CATALYTIC CONVERSION OF CHITIN TO LACTIC ACID IN HOT-COMPRESSED WATER

Miss Kodchakon Kun-asa

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Chemical Technology
Department of Chemical Technology
FACULTY OF SCIENCE
Chulalongkorn University
Academic Year 2020

การเปลี่ยนไคตินเป็นกรดแลกติกโดยใช้ตัวเร่งปฏิกิริยาในน้ำร้อนอัดความดัน

น.ส.กชกร ขันอาสา

Thesis Title	CATALYTIC CONVERSION OF CHITIN TO LACTIC ACID IN HOT-COMPRESSED WATER
By	Miss Kodchakon Kun-asa
Field of Study	Chemical Technology
Thesis Advisor	Associate Professor PRASERT REUBROYCHAROEN, Ph.D.
Thesis Co Advisor	Aritomo Yamaguchi, Ph.D.

Accepted by the FACULTY OF SCIENCE, Chulalongkorn University in Partial Fulfillment of the Requirement for the Doctor of Philosophy

.... Dean of the FACULTY OF SCIENCE

(Professor POLKIT SANGVANICH, Ph.D.)

DISSERTATION COMMITTEE

.... Chairman

(Associate Professor PRAPAN KUCHONTHARA, Ph.D.)

.... Thesis Advisor

(Associate Professor PRASERT REUBROYCHAROEN, Ph.D.)

.... Thesis Co-Advisor

(Aritomo Yamaguchi, Ph.D.)

.... Examiner

(Professor THARAPONG VITIDSANT, Ph.D.)

.... Examiner

(Professor NAPIDA HINCHIRANAN, Ph.D.)

.... External Examiner

(Associate Professor Chanatip Samart, Ph.D.)

กชกร ขันอาสา : การเปลี่ยนไคตินเป็นกรดแลกติกโดยใช้ตัวเร่งปฏิกิริยาในน้ำร้อนอัดความดัน. (CATALYTIC CONVERSION OF CHITIN TO LACTIC ACID IN HOT-COMPRESSED WATER) อ.ที่ปรึกษาหลัก : รศ. ดร.ประเสริฐ เรียบร้อยเจริญ, อ.ที่ปรึกษาร่วม : ดร.อะริโตโมะ ยามากูชิ

ไคตินคือไบโอโพลีเมอร์ที่พบมากเป็นอันดับสองรองจากเซลลูโลสซึ่งพบมากในส่วนประกอบของสัตว์สัตว์ที่มีเปลือกแข็ง ไคตินหรือ *N*-acetyl-D-glucosamine ซึ่งเป็นโมโนเมอร์หลักของไคตินสามารถที่จะเกิดปฏิกิริยาการเปลี่ยนแปลงไปสู่สารเคมีที่มีมูลค่ามากขึ้นโดยใช้ตัวเร่งปฏิกิริยาเอกพันธ์ โดยทั่วไปไคตินจะถูกผลิตขึ้นในอุตสาหกรรมอาหารและทำการปรับสมดุลและกลายเป็นขยะในอุตสาหกรรม ซึ่งการเปลี่ยนแปลงของไคตินเป็นสารเคมีที่มีมูลค่ายังมีการศึกษาที่น้อยเมื่อเทียบกับเซลลูโลส ดังนั้นในงานวิจัยนี้ได้ทำการศึกษาการเปลี่ยนแปลงของไคติน ซึ่งผลการศึกษาได้แบ่งออกเป็น 4 ส่วน โดยในส่วนแรกพบว่าการปรับสภาพด้วยวิธีการบดละเอียดสามารถที่จะเพิ่มการเปลี่ยนแปลงของไคติน ซึ่งความเป็นผลึกในโครงสร้างของไคตินลดลงเนื่องจากการปรับสภาพโดยการบดละเอียดซึ่งส่งผลให้การเปลี่ยนแปลงของไคตินเพิ่มมากขึ้น ในส่วนที่สองการใช้น้ำร้อนอัดความดันโดยไม่ใช้ตัวเร่งปฏิกิริยาสามารถเพิ่มการเปลี่ยนแปลงของไคตินแต่ผลิตภัณฑ์ไม่มีความจำเพาะเจาะจงที่กรดแลกติค ในส่วนที่สามได้ทำการศึกษาผลของโลหะออกไซด์ในการเปลี่ยนของไคตินเป็นกรดแลคติค โดยผลการศึกษาพบว่าตัวเร่งปฏิกิริยาแมกนีเซียมออกไซด์ให้ร้อยละผลได้ของกรดแลกติคสูงที่สุด คือ 10.8 % ซึ่งสภาวะที่มีความเหมาะสมในการเปลี่ยนแปลงของไคตินคือ อุณหภูมิในการทำปฏิกิริยา 533 เคลวิน เวลาในการทำปฏิกิริยาคือ 6 ชั่วโมง และปริมาณของตัวเร่งปฏิกิริยาแมกนีเซียมออกไซด์ร้อยละโดยมวล 1 % ในส่วนสุดท้ายได้มีการศึกษากลไกการเกิดปฏิกิริยา ซึ่งพบว่าคุณสมบัติความเป็นเบสของตัวเร่งปฏิกิริยามีความสำคัญต่อการเปลี่ยนแปลงของไคติน นอกจากนี้ตัวเร่งปฏิกิริยาแมกนีเซียมออกไซด์สามารถที่จะนำมาใช้ใหม่ได้ถึง 2 ครั้ง โดยร้อยละผลได้ของกรดแลกติคไม่เปลี่ยนแปลง

สาขาวิชา	เคมีเทคนิค	ลายมือชื่อนิสิต	....
ปีการศึกษา	2563	ลายมือชื่อ อ.ที่ปรึกษาหลัก	....
		ลายมือชื่อ อ.ที่ปรึกษาร่วม	....

iv

6072837523 : MAJOR CHEMICAL TECHNOLOGY

KEYWORD: Chitin Magnesium oxide Lactic acid

Kodchakon Kun-asa : CATALYTIC CONVERSION OF CHITIN TO LACTIC ACID IN HOT-COMPRESSED WATER. Advisor: Assoc. Prof. PRASERT REUBROYCHAROEN, Ph.D. Co-advisor: Aritomo Yamaguchi, Ph.D.

Chitin is the second most available polysaccharide after cellulose. Chitin and *N*-acetyl-D-glucosamine polysaccharide, can be converted to valuable products by using homogeneous catalysis, most of the chitin generated by food processing is treated as industrial waste. For chitin conversion to useful chemicals has been investigated less than cellulose conversion. Therefore, in this research, chitin conversion was investigated. The result was divided into four part. The first part, the result showed that ball milled pretreatment could increase the conversion of chitin, which indicated that the crystallinity of the chitin had been reduced by the ball milled pretreatment. In the second part, hot compressed water for chitin conversion without catalyst could be converted to other chemicals, but the product not selective with lactic acid. Moreover, the effect of metal oxides was studied on chitin conversion into lactic acid. The result showed that MgO gave the high yield of lactic acid. 10.8 % yield of lactic acid was obtained by using MgO. The optimal condition for chitin conversion was 533 K reaction temperature 6 h reaction time and amount of MgO 1%wt. In the final part, the reaction mechanism was investigated. The base site of the catalyst played an important role in chitin conversion. The MgO catalyst could be recovered after the reaction and reused twice with no decrease in the lactic acid yield.

Field of Study:	Chemical Technology	Student's Signature	....
Academic Year:	2020	Advisor's Signature	....
		Co-advisor's Signature	....

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

LIST OF FIGURE

LIST OF TABLE

CHAPTER I

GENERAL BACKGROUND

1.1 Introduction

Biomass comes from plants and animals that is important option for replacing fossil fuels. Most of the food is biomass such as rice, wheat, and also meat. It is abundant cheap and widely available in the world. Biomass could be used to produce electricity, heat, and valuable chemicals. However, biomass is one of the food. It is important to allow using of edible biomass for production of energy or valuable chemicals. Cellulose is most polysaccharide in the world that has been reported considerably to be converted to valuable products and fuel has been extensively studied [1-9]. Polysaccharide is monomer is found in chitin in second

most after cellulose, and it is the main component of crustacean shells, such as fungi, algae cell walls, insects' exoskeletons, and crustaceans' shells.[10, 11]

"Shell biorefinery" is the idea that has been suggested in transformation of chitin biomass into valuable chemicals. [12, 13] Nitrogen-containing chemicals were produced from chitin and derivatives such as *N*-acetyl-D-glucosamine and D-Glucosamine.by many methods which, was developed by researchers [14-17]. In addition, cellulose was used to produce non-nitrogen valuable chemicals such as 5-hydroxymethylfurfural (5-HMF) and levulinic acid which, it was also produced from chitin. Specifically, 5- HMF and levulinic acid could produce from chitosan by using microwaving in an aqueous solution [17]. Coversion of chitin-derived to 5-HMF was studied to increase 5-HMF yield by using iron chloride [18], and ionic liquid [19]. Moreover, Zirconium oxychloride and ionic liquid were used in the conversion of chitin to produce levulinic acid by using sulfuric acid catalyst [20-22]. Homogeneous catalysts are needed to use in the processes. Although, the problem of homogeneous catalysts were recyclability and separation of catalyst from all product, so the research of heterogeneous catalysts requires more studying.

Lactic acid is an important valuable chemicals from biomass because it is wildly used in many industries such as food, chemical industries, cosmetic, pharmaceutical, polylactic acid production. [23] Moreover, the conversion of chemicals such as acrylic acid and propylene glycol was produced from lactic acid [24, 25]. Normally, saccharification-fermentation process is used to produce lactic

acid from polysaccharides in biomass such as starch and cellulose. [26] In present, the demand of lactic acid is increasing. [27] The requirement of purification and neutralization of product in pH around 5 – 7 need to use in this process, and starting material in this process is edible carbohydrates, and also production rate is low which is some disadvantage of the fermentation process. [27]

On the other hand, homogeneous catalysts were used for the conversion of chitin such as H_2SO_4 and HCl [28]. The problem of homogeneous catalysts is difficulties to separation from product and also hard to recycle. Heterogeneous catalysts are highly to choose for conversion of chitin by reason of easy to separate from product. Although, heterogeneous catalysts are still a little attention from researchers. In this research, I studied the conversion of chitin into lactic acid by using metal oxides. Chitin conversion into lactic acid in this research used metal oxide to increase chitin conversion. In my hypothesis chitin could be converted to lactic acid which this chemicals is importance starting material especially for polylactic acid production [29]. In addition, other chemicals could be converted from chitin such as propylene glycol and acrylic acid [30]. Previously lactic acid production was reported that ZrO^{2-} show good activity for cellulose conversion [31]. However, lactic acid from chitin conversion never been reported. In this work, conversion of chitin into lactic acid and simple metal oxides catalysis using were investigated. The result showed that the best performance of metal oxide is MgO. This metal oxide

able to produce high yield lactic acid and also reused the catalyst two times by activity was not change [32].

1.2 Scope of this work

In this work, chitin conversion was investigated to produce lactic acid. The effect of reaction temperature, reaction time amount of catalyst, and type of metal oxide were investigated. Many metal oxides were used in reaction to increase chitin conversion into lactic acid. This research work was scope as follows:

1) To study the effect of the difference of metal oxides on chitin conversion

2) To study reaction parameters of conversion of chitin to lactic acid.

3) To study the effect of the difference of metal oxides.

4) To study catalytic performance of the difference of the grades of magnesium oxide.

5) To understand the properties of magnesium oxide into chitin conversion to lactic acid yield.

6) To understand the reaction pathway of chitin conversion into lactic acid.

7) To understand the role of acid and base to chitin conversion.

1.3 Objectives

1) To find the optimal condition for chitin conversion into lactic acid using hot compressed water

2) To find simple metal oxides to obtain the high yield of lactic acid from chitin conversion.

3) To understand the effect of metal oxides properties on conversion of chitin using hot compressed water.

4) To propose the reaction mechanism of chitin conversion to lactic acid

CHAPTER II
THEORY AND LITERATORE REVIEWS
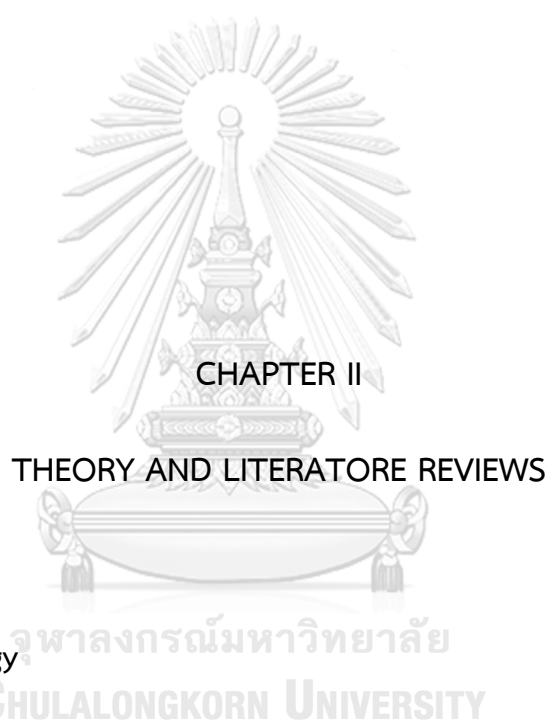
2.1 Renewable energy

Renewable energy is energy that can be produce from plants, sunlight, and wind, etc. Nevertheless, whether and time are factor to their ability. New technology is produced in order to using renewable energy, for example, heating, lighting, and etc. Researchers try to develop renewable energy to sustainable energy and replaced dirty energy sources such as fracked gas and coal. However, biomass investigation for using to be renewable energy must be carefully established because of some material is edible biomass [33-35].

