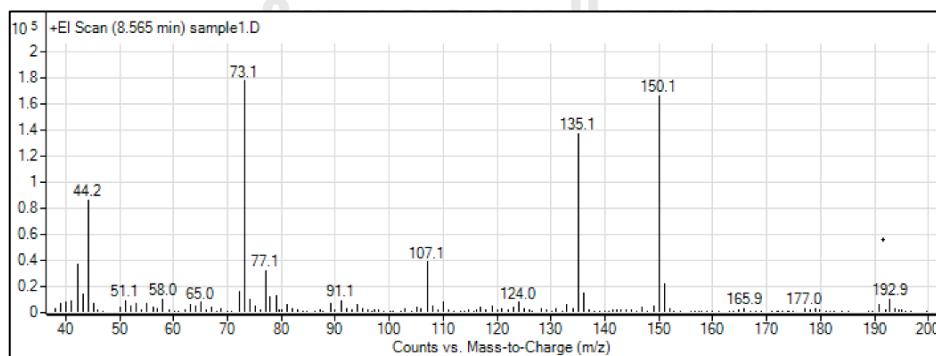
Mass spectrum of phenol.



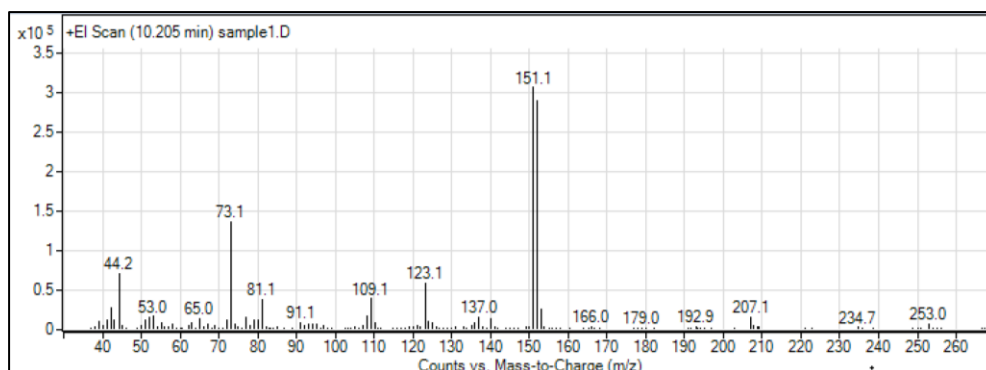
Mass spectrum of guaiacol.



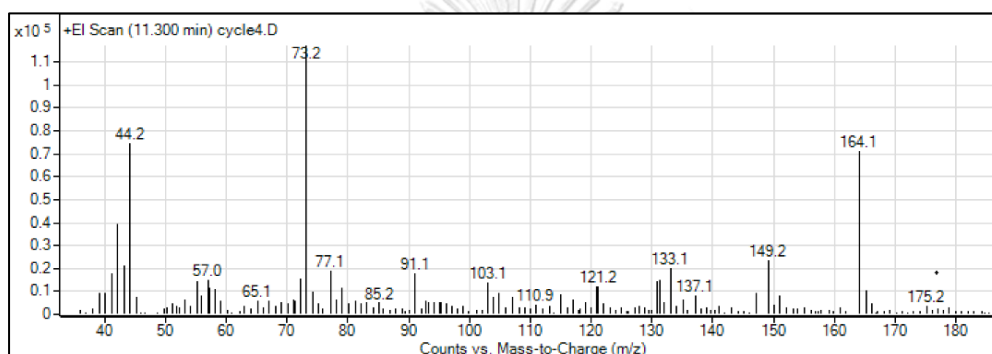
Mass spectrum of Vinyl guaiacol.



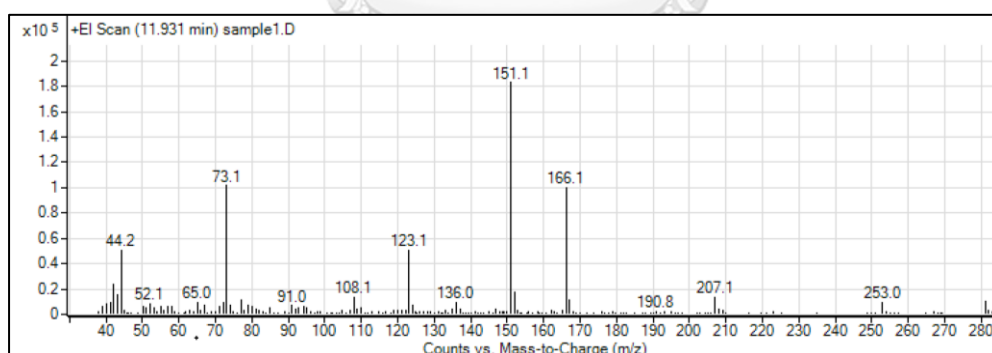
Mass spectrum of Vanillin.