2.2 Biomass

Organic material is the main component in biomass that find in waste wood plants, animals, crops, and trees. The heat from burning biomass is released from the chemical energy and could be generated to electricity by using the steam turbine. This material from plants or animals such as wood chips and agricultural waste could be used to produce electricity [36-38]. This includes sources such as crops, wood, and other biodegradable leftovers found in all communities. Moreover, Biomass can be converted to biofuel by many methods such as thermal, chemical, and biochemical methods [39, 40]. The burning of biomass also generates such as carbon dioxide and carbon monoxide to the atmosphere [41]. The pollution from biomass combustion has higher than burning coal. However, biomass is a new energy source in the world because biomass is abundant, cheap and it has widespread worldwide availability. Chemical products. Lignocellulose is one of the plant fibers these materials have been widely investigated [42]. However, chitin is animal fiber cloud be found in second biopolymer still less attention in the present research. The structure of chitin in shrimp shell was shown in **Figure 2.1**
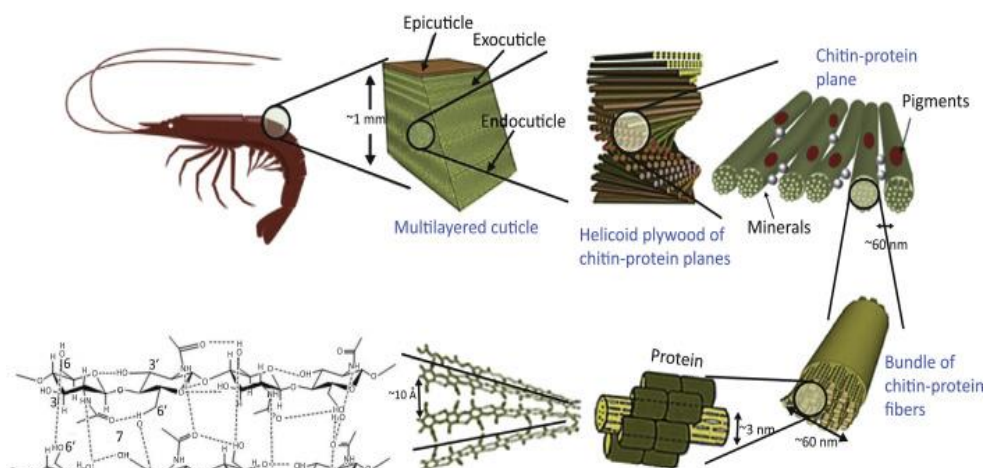
Figure 2.1 The composition and structure of chitin in shrimp shell [43].

2.1.1. The processing for biomass conversion

Pathway for biomass conversion to produce renewable energy sources has many routes such as biochemical processing, hydrothermal processing, aqueous phase processing and thermal processing. Thermal processing is process for production of fuels while aqueous phase processing is effective to produce high valuable chemical products. Moreover, both processing chemical and biochemical processing is also a route for the conversion of biomass. The intermediate substances can be subsequently upgraded to high value-added chemicals and fuels for the transportation sector. Overview of biomass conversion showed in **Figure 2.2**
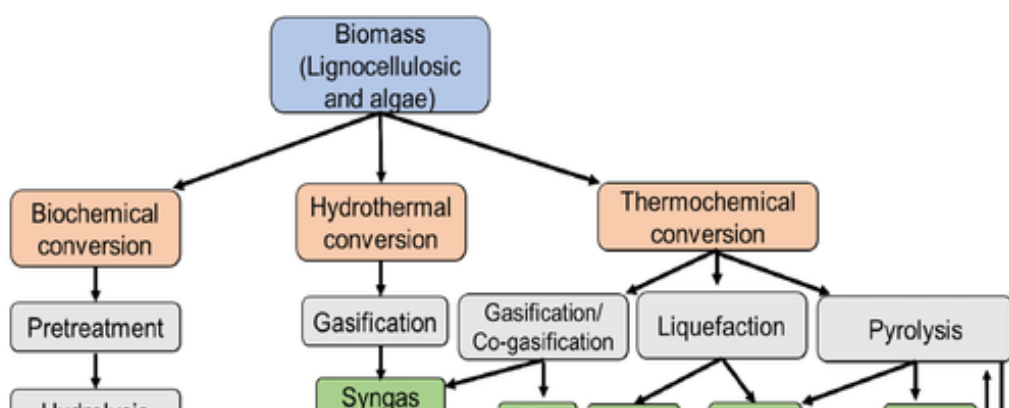
Figure 2.2 Overview of biomass conversion [44]

2.1.1. Thermochemical conversion

Three pathways (combustion, gasification, and pyrolysis) are thermochemical conversion of biomass [45-47].

1. Pyrolysis

Thermal and chemical decomposition of biomass is called pyrolysis which, No addition of oxygen gas to produce bio oil. Fuels such as charcoal, bio-oil, diesel, methane, and hydrogen are produced from the pyrolysis of biomass. Various lengths hydrocarbons are produced from pyrolysis, but the product give more oxygenated compound than the product from petroleum. Bio-oil from pyrolysis has to upgrade quality before use to be fuel [48]. The bio-oil from pyrolysis comes from organic material is heated in a non-oxygen atmosphere condition. The reaction temperature ie used to decompose the biomass in the range of 400 - 800 ℃ in the absence of

oxygen [49, 50]. Smaller molecules in the gas products, vapors, and solid charcoal all of product are broken down from the hydrogen, organic carbon, and oxygen compounds [51]. Product and rate of decomposition depend on many factors including type of reactor, heating rate, pressure, feedstock etc [52]. Biochar is main product when using low temperatures less than 450 ^{0}C. When using slow heating rate, the main product is gases. At rapid heating rates and a high temperature more than 800 ^{0}C, the main product is bio-oil [49].

2. Hydrothermal Liquefaction

One of the decomposition process is hydrothermal Liquefaction that undergoes a wet feedstock. Conditions are used slurry under temperature 300-400 °C and pressure around 10-25 MPa. The produce from this process is liquefaction bio-oil. Starting material is treated by water before use in this process. Some the water was used to treat starting material before used in the reaction and non-water solvents may also be entering to reactor [53]. The main composition of hydrothermal liquefaction is bio-oil and, gaseous, aqueous, and solid phase are by-products [54].

3. Gasification

Gasification is the thermal decomposition process at high temperature in air or an oxygen and sometimes steam [55]. Syngas is generated from gasification but

not only syngas also other valuable chemicals such as fatty acids, methane, ethylene

and detergents. [56-59]. Gasification process show in **Figure 2.3**

Synthesis gas consisting of CO, H_2 and CH_4 is valuable gas could be produced

from gasification process which is the partial oxidation of biomass [60]. To increase

amount of H_2, steam gasification is developed. Co-reactive agent is added to increase

char [61, 62]. Particle size, moisture content, heating value, carbon content and ash

content are parameter effect to gasification process.[63].
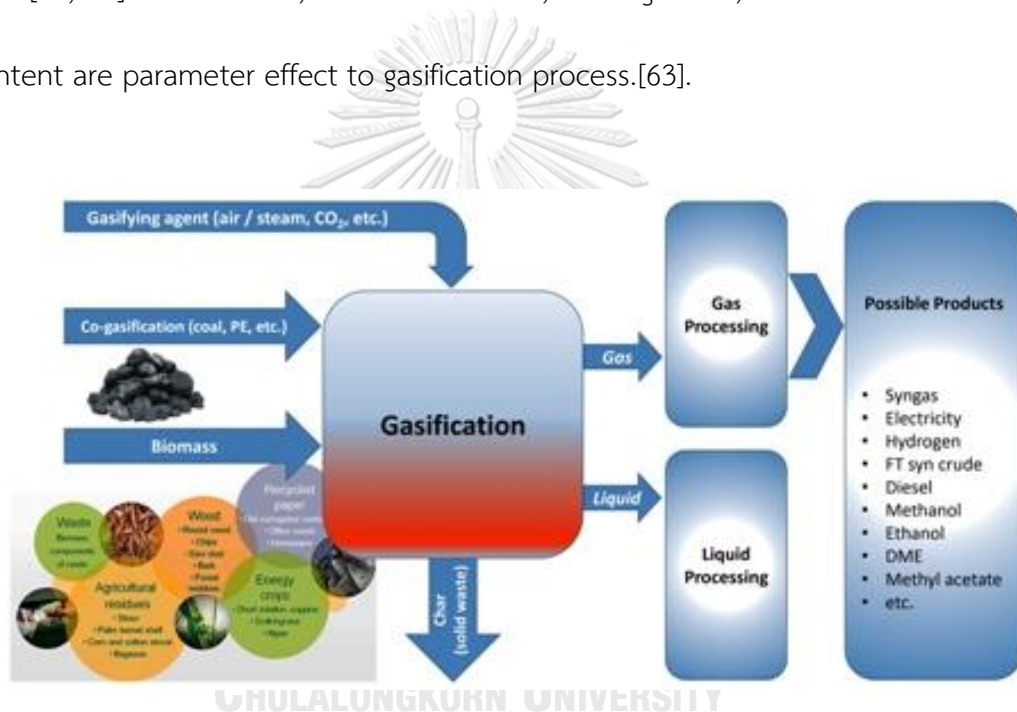
Figure 2.3 Overview of gasification process [64]

4. Combustion

Combustion process is one method for biomass conversion. Burning wood

and agricultural residues are method for combustion process in order to obtain heat

and light. Normally, conversion of lignin is used combustion method [65, 66].

Comparing combustion process with other process, the combustion is low selectivity

process. The main composition of combustion process is water and CO_2 which amount of product and by-product depend on starting material and process parameter. Inorganic in biomass is one importance factor to design the system. Amount of volatile matter are found in the combustion process more than fossil which, volatile in the process influence to decomposition of biomass effect to occurring of char in the process [67].

2.1.2 Biochemical conversion

Biocatalysts, such as enzymes is used in biochemical conversion to convert the carbohydrate such as hemicellulose and cellulose into sugar. This sugar occur from biochemical conversion is importance starting material to synthesis some valuable chemicals and also to be catalyst for production of biofuels. However target of this process is produce other chemicals to replaced petroleum product which, this technology clean when compare with other conversion method [68, 69].

2.1.3 Chemical processing

Chemical processing is technology for produce energy or chemicals from biomass. One of chemical process is Fischer-Tropsh which the technology to produce olefin and methanol.[70]. In one process each part of the process has difference reaction. Oxidation reaction, acid-base reaction, reduction reaction are chemical reaction. Several chemical reaction could be used to combine in chemical process in order to receive the target product and increase product yield.

2.3 Pretreatment

Preparation of feedstock are called pretreatment which, pretreatment could be mechanical and chemical processing and separation of starting material. Physical structure of plant are changed by using this process which, effect to conversion of sugar polymers and other components [71-73]. For the long time, advantage of pretreatment are investigated [71]. The target of the pretreatment method is to destroy hemicellulose and lignin, enhance the porosity of the lignocellulose, and decrease the crystallinity.

Mechanical comminution of materials is chipping, grinding, and milling could be used to decrease cellulose crystallinity. Normally, 10-30 mm after chipping and 0.2-2 mm after milling or grinding this is the size of the materials [74]. The final particle size depend on the power of mechanical comminution. β-1,4-glycosidic bonds were cleavage, this reason effect to a high surface area and a low crystallinity [75]. Pretreatment in the conversion of biomass show in **Figure 2.4**
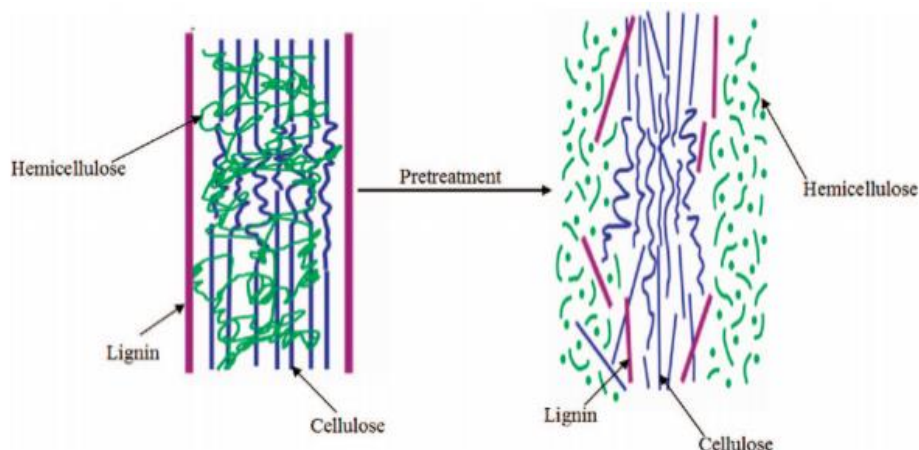
Figure 2.4 Pretreatment in the conversion of biomass [61].