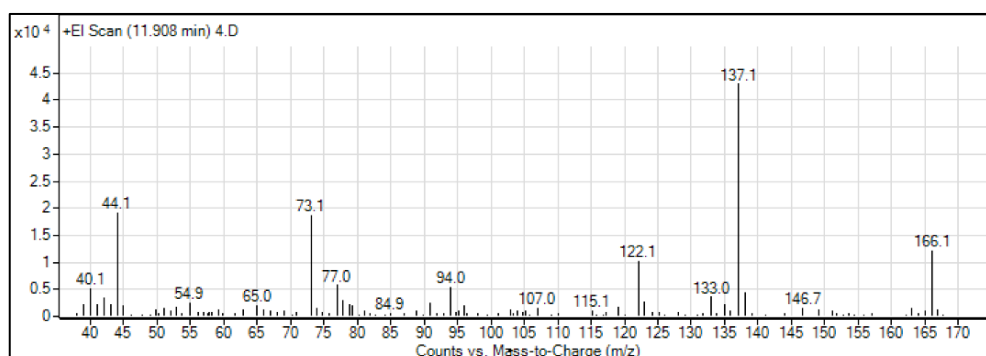
Mass spectrum of Eugenol.



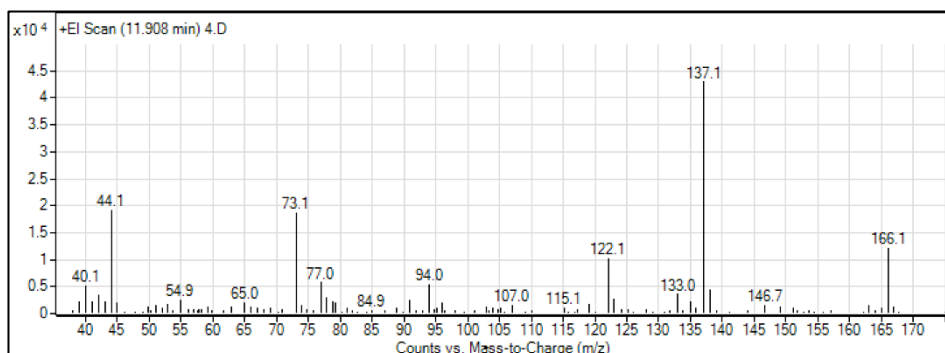
Mass spectrum of Acetoguaiacone.



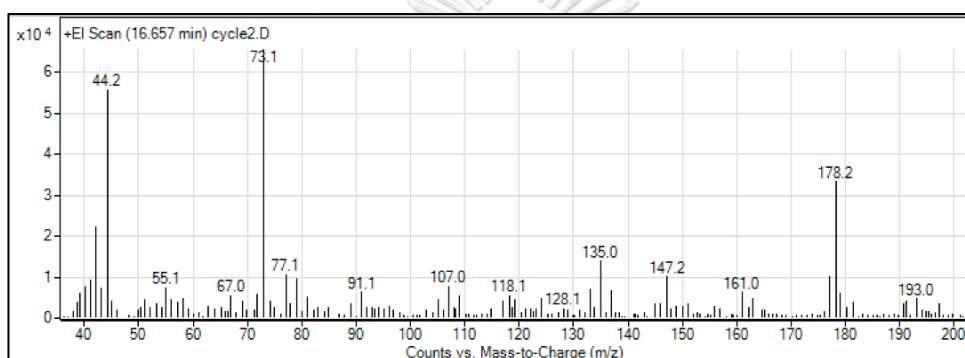
Mass spectrum of propylguaiaacol.



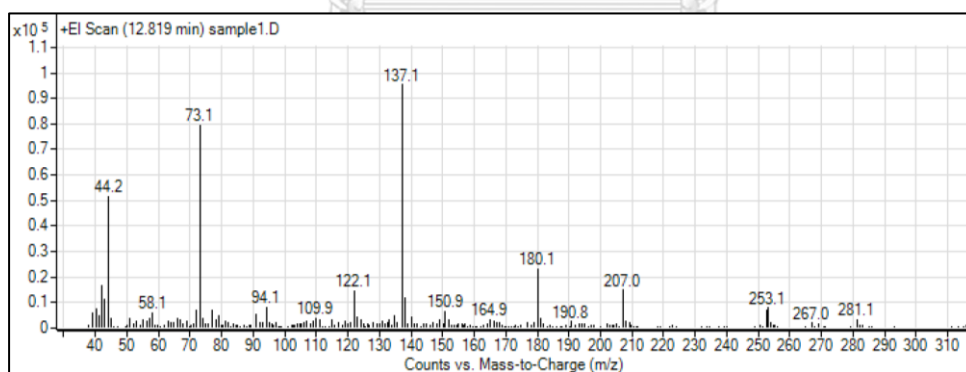
Mass spectrum of propylguaiacol.



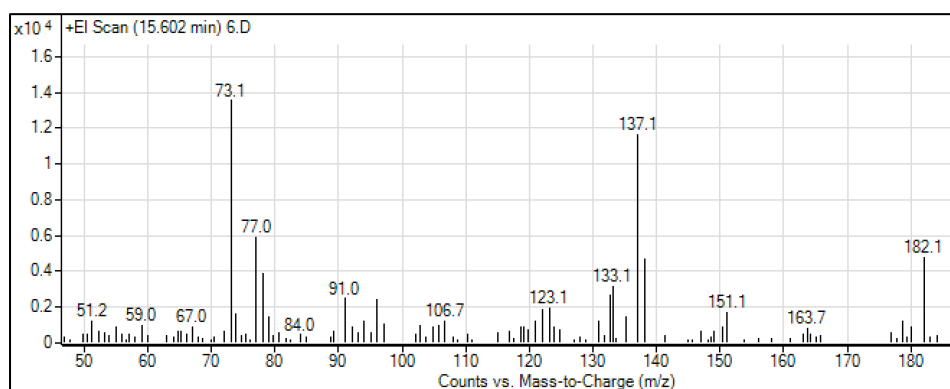
Mass spectrum of coniferyl aldehyde.



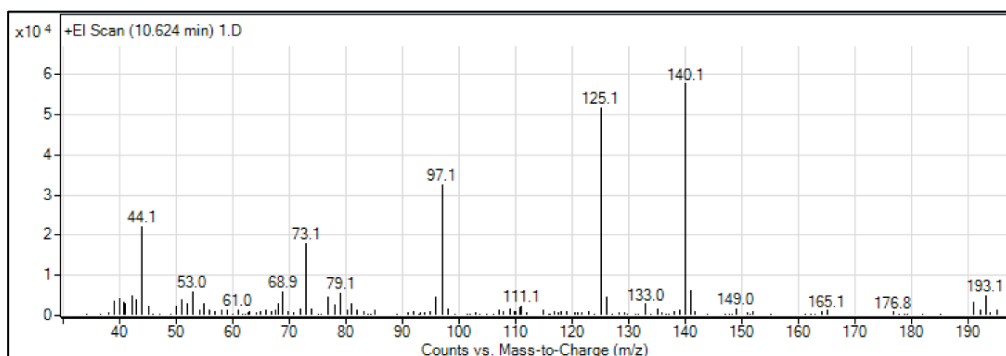
Mass spectrum of guaiacylacetone.



Mass spectrum of Homovanillic acid

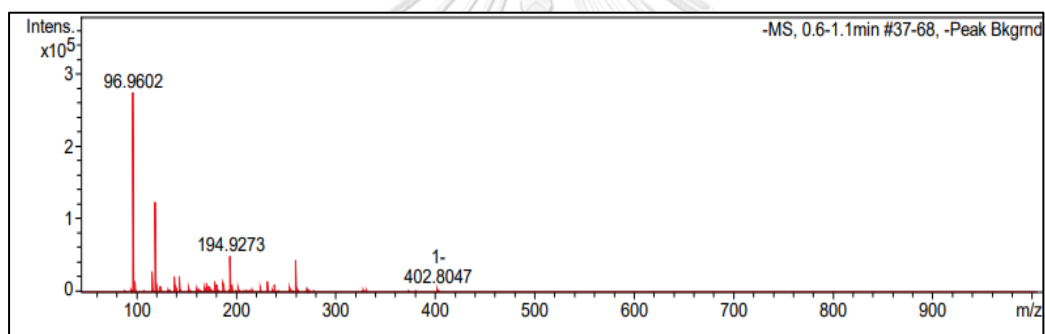


Mass spectrum of catechol guaiacol.

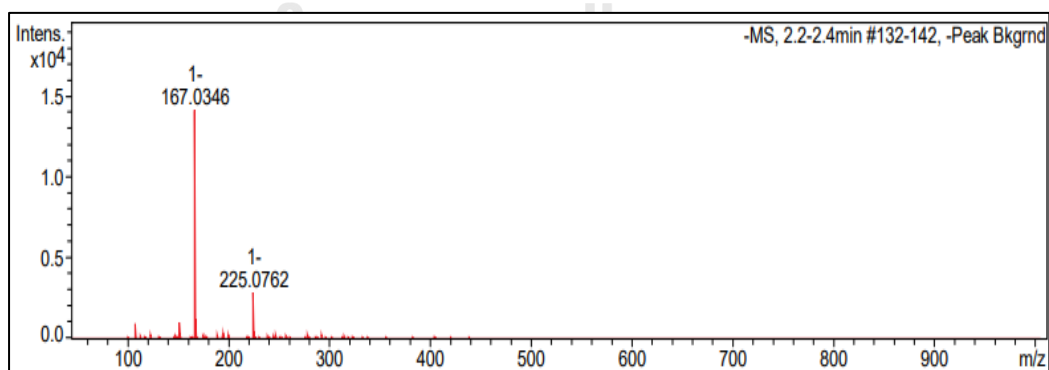


Dimer products analytical by Liquid chromatography with mass spectrometry.