2.4 Hydrolysis

Hydrolysis is the breakdown process of organic compound by using enzymatically or chemically into other molecules suitable for use as fuels or building-block chemicals [6]. The process is remarkable to produce high value-added chemicals by using water as a solvent. The system of this process is operated under high pressure in order to maintain condition of liquid phase. Biomass is treated and is converted to products under liquid phase. The advantage of this process is the catalysts can be used to increase the yield of products without the problem and using the catalyst can be decreased reaction temperature. The disadvantage of this process is needed to use under high pressure. Mechanism hydrolysis cellulose show in **Figure 2.5**
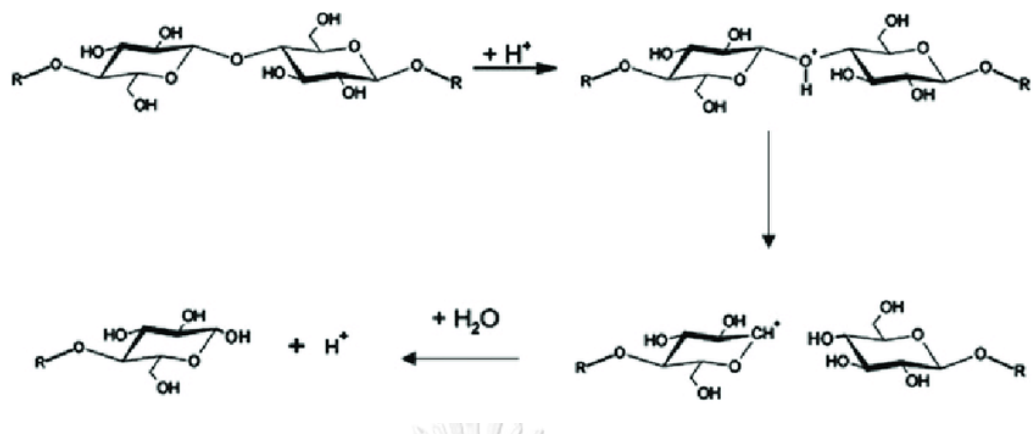
Figure 2.5 Reaction mechanism of acid hydrolysis of cellulose [76]

2.3. Chitin biomass

Chitin is polysaccharide, Second most polysaccharide in the world after cellulose is chitin, which, was found in the cell walls of fungi and exoskeletons of crustaceans and insects. Normally, chitin is waste stream. Amount of chitin around the world is 1011 tones. Chitin is found in seafood industries around 106 tones, In recently, chitin waste have to change to low value material such as fertilizers, pet foods and fishmeal [77].

Chitin biomass has monomers N-acetyl-glucosamine (GlcNAc) and D-Glucosamine (GlcNH$_2$). The structure show in **Figure 2.6**. Although, chitin is defined to a polymer of N-acetyl-D-glucosamine monomer [78]. Chitin is insoluble in aqueous because many of hydrogen bonds between acetamido groups in polymer chains. More advantage of chitin it could be used as a material for the purification of enzymes [79, 80]. Chitin have in three forms- **α**, **β** and **γ** chitin (**Fig.2.6**). Only **α**-chitin could extractable, and was found in crustaceans and cell wall of fungi which, this form have most abundance in the world. Conversion of chitin to chitosan could be by remove acetyl groups from chitin. The main source of chitosan is chitin which chitin is a waste from the seafood industry [81].
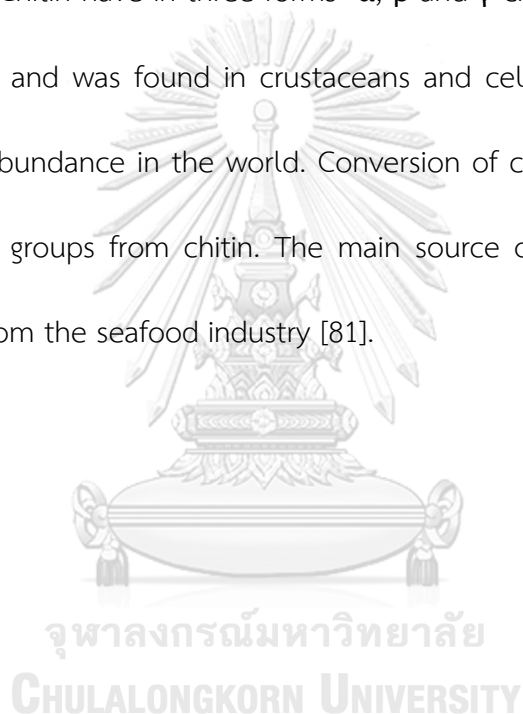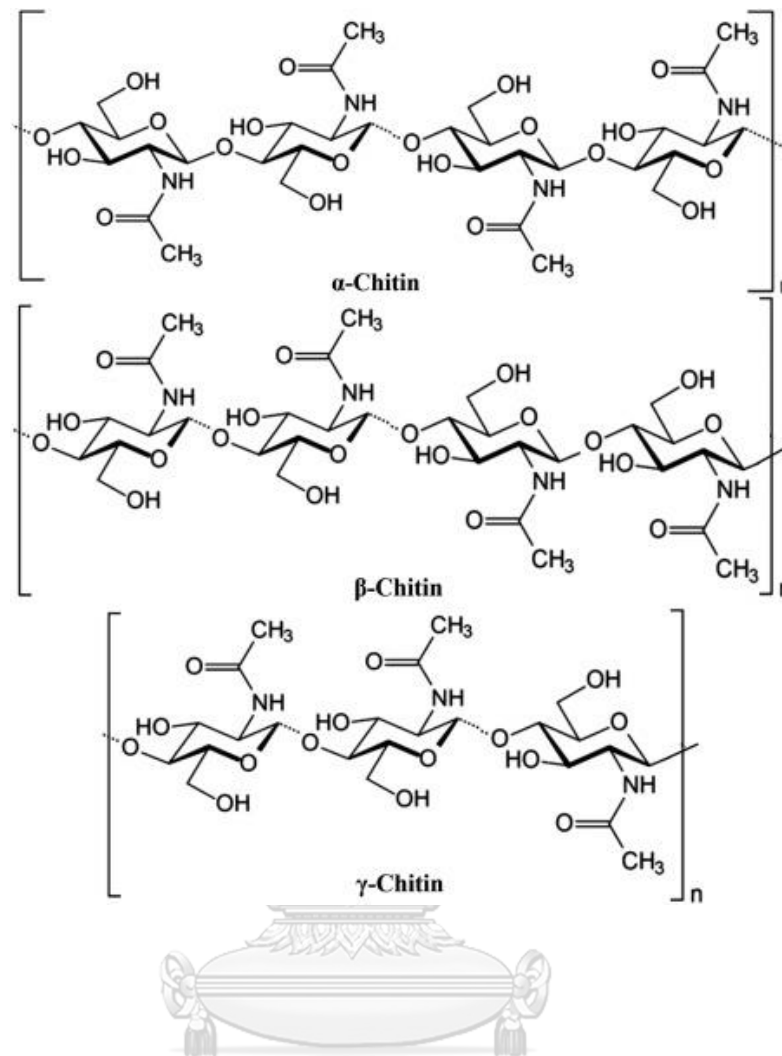
Figure 2.6 Structure of chitin form [82]

2.4. Chitosan

Chitin convert to chitosan from by deacetylation reaction. **Fig. 2.7** show the difference structure of chitin and chitosan. Chitosan could soluble in dilute acids. Chitosan is decomposition by lysozyme and degree of crystallinity increase decomposition of chitosan decrease. Decomposition of chitosan can be given lower *N*-acetyl-D-glucosamine, molecular weight, and chitooligomers [83].

The degree of deacetylation of chitin higher 50%, this material can be soluble in acidic solution and is called chitosan which, effect to protonation of the –NH$_2$ function of the D–glucosamine this reason of chitosan soluble. Ability soluble of chitosan in aqueous solutions in result of we can used different applications of chitosan such as solutions, films, and fibers [83].
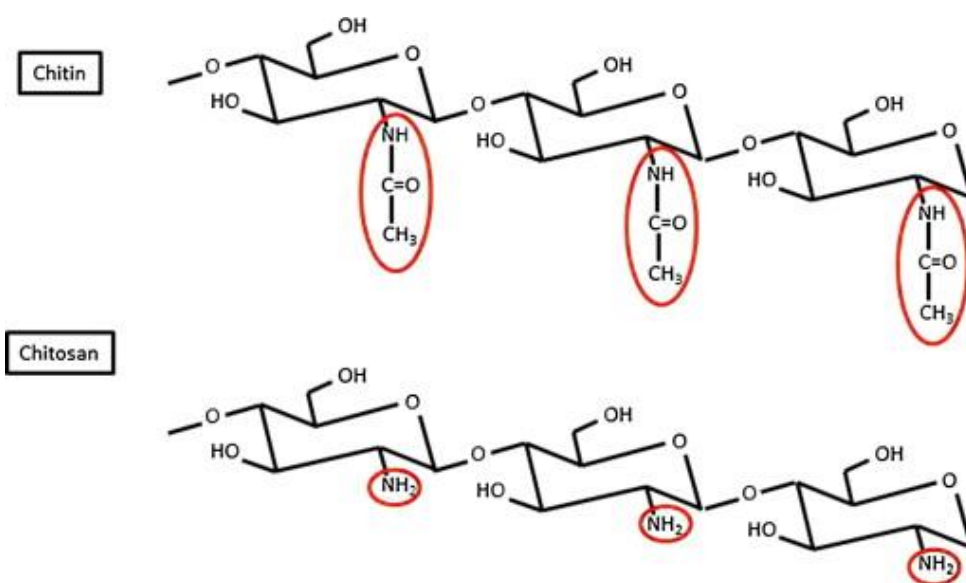
Figure 2.7 chemical structure of chitin and chitosan [84].

4. Shell biorefinery

Conversion of chitin into many valuable chemicals was called 'shell biorefinery'. Insects and crustaceans have high chitin content and also have protein or calcium carbonate. For concept of shell biorefinery, is upgraded chitin and derivative into valuable chemicals which could be used to apply in biorefinery. Crustacean shells usually have calcium carbonate around 20–50% and protein around 20–40% and higher to 15–40% in chitin (**Fig. 2.9**).
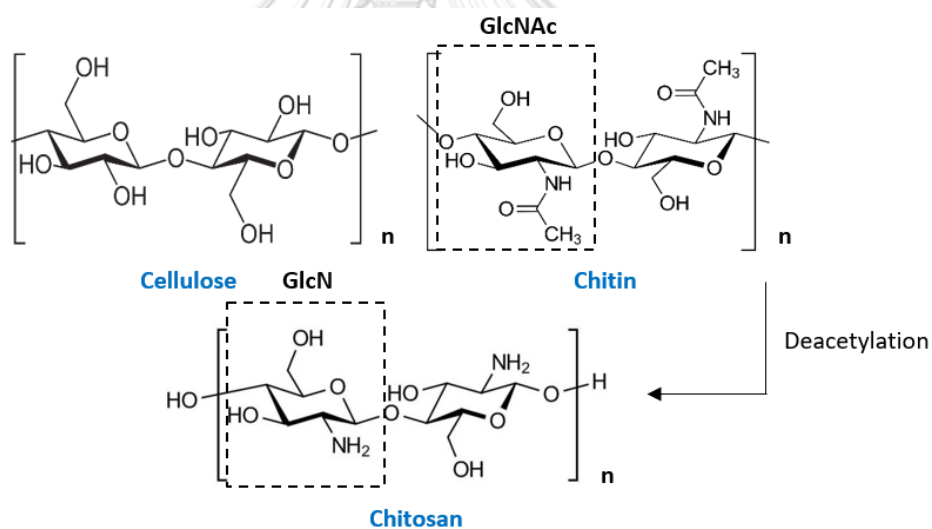
Figure 2.8 Chemical structures of cellulose, chitin and deacetylated chitosan.
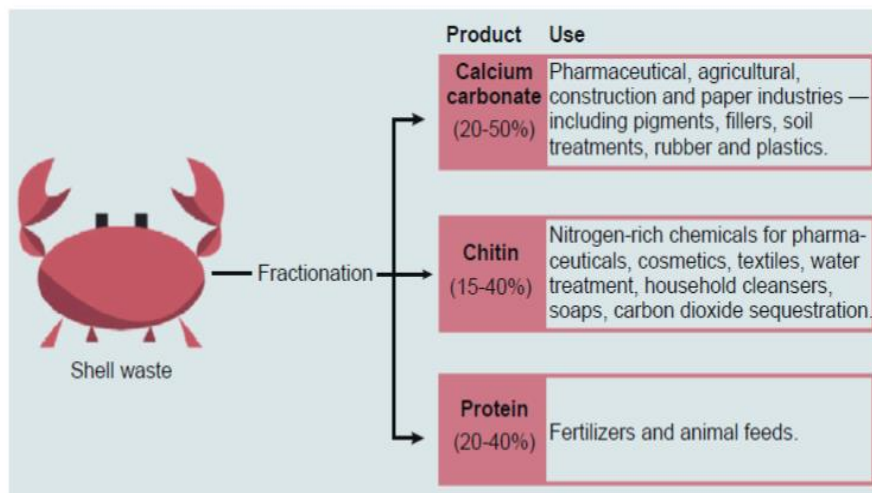
Figure 2.9 Components of shell biomass [43].