402  $m/z$

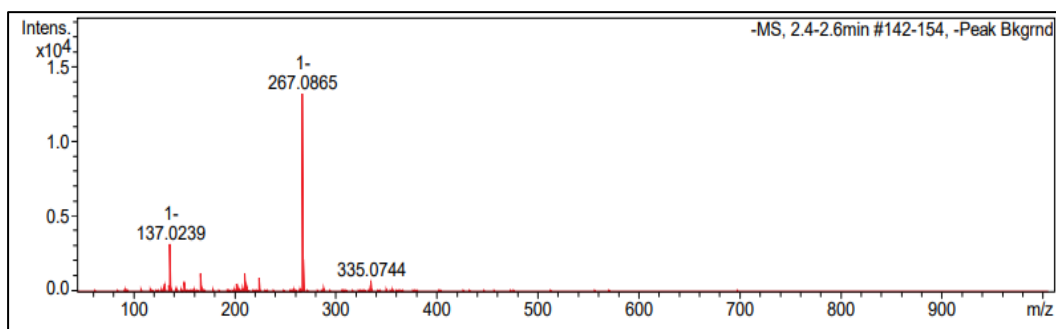


225  $m/z$

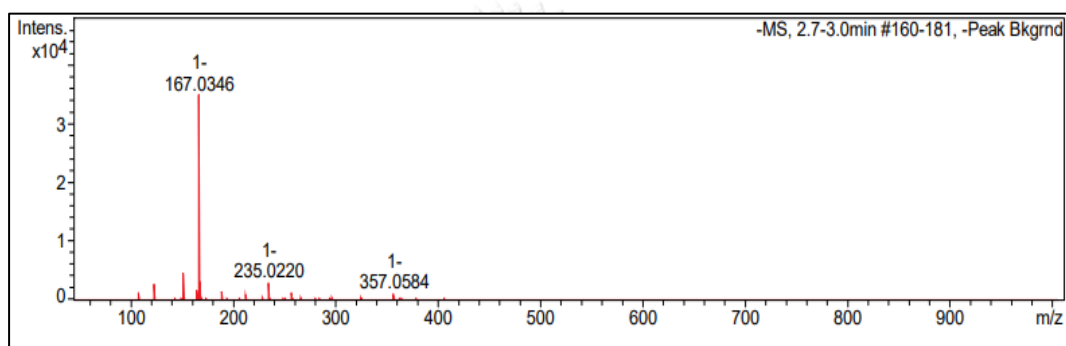




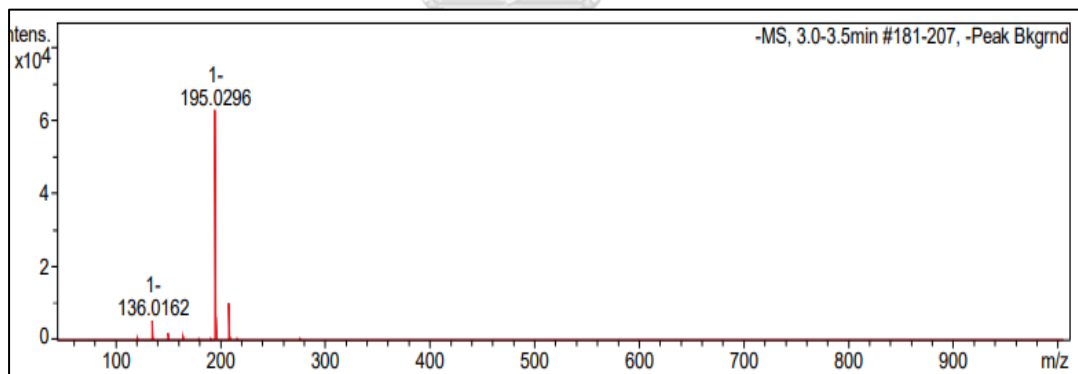
268 m/z



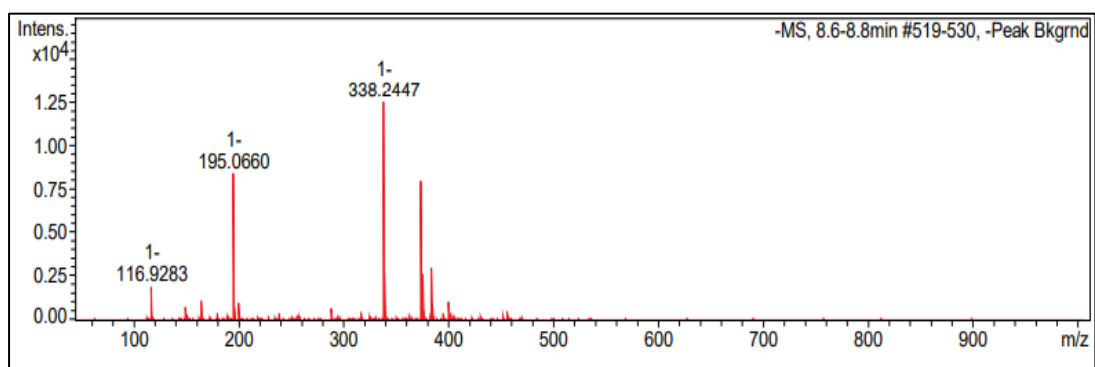
360 m/z



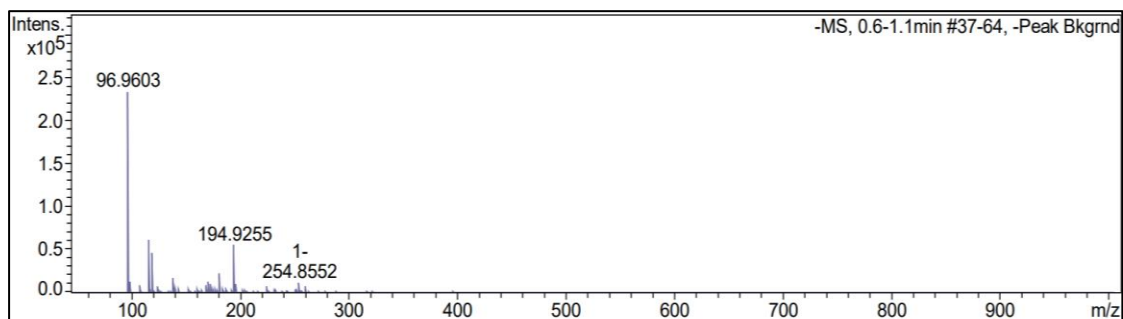
209 m/z



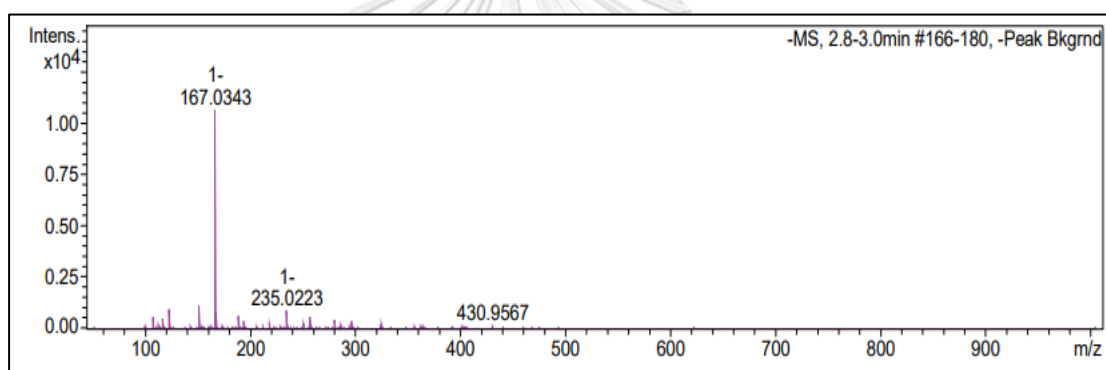
334 m/z



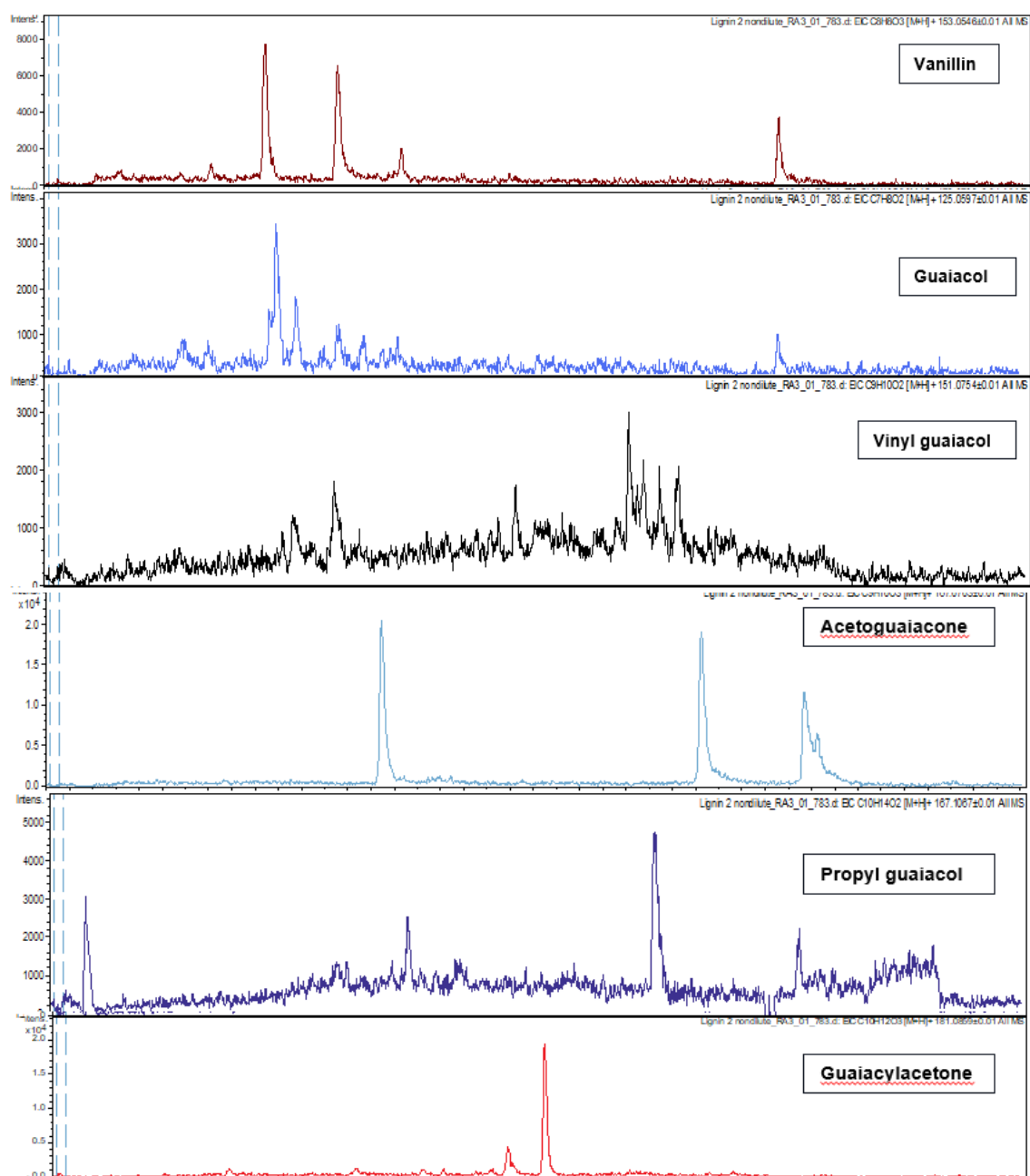
257 m/z

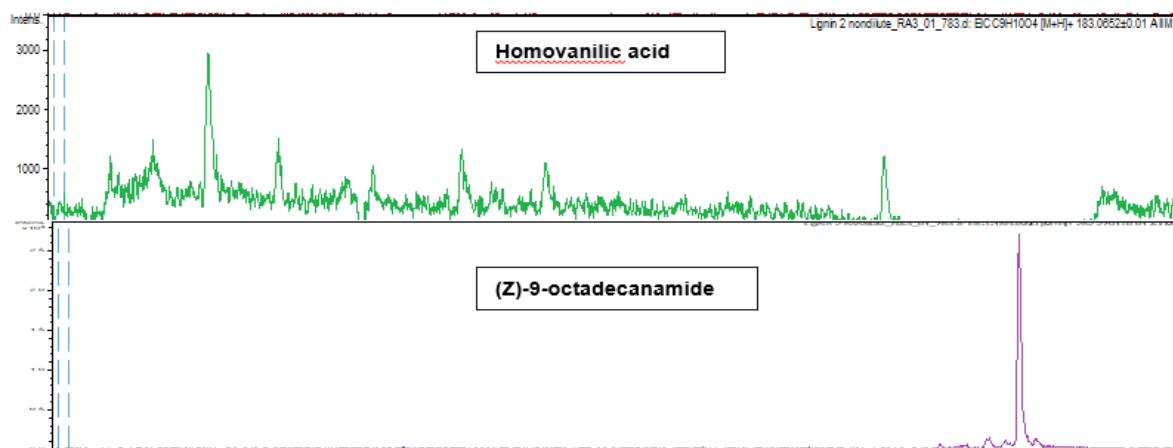


235 m/z

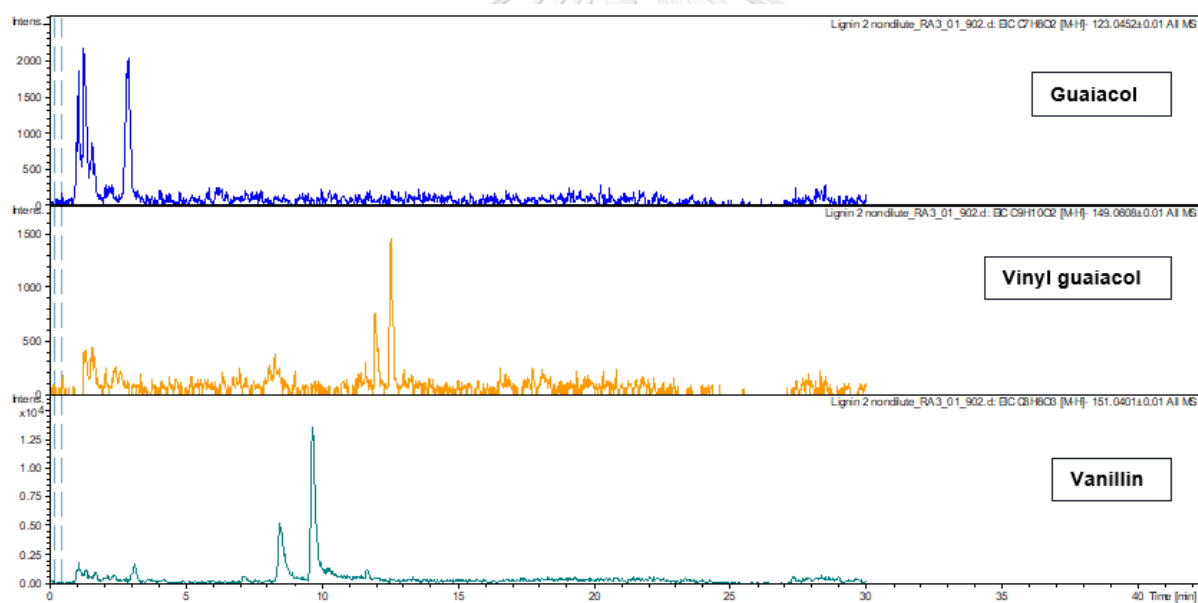