2.5 Chitin conversion into chemicals

Conversion of chitin has been few investigated [85-87]. **Figure.2.10** show that chitin covert to oxygen and nitrogen contain compound and chitosan. However, the nitrogen compounds cloud easier convert to nitrogen-containing chemicals but, oxygen-containing chemicals is used into existing biorefinery.

From literature review conversion of chitin to valuable chemicals have been investigated. Lactic acid or formic acid cloud be obtain in high yield when using cellulose to be starting material [88, 89]. In NaOH solvent, conversion of shrimp shell waste using copper oxide in oxidation reaction show high acetic acid yield [86].

Levulinic acid was produce from microwave method by using sulfuric acid this result show that chitin cloud be produced levulinic acid around 37% [21]. 5-Hydroxymethylfurfural (5-HMF) was produce from sugar by using some acid catalysts (as zinc or iron chloride) in polar solvent.[90]. N-acetylmonoethanolamine and polyols were converted from chitin with high yield at reaction temperature lower than 180°C [91]. Moreover, N-acetylglucosamine was converted from chitin by co-solvent[17]. Chitin conversion can be produced ethylene glycol and several monomeric sugar show high conversion at reaction temperature 165 °C and reaction time 90 min [92]. Overall of product can convert from chitin or chitosan show in **Figure 2.10.**
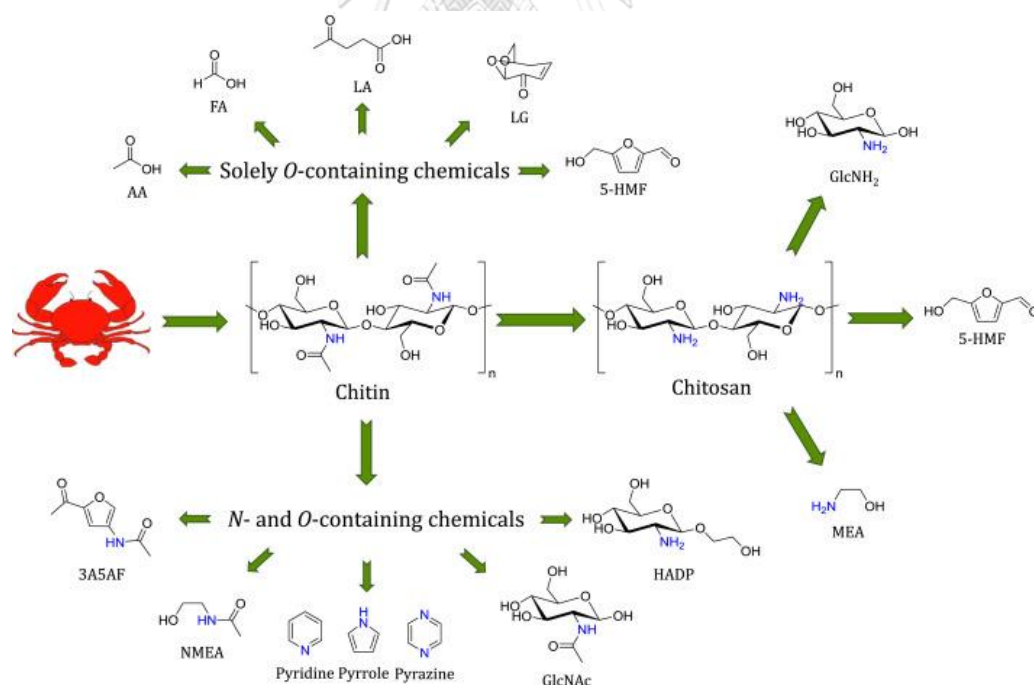
Figure 2.10 Nitrogen and oxygen contain compounds convert from chitin or chitosan[43]

2.6. Hot-compressed water

Hot-compressed water has many advantage and could be used in various reaction. Conditions of temperature and pressure were parameter influence with hot-compress water process. Difference of Hot-compressed water properties has influence to chemical reaction. However, ability of water in each reactions is difficult to indicate. Water at sub- and super-critical temperature condition was investigated in order to use the advantage of ionic product [93-95]. Temperature and density are parameter influence with properties of . hot-compressed this means that when improving temperature properties in hot-compressed water changed. At lower temperature critical point and at high pressures water in hot-compressed water is an acid/base catalyst precursor. Many synthesis reactions used this point. However, biomass liquefaction which is degradation reactions in hot-compressed show properties of a non-polar solvent. At not too high temperature C–C bond formation occur which this reaction can be performed in organic solvent. In addition, structure and polarity of water still not change. This is compressibility of hot-compressed water which is influence of solute which effect with chemical reaction. [96].

2.7. Metal oxides

Metal oxides is one type of heterogeneous catalyst. In recently, metal oxides are used in many chemicals industries. This material are very importance because metal oxide can be used to be catalysts and also used in role of support. Many functions were made from the properties of metal oxide. Many reactions for synthesis used metal oxide for example, gas synthesis or conversion of chemicals.

2.7.1 Magnesium oxide

Magnesium oxide (MgO) is important metal oxides for catalyst. MgO is usually basic support and also can be increased performance of dehydrogenation of short-chain alkanes [97]. The interesting feature of MgO is electropositive cation property (Mg^{2+}), and the anion of oxygen. Structure of MgO is a rock salt structure, A Mg^{2+} atom is surrounded by five O^{2-} ions. Structure of MgO show in **Figure 2.11**. MgO forms in the water (MgO + $H_2O \longrightarrow Mg(OH)_2$) can be change to Magnesium hydroxide ($Mg(OH)_2$), but it can be reversed by heating it to remove moisture.
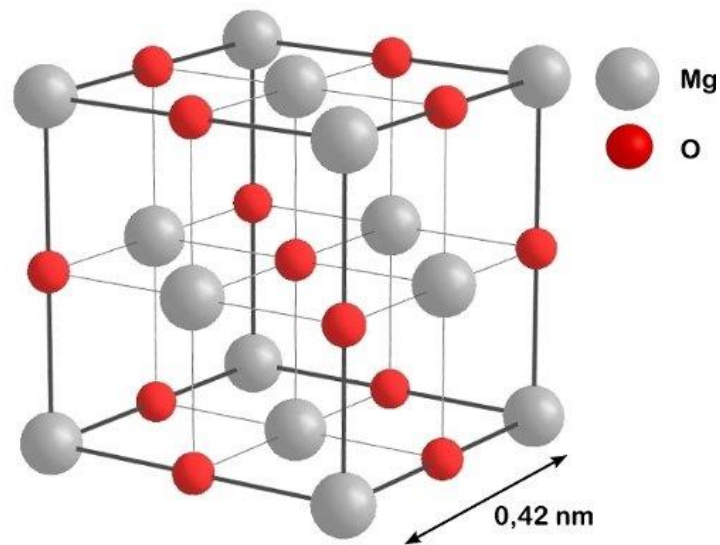
Figure 2.11 MgO structure [98]

2.7.2 Aluminium oxide

Nature of alumina or aluminum oxide (Al_2O_3) is white or colorless crystalline this material is used as catalyst and starting material for the production of aluminum metal. In addition, alumina is used in ceramic industrial and as reagent in chemical process. Moreover, alumina is used as adsorbent and catalyst as well as the adsorption of catalysts in polyethylene production [99], as a adsorbent for many chemicals such as arsenic, fluoride, in sulfur removal [100-102].

2.8 Literature reviews

Kobayashi et al. [5] studied cellulose hydrolysis. Supported metal catalysts were used to increase cellulose conversion. This method has been improved hemicellulose conversion and bio-oils yield. These methods have achieved in higher yields of sugar and alkanes. Sugar is used for produce bio-plastics.

Zhang et al. [90] evaluated conversion of N-acetyl-D-glucosamine to 5 - hydroxymethylfurfural. Ionic liquid catalysts and water mixed with dimethyl sulfoxide solvent were used in this reaction. Many reaction foctor, (temperature, time, solvent ratios and amount of catalyst) were studied. The main product was changed from N-acetyl-D-glucosamine to D-glucosamine and monosaccharides but, amount of 5 - hydroxymethylfurfural still lower than N-acetyl-D-glucosamine. Sulfate ($[Hmim][HSO_4]$) show highest effective.

Shen et al. [18] investigated method for production of lactic acid from chitosan. Acidic ionic liquids catalysis was used in the reaction. The result show that dilution effect was influenced. The correlation between ionic liquid and lactic acid yield was investigated. The result show that acidity of ionic liquid influenced with production of chitosan to lactic acid. Moreover, SEM and IR were used to investigate morphology and structure of solid residues. The mechanism were start with chitosan first quaternizes and decomposition to D-glucosammonium salt, and NH_3 elimination effect to the material convert to lactic acid.

Zhang et al. [103] demonstrated a role of magnesium hydroxide on Pt/SiO$_2$ to produce 1,2-propylene, including increasing of isomerization of glucose into fructose, and reduce convertion hexitol into 1,2-propylene glycol which is by-product. The Pt/SiO$_2$@Mg(OH)$_2$ prepared to be core-shell structure by hydrothermal process.The result shoe showed good performance and stability of Pt/SiO$_2$ @Mg(OH)$_2$ and magnesium hydroxide on Pt/SiO$_2$.

Yamaguchi et al. [104] studied gasification of cellulose and recycled paper. Cellulose powder was used to be starting material at 523 K in water by using many metal catalysts. The most activity catalyst in gasification process of paper and cellulose is charcoal-supported ruthenium catalyst. The optimal condition of gasification was reaction temperature 573 K reaction time 10 minute charcoal-supported ruthenium catalyst and paper was starting material. Ball milling treatment was used increased yield. The result indicated that decreasing crystallinity and particles sizes provided high gas yields. From this research found the new route for produce fuel gas.

Abdullah et al. [105] studied kinetic behaviors and effects of crystalline celluloses on hydrothermal decomposition by using semi hot-compressed water. Decomposition of various crystalline celluloses was indicated by rate and Ea are; however, the Ea were calculated by empirical relationships of Arrhenius equation.

Wattanapaphawong et al. [88] studied many metal oxides catalyst (ZrO_2, Al_2O_3, TiO_2, Fe_3O_4, V_2O_5, CeO_2, Y_2O_3, Tm_2O_3, HfO_2, Ga_2O_3, MgO, La_2O_3, Nb_2O_5, and Ta_2O_5) for conversion of cellulose to lactic acid. Lactic acid production from cellulose was obtained by ZrO_2 at reaction condition 473 K reaction time 6 h. Moreover types of ZrO_2 were investigated. The result show that acid and base sites on the ZrO_2 influence to lactic acid yields.

Dumesic et al. [106] investigated production of 5-Hydroxymethylfurfural from glucose by using a mixed of Amb-70 and Sn-β as solid acid catalysts. Moreover, this research used homogeneous catalysts and salts. The result show high yield of 5-Hydroxymethylfurfural. Distillation for THF can be as the solvent can be achieved to separation and purification of 5-Hydroxymethylfurfural.

Xiaoyun et al. [86] investigated conversion of chitin to acetic acid. Non-noble metal catalysts were used in conversion reaction which, from the reaction provide high yield acetic acid yield. In addition, untreated shrimp shell powder also provided high yield. Oxygen was used to be oxidant in catalytic reaction. Conversion of chitin was achievable to provide a new route for produce acetic acid from renewable resources.