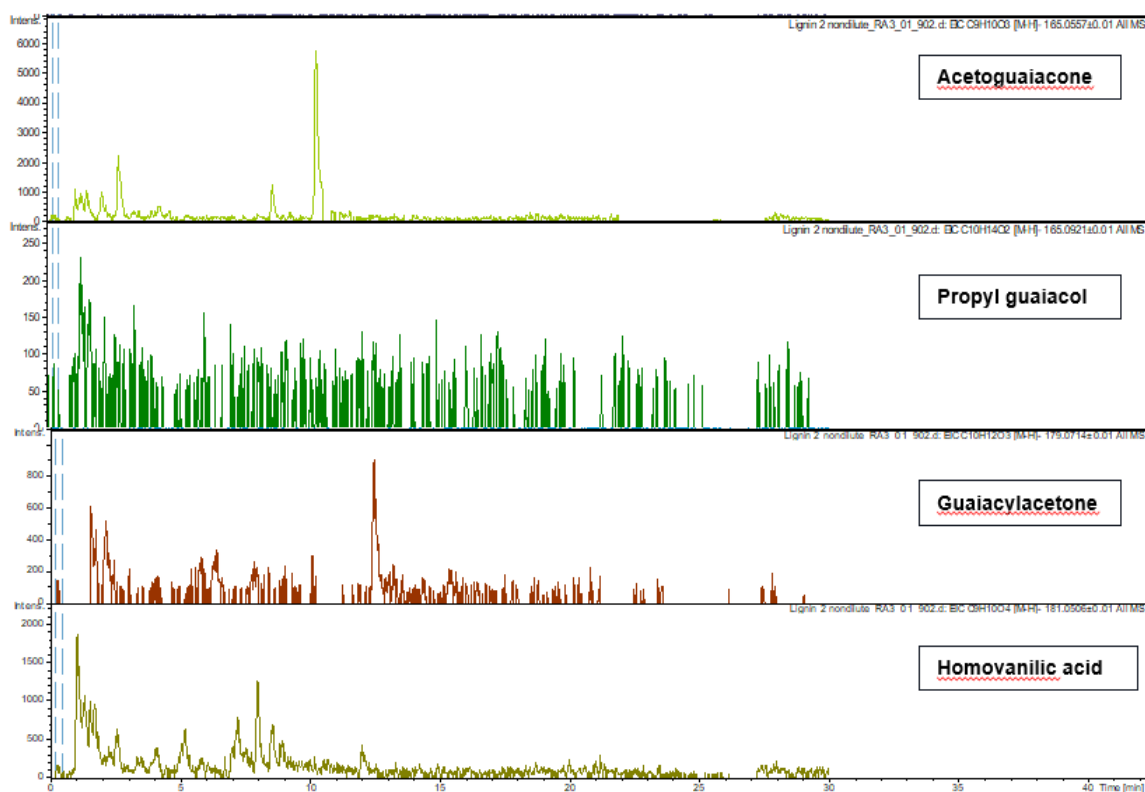
## Data of monomer products: analytical by EI scan with LC-MS

Positive mode (MS<sup>+</sup>)

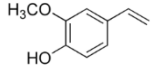
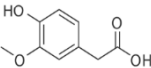
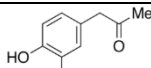
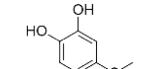


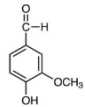
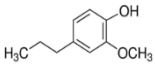
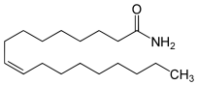
Negative mode (MS-)





Application for useful chemical.