Yabushita et al. [87] studied a fast conversion of chitin to monomers. Homogeneous catalysts were used in this reaction with remaining of N-acetyl groups by mixing between mechanochemistry and homogeneous catalysis. Mechanochemistry was also used combine with homogeneous catalyst which, H_2SO_4 show soluble short-chain oligomers product. The result show that hydrolysis of the ball milled chitin given yield of *N*-acetyl-D-glucosamine (53 %), and methanolysis provied yield of 1-O-methyl-N-acetylglucosamine (70 %). Amount of acid was decreased by methanolysis (99.8%) when compared with conventional process.
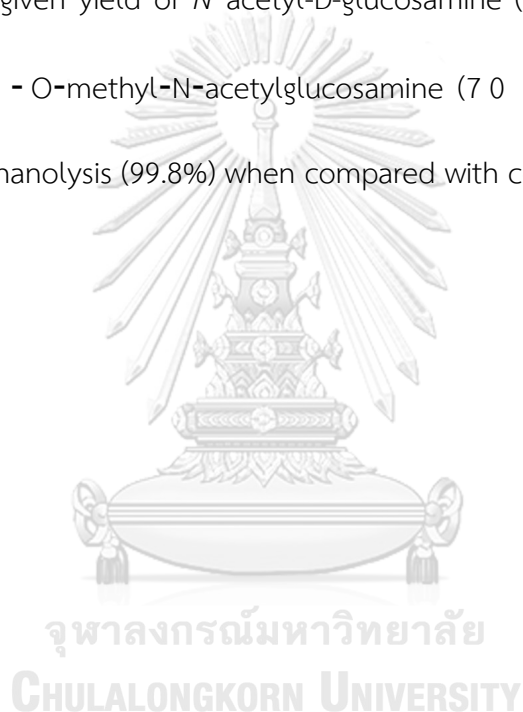
CHAPTER III

EXPERIMENTAL

3.1 Materials and reagents

Materials and reagents are used in this study are listed in **Table 3.1**

Table 1 List of chemicals and catalyst

Chemicals	Source
Aluminium oxide	Sumitomo Chemical Co.
Zirconium oxide	Daichi kigenso kagako kotyo co.,ltd
Titanium oxide	Ishihara Sangyo Kaisha Ltd.
Magnesium oxide	Ube Industries
Cerium oxide	Daiichi Kigenso Kagaku Kogyo Co.
Calcium hydroxide	FUJIFILM Wako Pure Chemical Corporation
Sodium carbonate	FUJIFILM Wako Pure Chemical Corporation
Zinc oxide	FUJIFILM Wako Pure Chemical Corporation
Hydrotalcite	FUJIFILM Wako Pure Chemical Corporation
Calcium carbonate	FUJIFILM Wako Pure Chemical Corporation
Magnesium hydroxide	FUJIFILM Wako Pure Chemical Corporation
Magnesium carbonate	FUJIFILM Wako Pure Chemical Corporation
Silicon dioxide	FUJIFILM Wako Pure Chemical Corporation
Chitin unbleached	MP Biomedicals
Chitin Practical Grade	Toronto Research Chemicals
Chitin 1st Grade	FUJIFILM Wako Pure Chemical Corporation
N-Acetyl-D Glucosamine	FUJIFILM Wako Pure Chemical Corporation
D-Glucosamine Hydrochloride	FUJIFILM Wako Pure Chemical Corporation
D-Glucose	Kanto Chemical Co.
Chitosan	Sigma-Aldrich Co.

3.2 Ball milling pretreatment

In this research, Effect of ball milling pretreatment was investigate. Chitin was entered into ball milling pot and then zirconium oxide ball was also added into ball milling pot. In final step ball milling was set ball milling time and roll.

3.3 Reaction test

3.3.1 Ball milling pretreatment

In this research, Ball milling is used for pretreatment chitin before used as a starting material. Chitin (Chitin 1st Grade, Chitin unbleached, Chitin Practical Grade) 10g was added into ball milled pot. Zirconium balls were added into ball milling pot. Then ball milling pot was set time and start milling roll. Finally, ball milled chitin was obtained.

3.3.2 Effects of reaction conditions chitin conversion in the hot-compress water

Batch reactor (OM Lab-Tech, MMJ-100) from stainless steel the volume inside of 100 cm^3 was used in conversion of chitin. In a generally experiment, 0.5 g of chitin, and 50 g of water were entered to the reactor. In next step, Nitrogen was carried on inside the reactor. The reactor was heated and also used screw stirring at one temperature which, temperature in range 473 – 553 K and reaction time 1 - 24 h were study. After reaction, combination of liquid and solid was recovered. Combination of product were filtered which, solid residue and liquid fraction were obtained. The solid residue was heated to make dry solid overnight at 373 K, and the

weight of the dry solid residue and liquid fraction were recorded. The investigated parameters are as follows:

- Three types of chitin will be used as starting material in order to study differences between chitin sources. ('chitin, practical grade' from Toronto research chemicals Inc., as well as 'chitin reagent' and 'chitin unbleached' from Wako Co. Ltd.)

- Reaction temperatures within the range of 473-553 K was studied in order to find suitable reaction conditions.

- Reaction time within the range of 1-16 h was studied in order to find suitable reaction conditions.

3.3.3. Effects of catalysts on chitin conversion reaction

Batch reactor (OM Lab-Tech, MMJ-100) from stainless steel the volume inside of 100 cm^3 was used in conversion of chitin. In a generally experiment, 0.5 g of chitin, catalyst 0.2 – 1 and 50 g of water were entered to the reactor. In next step, Nitrogen was carried on inside the reactor. The reactor was heated and also used screw stirring at one temperature which, temperature in range 473 – 553 K and reaction time 1 - 24 h were study. After reaction, combination of liquid and solid was recovered. Combination of product were filtered which, solid residue and liquid fraction were obtained. The solid residue was heated to make dry solid overnight at 373 K, and the weight of the dry solid residue and liquid fraction were recorded.

The investigated parameters are as follows:

- MgO, Al$_2$O$_3$, ZrO$_2$, TiO$_2$, SiO$_2$, ZnO, CeO$_2$, Hydrotalcite, CaCO$_3$, Mg(OH)$_2$, MgCO$_3$, NaCO$_3$, Ca(OH)$_2$ were used in conversion of chitin.

- The catalyst that show highest yield were used to test effect of catalyst weight in range 0.2-1.0 g.

- Recycle of catalyst (1-3 times) were studied to test stability of the catalyst.
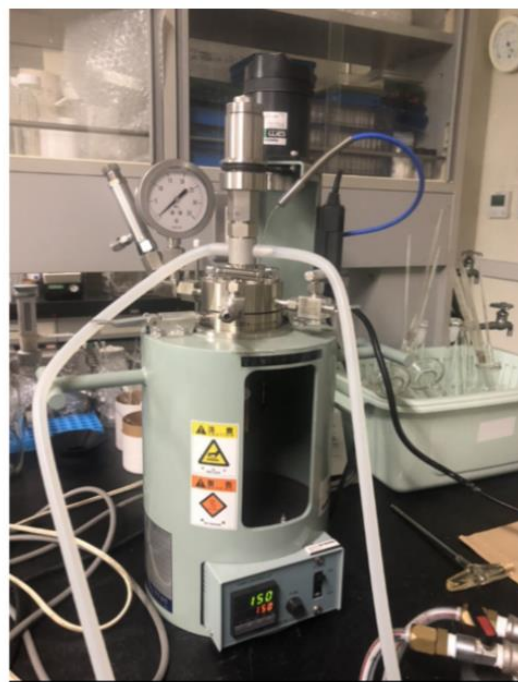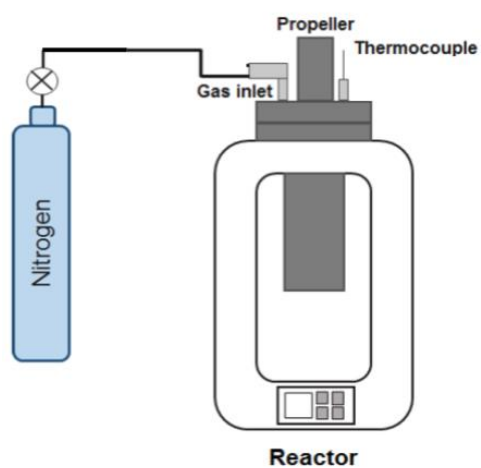
Figure 3.1 Reactor system for chitin conversion

3.3.4. Effects of catalysts on chitin conversion reaction

Batch reactor (OM Lab-Tech, MMJ-100) from stainless steel the volume inside of 100 cm^3 was used in conversion of chitin, chitosan, D-glucose, D-Glucosamine or *N*-Acetyl-D Glucosamine.In a generally experiment, 0.5 g of chitin, catalyst 0.2 – 1 and 50 g of water were entered to the reactor. In next step, Nitrogen was carried on inside the reactor. The reactor was heated and also used screw stirring at one temperature which, temperature in range 473 – 553 K and reaction time 1 - 24 h were study. After reaction, combination of liquid and solid was recovered. Combination of product were filtered which, solid residue and liquid fraction were obtained. The solid residue was heated to make dry solid overnight at 373 K, and the weight of the dry solid residue and liquid fraction were recorded.
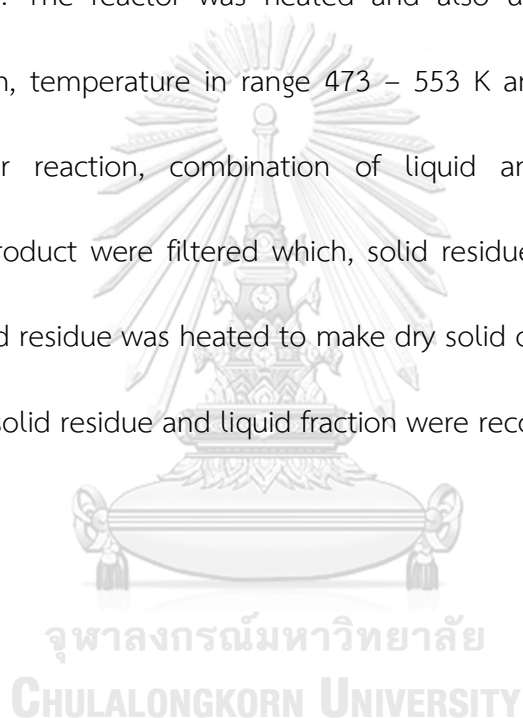
Quantitative composition of liquid product such as lactic acid, acetic acid, levulinic acid, 5-hydroxyfurfural (5-HMF), D-glucosamine, and *N*-acetyl-D-glucosamine were analyzed by high-performance liquid chromatography (HPLC). Total organic carbon (TOC) in the liquid product was analyzed with a TOC analyzer. The TOC (%) was calculated number of carbon mole in starting matherial. The conversion, TOC and product yields (%) were calculated based on the dry weight and mole of carbon by equation (1, (2) and (3) :

$$\text{Product yield (\%)} = \left(\frac{\text{moles of C in product}}{\text{moles of C in initial reactant}}\right) \times 100 \qquad (1)$$

$$\text{TOC (\%)} = \left(\frac{\text{Mole of total organic carbon in product}}{\text{moles of C in initial reactant}}\right) \times 100$$

$$\text{Conversion (\%)} = \left(1 - \frac{(\text{Weight of solid residue}) - (\text{weight of solid catalyst})}{\text{Weight of initial substrate}}\right) \times 100 \qquad (2)$$

3.4 Product analysis and Characterization

3.4.1 High-performance liquid chromatography (HPLC)

High-performance liquid chromatography (Shimadzu) equipped with a refractive index detector (Shimadzu, RID-10A), a UV–vis detector (Shimadzu, SPD-20AV), and an ICSep COREGEL-107H column. The equipment were used to identify chemicals such as *N*-acetyl-D-glucosamine, D-glucosamine, 5-Hydroxymethylfurfural, Levulinic acid and Lactic acid.

3.4.2 Elemental Analyzer

Quantitative of carbon in various chitin was analyzed by an elemental analyzer (PerkinElmer 2400 II).

3.4.3 X-ray diffraction (XRD)

The catalysts and the reactants were analyzed by X-ray diffraction (Rigaku SmartLab). X-ray diffraction system is Cu Kα radiation (λ= 0.15406 nm) in the 2θ range of 5–90°.with a 2θ step size of 0.02° in condition current 30 mA and voltage 40 kV.

3.4.4 Thermogravimetry–differential thermal analysis (TG-DTA)

Thermogravimetry–differential thermal analysis (TG-DTA) was used to analyze of the catalysts and solid residue. After the reaction the solid residue or catalysts was entered into a Thermo plus EVO2 TG-DTA8122 (Rigaku) in flowing dry air and heating rate of 10 K min^{-1}. Optional direct monitoring system recorded images in real time of the samples.

3.4.5 Atomic emission spectrometry

In the liquid fraction, amount of oxide metal in the liquid phase was analyzed by inductively coupled plasma atomic emission spectrometry (SPS4000, SII NanoTechnology).

3.4.6 Total organic carbon analyzer (TOC)

Total organic carbon analyzer (Shimadzu, TOC-V$_{CSN}$) were used to calculate the amount of organic carbon in solution.

Figure 3.2 Picture of total organic carbon analyzer (Shimazu)

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

CHAPTER IV

RESULT AND DISCUSSION

The study in this chapter is divided into four parts. The first part is the investigation for pretreatment of chitin. In second, chitin conversion without catalyst was investigated. In addition, Reaction condition for chitin conversion were studied in this part. In third part is investigation of catalytic performance as well as reaction using catalyst was compared with non-catalyst in the reaction. Moreover, the effect of reaction temperature, reaction time, amount of catalyst, chitin type and reusability of catalyst were studied. Final part, the reaction path way was investigated.

4.1 The effect of mall milled pre-treatment

First, the effect of ball milled pretreatment was studies. Chitin was ball milled at 24 h and 48 h. Ball milled pretreatment of chitin at 24 h and 48 h obtain higher conversion than chitin without ball milled pretreatment (55.0 and 56.6 %) respectively The result of product yields, conversion of chitin and TOC show in the **Table 4.1** and **Figure 4.1.**

Table 4.1 The effect of ball milled pretreatment on chitin conversion without catalyst

Ball milled time (hr)	Conversion (%)	TOC (%)	Product yield (%)		
			5-HMF	Acetic acid	Lactic acid
0	14.9	10.4	0.9	2.1	0.8
24	55.0	30	0.9	3.6	1.1
48	56.6	36.9	1.6	8.7	1.3

Reaction conditions: 0.5 g ball-milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, 473 K reaction temperature, and 16 h reaction time.

Figure 4.1 The effect of ball milled pretreatment on chitin conversion without catalyst Reaction conditions: 0.5 g ball-milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, 473 K reaction temperature, and 16 h reaction time.
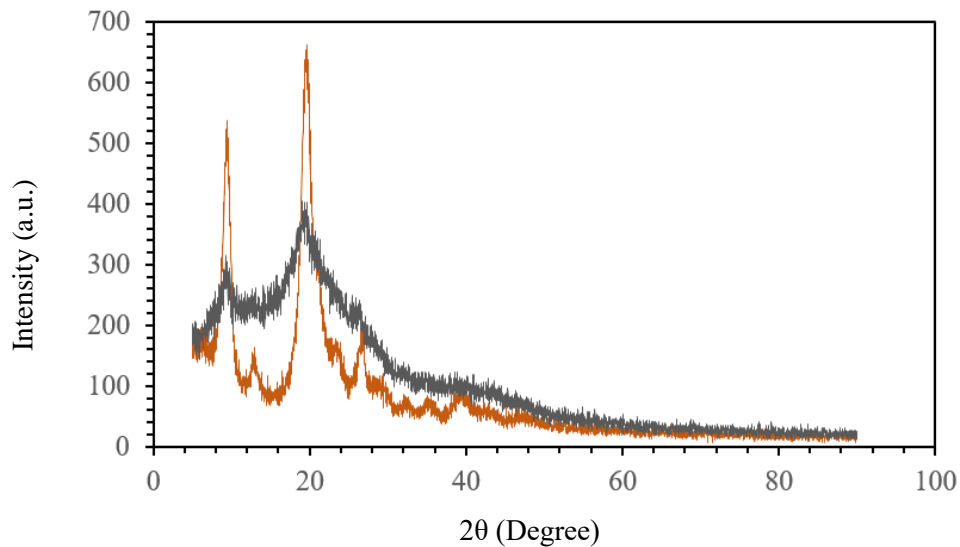
Figure 4.2 XRD patterns of chitin (orange) and (b) ball milled chitin (black) for 48 h.

Ball milled pretreatment was used for preparing of chitin before entering to reactor. Chitin and ball milled chitin (FUJIFILM Wako Pure Chemical Corporation) was investigated by using X-ray diffraction to analyze morphology of chitin, In **Figure 4.2,** chitin (orange line) showed importance peak at 2θ 9.6, 19.4 and 26.4 degrees, which related with the crystalline planes of (110), (130) and (013) this suggested that α-chitin [107]. From the result could identify structure of chitin [108, 109]. However, XRD pattern of chitin (Black line) showed board peak, which indicated that ball milling pretreatment decreased crystallinity of chitin. From the result, ball milling pretreatment led to cleavage of hydrogen bonding in chitin, which affect to crystallinity of chitin.

Composition of product in liquid fraction was determined by HPLC. 5-Hydroxymethylfurfural (5-HMF), acetic acid and lactic acid were detected in liquid solution. Other product (Levulinic acid, D-Glucose, glyceraldehyde hexose sugar and etc.) could be intermediary chemicals for produce acetic acid and lactic acid [32]. A decreasing of chitin crystallinity was related with the increasing TOC yield and conversion of chitin (**Table 4.1**). This finding is consistent with previous literature review which reducing of crystallinity by ball milling pretreatment can be enhanced conversion reaction in water solvent [110, 111].

4.2 Chitin conversion into lactic acid by hot compresses water without catalyst.

In this part, hot compressed water without solid catalyst were investigated.

4.2.1 Reaction condition of chitin conversion without catalyst

Table 4.2 show conversion of chitin and ball milled chitin at reaction temperature 473 K. The product from chitin conversion were acetic acid (2.1%), lactic acid (0.8%), and 5-HMF (0.9%). From the result N-acetyl-D-glucosamine and D-glucosamine could not detect in liquid product after the chitin conversion reaction. **Table 4.3** show conversion of chitin and ball milled chitin at reaction temperature 533 K. The product from chitin conversion were acetic acid (2.1%), lactic acid (0.8%), 5-HMF (0.9%). The product from chitin conversion were acetic acid (10.1%), lactic acid (1.8%), 5-HMF (0.5%). The product from ball milled chitin conversion were acetic

acid (14.6%), lactic acid (1.5%). From the result show that when increased temperature from 473 K to 533 K acetic acid yield also increased. From literature review strongly base catalyst such as sodium hydroxide was used for deacetylation reaction to convert chitin to chitosan. These reaction could be obtained acetic acid [112]. Moreover, acid catalysts were used in chitin conversion reaction, *N*-acetyl-D-glucosamine was converted to D-glucosamine by deacetylation to obtain acetic acid [113, 114].

In **Table 4.2** and **Table 4.3** I try to increase reaction temperature from 473 to 533 K and also reduce reaction time from 16 to 6 h. From the result show that at 473 K, 16 h reaction time, ball milled chitin was starting material, showed the high TOC yield increase from 10.4 to 37% and conversion of chitin increased from 14.9 to 55 %. Moreover at 533 K, 6 h reaction time was also obtained high TOC yield increase from 43.7 to 49.5 %. In both condition could be ball milled pretreatment influenced to conversion of chitin. However, amount of lactic acid yield was not significantly changed. Chitin conversion into lactic acid requires a catalyst to increase selectivity.

Table 4.2 The effect of ball milled pretreatment on chitin conversion without catalyst at 473 K [99].

Reaction time (h)	Chitin pretreatment	Conversion (%)	TOC (%)	Yield (%)		
				Acetic acid	Lactic acid	5-HMF
16	None	14.9	10.4	2.1	0.8	0.9
16	Ball milling	55	37.0	8.7	1.3	1.6

Reaction conditions:.0.5 g ball-milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, 473 K reaction temperature, and 16 h reaction time

Table 4.3 The effect of ball milled pretreatment on chitin conversion without catalyst at 533 K [99].

Reaction time (h)	Chitin pretreatment	Conversion (%)	TOC (%)	Yield (%)		
				Acetic acid	Lactic acid	5-HMF
6	None	88.2	43.7	10.1	1.8	0.5
6	Ball milling	89.8	49.5	14.6	1.5	0.0

Reaction conditions: 0.5 g ball-milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, 473 K reaction temperature, and 6 h reaction time.
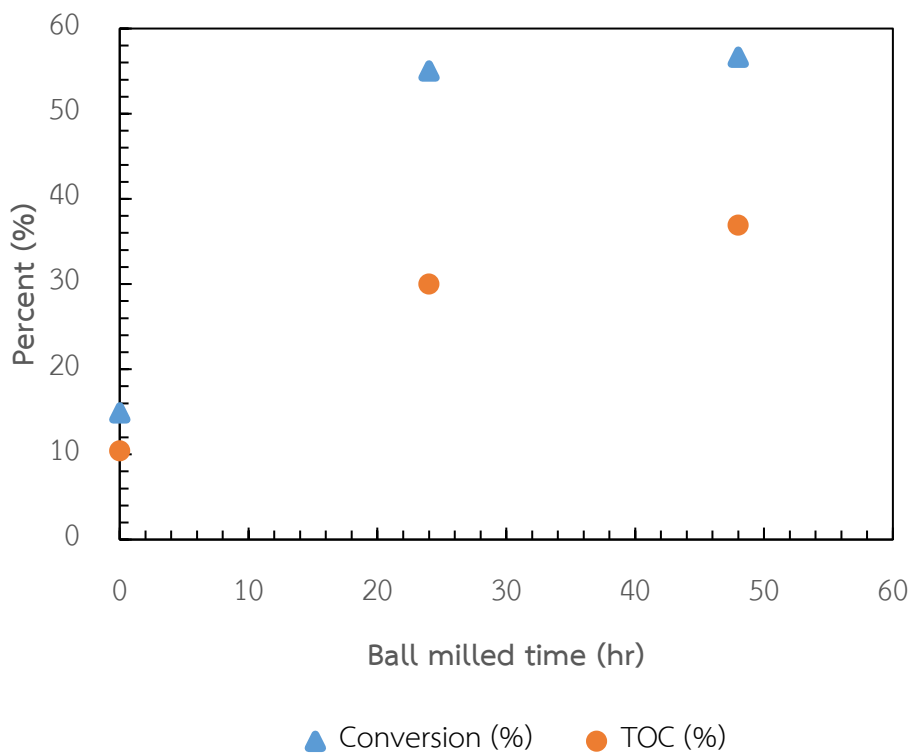
In the next step I will try to find optimal condition for conversion of chitin conversion without catalyst. The first parameter was reaction temperature. Reaction temperature in range 473-553 K was studied. 533 K showed high TOC yield (49.5 %) and high chitin conversion (84.8%), the result showed in **Table 4.4**. and **Figure.4.3**. TOC yield increased from 37 to 49.5 % with increasing of reaction temperature 473 to 533 K this attributed with conversion of chitin increased from 55 to 84.8 %. However, when increased temperature to 553 K TOC yield and conversion of chitin decreased (84.5 and 45.9 %) probably because of decomposition of organic carbon compound at the higher reaction temperature.
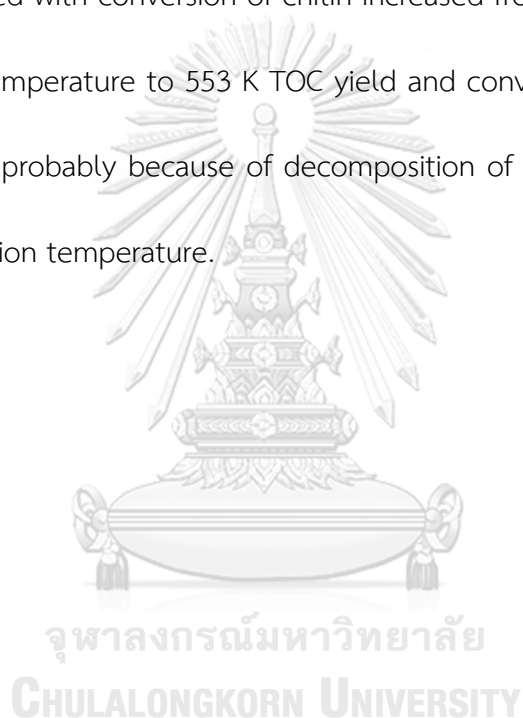
Table 4.4 The effect of reaction temperature on chitin conversion without catalyst

Temperature (K)	Conversion (%)	TOC (%)	Product yield (%)		
			5-HMF	Acetic acid	Lactic acid
473	55	37.0	0.9	2.1	0.8
483	48.6	28.1	0.9	10.2	3.0
493	60.6	43.1	0.8	10.2	2.4
503	74.7	36.5	0.7	13.6	3.1
513	79.8	44.1	0.7	13.9	3.3
533	84.8	49.5	0	14.6	1.5
553	84.6	45.9	0	14.4	0.9

Reaction conditions: 0.5 g ball milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, and 16 h reaction time.

จุฬาลงกรณ์มหาวิทยาลัย

**C**HULALONGKORN **U**NIVERSITY
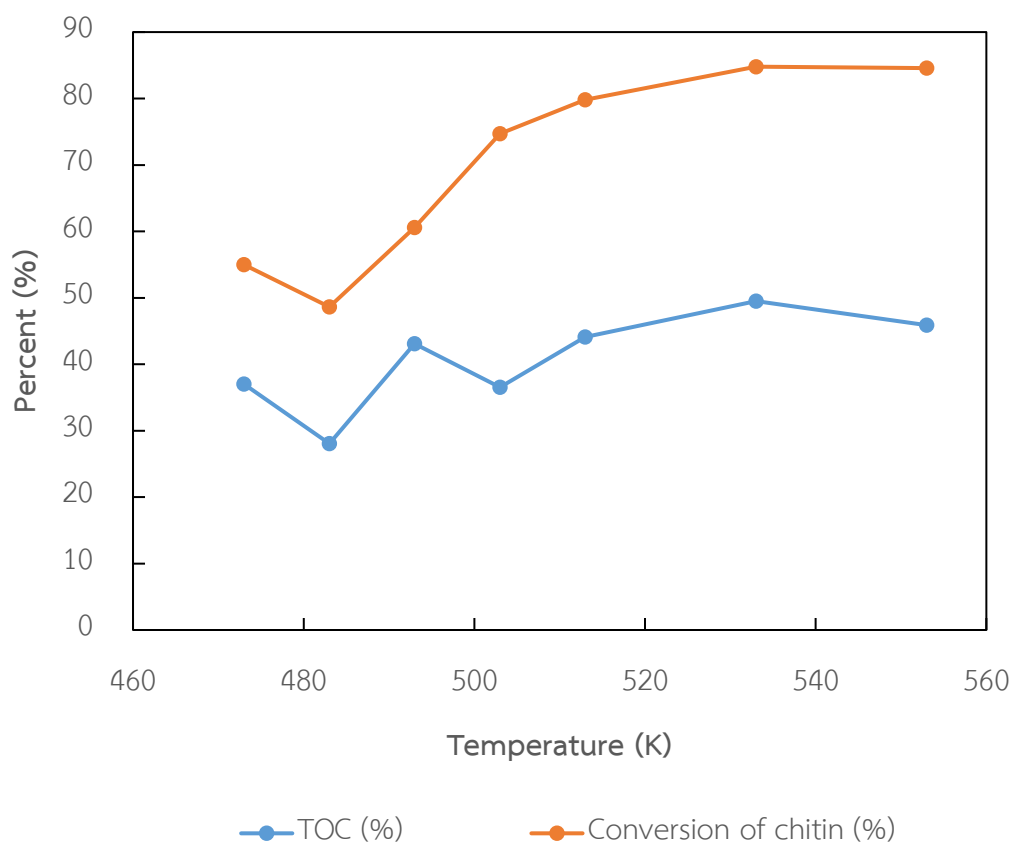
Figure 4.3 Conversion of chitin and TOC in the liquid solution obtained by various reaction temperature reaction conditions: 0.5 g ball-milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, and 16 h reaction time.