Identified products	Application
 <p><b>Vinyguaiacol</b></p>	Often used in the pharmaceutical industry. Has properties to reduce inflammation.
 <p><b>Homovanillic acid</b></p>	Often used in the medicine as a reagent to detect oxidative enzymes and is associated with dopamine levels in the brain.
 <p><b>Guaiacylacetone</b></p>	Often used in the chemical industry as a solvent for various substances.
 <p><b>Catechol guaiacol</b></p>	Often used in the pharmaceutical and food industry as a precursor to various sweeteners.

 <p><b>Vanillin</b></p>	Often used in the food industry as a flavoring agent in food.
 <p><b>Propylguaiacol</b></p>	Often used in the agricultural industry as a beneficial for plants to protect against bacteria.
 <p><b>(Z)-9-Octadecanamide</b></p>	Often used in the pharmaceutical industry as an ingredient in sleeping pills for humans.



## REFERENCES

1. Gomes, E.D. and A.E. Rodrigues, *Recovery of vanillin from kraft lignin depolymerization with water as desorption eluent*. Separation and Purification Technology, 2020. **239**.
2. Paananen, H., et al., *Base-catalyzed oxidative depolymerization of softwood kraft lignin*. Industrial Crops and Products, 2020. **152**.
3. Rana, M., et al., *Effects of Temperature and Salt Catalysts on Depolymerization of Kraft Lignin to Aromatic Phenolic Compounds*. Energy & Fuels, 2019. **33**(7): p. 6390-6404.
4. Movil-Cabrera, O., et al., *Electrochemical conversion of lignin to useful chemicals*. Biomass and Bioenergy, 2016. **88**: p. 89-96.
5. Roberts, V.M., et al., *Towards quantitative catalytic lignin depolymerization*. Chemistry, 2011. **17**(21): p. 5939-48.
6. Elumalai, P., et al., *Testing Metal–Organic Framework Catalysts in a Microreactor for Ethyl Paraoxon Hydrolysis*. Catalysts, 2020. **10**(10).
7. Laurichesse, S. and L. Avérous, *Chemical modification of lignins: Towards biobased polymers*. Progress in Polymer Science, 2014. **39**(7): p. 1266-1290.
8. Prothmann, J., et al., *Identification of lignin oligomers in Kraft lignin using ultra-high-performance liquid chromatography/high-resolution multiple-stage tandem mass spectrometry (UHPLC/HRMS(n))*. Anal Bioanal Chem, 2018. **410**(29): p. 7803-7814.
9. Liu, C., et al., *Catalytic oxidation of lignin to valuable biomass-based platform chemicals: A review*. Fuel Processing Technology, 2019. **191**: p. 181-201.
10. Malik, S.N., et al., *Pretreatment of yard waste using advanced oxidation processes for enhanced biogas production*. Biomass and Bioenergy, 2020. **142**.
11. Song, Y., et al., *Integrated individually electrochemical array for simultaneously detecting multiple Alzheimer's biomarkers*. Biosens Bioelectron, 2020. **162**: p. 112253.
12. Brebu, M. and I. Spiridon, *Co-pyrolysis of LignoBoost® lignin with synthetic*

- polymers. *Polymer Degradation and Stability*, 2012. **97**(11): p. 2104-2109.
13. Jiang, W., et al., *Near-critical water hydrothermal transformation of industrial lignins to high value phenolics*. *Journal of Analytical and Applied Pyrolysis*, 2016. **120**: p. 297-303.
  14. Ma, R., M. Guo, and X. Zhang, *Recent advances in oxidative valorization of lignin*. *Catalysis Today*, 2018. **302**: p. 50-60.
  15. Kumar, A., et al., *Effect of hydrogen peroxide on the depolymerization of prot lignin*. *Industrial Crops and Products*, 2020. **150**.
  16. Schutyser, W., et al., *Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading*. *Chem Soc Rev*, 2018. **47**(3): p. 852-908.
  17. Luo, Z., et al., *Liquefaction and Hydrodeoxygenation of Polymeric Lignin Using a Hierarchical Ni Microreactor Catalyst*. *ACS Sustainable Chemistry & Engineering*, 2019. **8**(5): p. 2158-2166.
  18. Liu, S., et al., *Selective depolymerization of liginosulfonate via hydrogen transfer enhanced in an emulsion microreactor*. *Bioresour Technol*, 2018. **264**: p. 382-386.
  19. Hou, Y., et al., *Feasibility of monomer aromatic substances as calibration standards for lignin quantitative analyses in Pyrolysis-GCMS*. *Journal of Analytical and Applied Pyrolysis*, 2013. **101**: p. 232-237.
  20. Ouyang, X.-p., Y.-d. Tan, and X.-q. Qiu, *Oxidative degradation of lignin for producing monophenolic compounds*. *Journal of Fuel Chemistry and Technology*, 2014. **42**(6): p. 677-682.



## VITA

NAME	chawakorn rittirong
DATE OF BIRTH	18 Nov 1996
PLACE OF BIRTH	Lopburi Thailand