Table 4.5 The effect of chitin type from three company on chitin conversion without catalyst

Ball milled time (hr)	Conversion (%)	TOC (%)	Product yield (%)		
			5-HMF	Acetic acid	Lactic acid
Type 1	14.9	10.4	0.9	2.1	0.8
Type 2	19.8	9.6	0.7	0.9	0.6
Type 3	17.1	9.8	0.5	0.7	0.6

Reaction conditions: 0.5 g chitin, 50 g water, 473 K reaction temperature, and 16 h reaction time.

Type 1 = Chitin reagent from Wako Co. Ltd.

Type 2 = Chitin unbleached from MP Biomedicals

Type 3 = Chitin Practical Grade Toronto research chemicals inc.

The result from CHN analyzer Chitin reagent from Wako Co. Ltd. (C=41.3 %, H=6.9%, N=6.1%) Chitin unbleached from MP Biomedicals (C=41.2 %, H=6.9%, N=6.2%) Chitin Practical Grade Toronto research chemicals inc. (C=41.1 %, H=6.9%, N=6.0%) showed almost similar. Moreover, chitin reagent from Wako Co. Ltd ., Chitin unbleached from MP Biomedicals, and Chitin practical grade from Toronto research chemicals inc. were investigated in conversion of chitin at 473 K for 16 h (**Table 4.5**). The conversion of chitin reagent from Wako Co. Ltd. was a lower than the conversion from chitin unbleached from MP Biomedicals and chitin practical grade from Toronto

research chemicals inc. However, chitin conversion and TOC yield from 3 type showed a little difference which related with the result from CHN analyzer.

Table 4.6 The effect of reaction time on chitin conversion without catalyst

Reaction time (h)	Conversion (%)	TOC (%)	Product yield (%)		
			5-HMF	Acetic acid	Lactic acid
2	20.3	30.2	0.4	0.2	0.4
4	30.6	36.5	0.2	0.5	0.5
6	67.1	55.3	1	9.3	3.1
16	84.8	49.5	0	14.6	1.5
24	81.6	39.4	0	13.8	3.2

Reaction conditions: 0.5 g ball-milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, 533 K reaction temperature.

The reaction time in range 2-24 h was investigated to find the optimal reaction condition. At reaction time 6 h showed high TOC yield (53.3 %) and chitin conversion (67.0%), the result showed in **Table 4.6** . and **Figure.4.4** . TOC yield increased from 30.2 to 55.3% with increasing of reaction time 2 to 6 h attributed with conversion of chitin increased from 20.3 to 67.0 %. However, when increased reaction time to 24 h, TOC yield decreased to 39.44 % which, organic carbon compound such as acetic acid and lactic acid might decompose at longer reaction time.
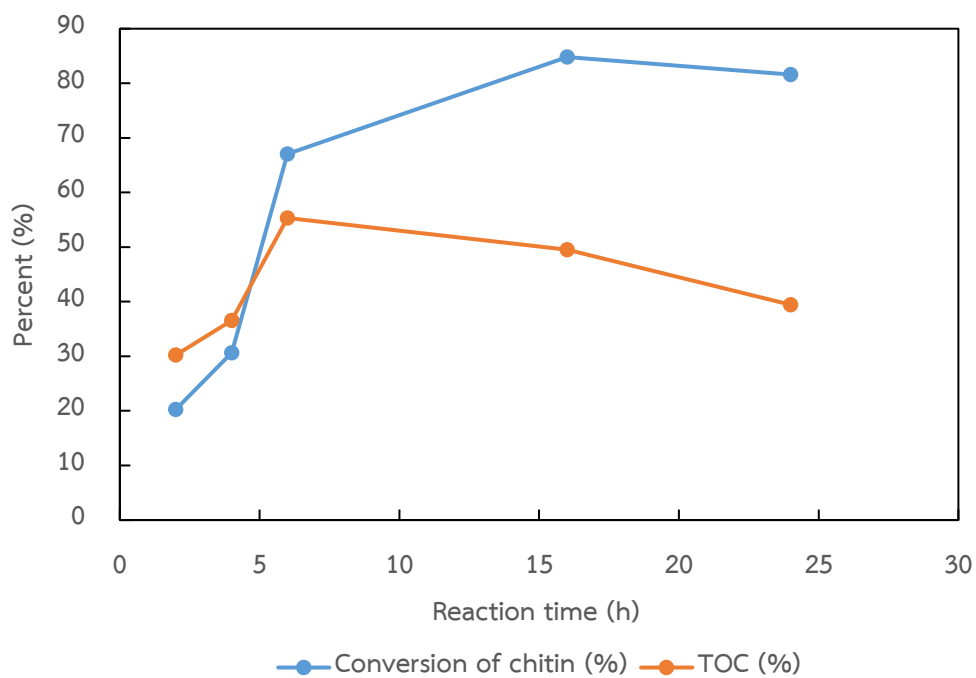
Figure 4.4 Conversion of chitin and TOC in the liquid product obtained by various

reaction time Reaction conditions: 0.5 g ball-milled chitin (Chitin reagent from Wako

Co. Ltd), 50 g water, 533 K reaction temperature, and 6 h reaction time

4.3. Chitin conversion into lactic acid by hot compressed water with catalysts

In this part, hot compressed water with solid catalyst were investigated.

4.3.1 Catalyst screening and reaction condition with catalyst

Next step, chitin conversion was demonstrated by using metal oxides (Al_2O_3, ZrO_2, ZnO, CeO_2, TiO_2, SiO_2 and MgO) at 533 K for 6 h. Chitin conversion without catalyst was used to be control condition. **Table 4.7** showed result from catalyst screening. Acetic acid yield changed when using metal oxide (Al_2O_3 (14.5%), ZrO_2 (14.3%), ZnO (13.9%), CeO_2 (14.1%), TiO_2 (13.1%), SiO_2 (13.1%) and MgO (13.5%)) when compared with non-using metal oxide (9.3%) , but the yield of lactic acid higher when using Al_2O_3 (6.2%), and MgO (10.8%) than without catalyst condition (3.1%). In addition, I also detected pH in liquid solution before chitin conversion reaction and liquid product after the reaction. I found that MgO catalyst obtained highest pH of liquid solution before and after the reaction, which indicated that high pH of catalyst in conversion of chitin attribute with production of lactic acid. Generally, from literature review MgO show very weak acid character both in site density and strength (base site = 2.59 μmol m^{-2} acid site = 0.07 μmol m^{-2}) [115]. In the result indicated that the basicity property of the catalyst was most important property. MgO catalyst have basicity property, but the other catalyst was acid or weak base catalyst, which might indicated that activity of catalyst in chitin conversion depended on basicity.

Table 4.7 The effect of metal oxides on chitin conversion

Catalyst	Conversion (%)	TOC (%)	Yield (%)		pH	
			Acetic acid	Lactic acid	Before	After
None	67.1	55.3	9.3	3.1	9.0	6.1
Al_2O_3	53.1	51.9	14.5	6.2	9.2	6.2
ZrO_2	98	53.1	14.3	3.9	9.1	6.7
ZnO	99	50.5	13.9	3.4	9.0	6.2
CeO_2	99	53.2	14.1	0.7	9.2	6.2
TiO_2	99	46.4	13.1	0.4	9.0	5.7
SiO_2	99	47.6	13.1	1.4	9.1	5.2
MgO-1	70.3	57.4	13.5	10.8	11.0	9.3

Reaction conditions: 0.5 g ball-milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, 533 K reaction temperature, 6 h reaction time, and 0.5 g catalyst weight.

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

Table 4.8 The effect of various type of chitin on chitin conversion

Catalyst	Conversion	TOC	Yield (%)		
	(%)	(%)	Acetic acid	Lactic acid	5-HMF
MgO-1	70.3	57.4	13.5	10.8	0.0
MgO-2	63.4	56.0	14.1	9.4	0.0
MgO-5	65.6	52.8	12.8	9.3	0.0

Reaction conditions: 0.5 g ball-milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, 533 K reaction temperature, 6 h reaction time, and 0.5 g catalyst weight.

In **Table 4.8** showed the effect of various type of chitin on chitin conversion. MgO-1 obtained highest chitin conversion (70.3%) and TOC yield (57.4%), but amount of acetic acid (13.5%) and lactic acid (10.8%) was not different with MgO-2 and MgO-5. When compared physical property of each chitin such as specific surface area, MgO-1 (13–19 m^2/g), MgO-2 (7–8 m^2/g) and MgO-5 (28–38 m^2/g). From the result could indicate that specific surface area of MgO catalyst was not attributed with lactic acid production.

Table 4.9 The effect of other catalyst on chitin conversion

Catalyst	TOC (%)	Product yield (%)	
		Acetic acid yield	Lactic acid
MgO	57.4	13.4	10.8
$Ca(OH)_2$	73.3	13.2	18.0
Na_2CO_3	80.9	14.6	16.0
Hydrotalcite	55.2	12.9	6.7
$CaCO_3$	63.8	13.1	15.5
$Mg(OH)_2$	57.2	13.8	8.2

Reaction conditions: 0.5 g ball-milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, 533 K reaction temperature, 6 h reaction time, and 0.5 g catalyst weight.

To proof assumption about basicity affected to production of lactic acid, $Ca(OH)_2$, Na_2CO_3, Hydrotalcite, $CaCO_3$, and $Mg(OH)_2$ were investigated to be catalyst in chitin conversion, the result showed in **Table 4.9**. $Ca(OH)_2$ showed highest lactic acid yield (18.0 %), which is strongly basic chemicals and low solubility in water. This result could confirm that basicity related with chitin conversion into lactic acid. However, $Ca(OH)_2$ obtained the highest yield of lactic acid, but $Ca(OH)_2$ catalyst was not friendly with environmental to recycle because pH of $Ca(OH)_2$ is high. In the next step still focused on MgO catalyst for chitin conversion.

Moreover, I also tested Mg(OH)$_2$ to be catalyst in chitin conversion, the result showed in **Table 4.9.** Mg(OH)$_2$ obtained TOC yield and amount of lactic acid in yield of 57.2 and 8.2 % respectively. However, when compared with MgO which, amount of lactic acid was 10.8 %, Mg(OH)$_2$ showed similar with lactic acid yield in MgO. This result indicated that Mg(OH)$_2$ and MgO could be increased amount of lactic acid.
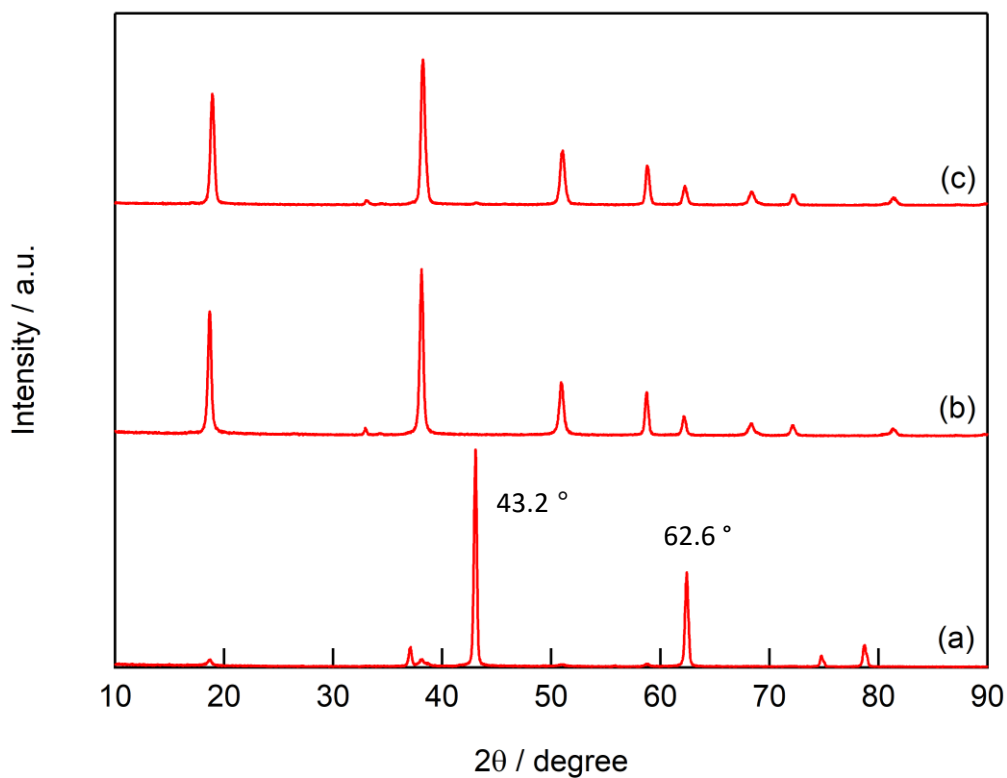
Figure 4.5 XRD patterns of (a) MgO catalyst (b) solid residue from chitin conversion reaction (condition : 0.5 g ball milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, 533 K reaction temperature, and 6 h reaction time 0.5 g MgO) ,and (c) $Mg(OH)_2$ [32].

Figure 4.5 showed XRD patterns of MgO catalyst, solid residue from chitin conversion reaction (0.5 g ball milled chitin, 50 g water, 533 K reaction temperature 0.5 g catalyst weight), and $Mg(OH)_2$. Xrd pattern of MgO showed important peak at 2θ of 43.2 and 62.6 degrees, which related with the crystalline planes of (002) and (022) respectively [116]. In addition, XRD pattern of the dry solid residue from chitin conversion showed similarity with XRD pattern of $Mg(OH)_2$ reference, which indicated that MgO was converted to $Mg(OH)_2$ by hydrolysis reaction on conversion of chitin.

a

b

(a) (b) (c)

(d) (e) (f)
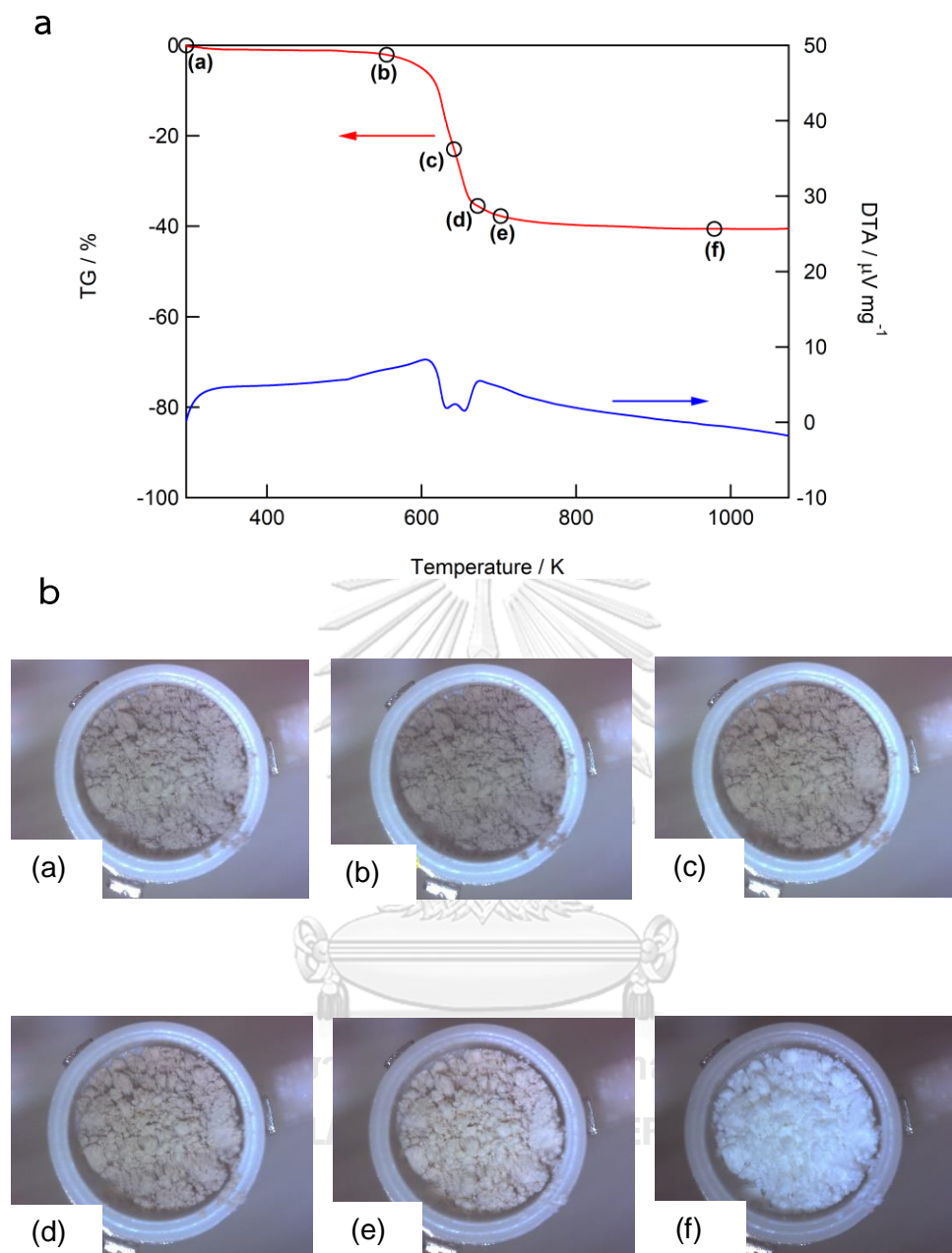
Figure 4.6 Characterization of TG-DTA (a) TG-DTA curves of solid residue (condition :

0.5 g ball milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, 533 K reaction

temperature, and 6 h reaction time, and 0.5 g MgO) (b) picture of samples from TG-

DTA analysis. [32]

Figure 4.6 showed TG-DTA curves of solid residue and picture of samples from TG-DTA analysis. TG-DTA in dry air was used to analyze property of solid residue from chitin conversion, and picture of sample were reported in real time during the analysis. After chitin conversion reaction, color of solid residue was brown. At temperature around 600 to 680 K, weight of sample was lost, which related with MgO was hydrolyzed to $Mg(OH)_2$ [116, 117]. These result related with characterization of solid residue by using XRD. However, at 680 K picture of sample showed sample color was still brown (**Figure 4.5(b)-d**). The solid residue was more heated the color became to white solid at 1000 K. This result suggested that carbonaceous substance or coke on surface was decomposed by heating at temperature more than 680 K. This result found that solid residue after conversion of chitin was $Mg(OH)_2$ and coke on $Mg(OH)_2$ surface.
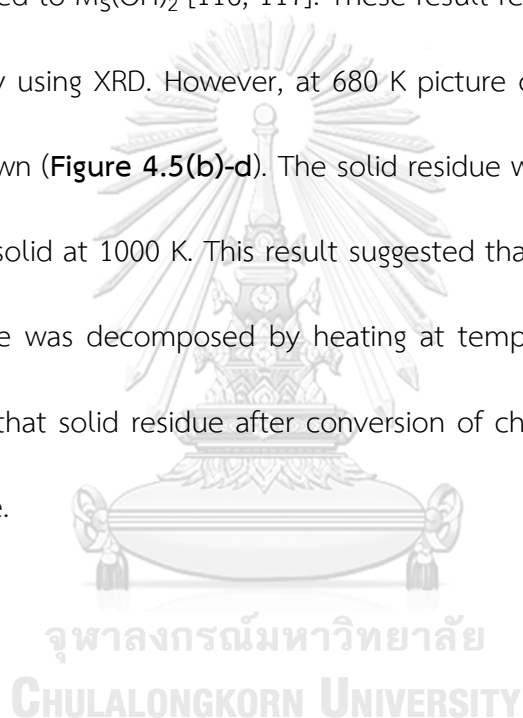
4.3.1 Reaction condition of chitin conversion with catalyst

To produce high lactic acid yield, reaction time, reaction temperature, and amount of catalyst were investigated to find optimal condition.

Reaction time for chitin conversion by using MgO catalyst were investigated to find the optimal reaction condition. Reaction time in range 1-10 h was studied. At reaction time 6 h showed high TOC yield (10.8 %) and chitin conversion (71.6%), the result showed in **Table 4.7**. TOC yield improved from 8.6 to 10.8% with increasing of reaction time 1 to 6 h attributed with conversion of chitin increased from 20.3 to 67.0 %. However, when increased reaction time to 10 h, lactic acid yield decreased to 8.4 % because organic carbon compound such as acetic acid and lactic acid might decompose at longer reaction time.
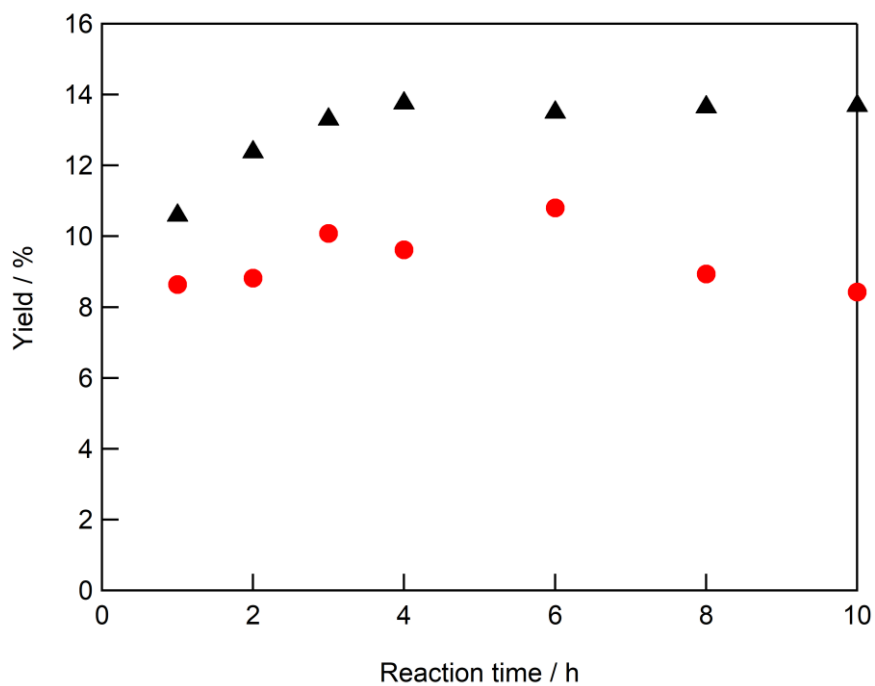
Figure 4.7 The effect of reaction time and product chitin conversion product: lactic

acid yield (red circle) acetic acid (black triangle) at condition: 0.5 g ball milled chitin

(Chitin reagent from Wako Co. Ltd), 50 g water, 533 K reaction temperature 0.5 g MgO

[32].

Table 4.10 The effect of reaction temperature on chitin conversion without catalyst

Reaction temperature (h)	Conversion (%)	TOC (%)	Product yield (%)		
			5-HMF	Acetic acid	Lactic acid
473	15.4	24	0.23	5.9	2.7
513	44.5	44.5	0	11.4	10.4
533	70.3	57.4	0	13.5	10.8
553	78.8	68.3	0	14.4	6.7

Reaction conditions: Chitin reagent from Wako Co. Ltd. 0.5 g ball-milled chitin (Chitin reagent from Wako Co. Ltd), 50 g water, 6 h reaction time, 0.5 g MgO

In the next step I tried to find optimal condition for conversion of chitin conversion without catalyst. The parameter was reaction temperature. Reaction temperature in range 473-553 K was studied. 533 K showed high lactic acid yield (10.8%), the result showed in **Table 4.10**. lactic acid yield improved from 2.7 to 10.8% with increasing of reaction temperature 473 to 533 K attributed with conversion of chitin increased from 15.4 to 70.3 %. However, when increased temperature to 553 K lactic acid yield decreased (6.7 %) probably because of decomposition organic carbon compound at the high reaction temperature

Table 4.11 The effect of MgO weight on chitin conversion

Weight of catalyst (%wt.)	TOC (%)	Yield / %	
		Acetic acid	Lactic acid
1	57.4	13.5	10.8
0.5	57.1	12.9	9.1
2	57.8	12.9	10.5

Reaction conditions: Chitin reagent from Wako Co. Ltd. 0.5 g ball-milled chitin, 50 g water, 6 h reaction time, and 533 K reaction temperature

Table 4.11 showed investigation of amount of MgO in range 0.5-2 %wt. on chitin conversion, 1 %wt of MgO showed highest TOC yield and lactic acid yield (57.4 and 10.8 %), although the effect of catalyst weight on lactic acid production from chitin was small.

Table 4.12 The effect of chitin type from several companies on chitin conversion [99]

Reactant	TOC (%)	Yield (%)		
		Acetic acid	Lactic acid	5-HMF
1st grade (FUJIFILM Wako Pure Chemical)	57.4	13.5	10.8	0.0
Practical grade (Toronto Research Chemicals)	56.0	12.7	8.4	0.0
Unbleached grade (MP Biomedicals)	56.1	13.2	10.5	0.0
Chitosan (Sigma-Aldrich)	51.1	5.5	9.5	0.0

Reaction conditions:. 0.5 g starting material, 50 g water, 533 K reaction temperature 6 h reaction time, 0.5 g MgO.

Various types of chitin was investigated, which were got from several companies. In addition, chitosan was tested as a control condition, the result showed in **Table 4.12**. Practical-grade chitin from Toronto Research Chemicals obtained lowest lactic acid yield, but the difference was not large.

4.4 Reaction mechanism of chitin conversion by using hot compressed water

Figure 4.8 showed proposed reaction mechanism of chitin conversion reaction to produce lactic acid. *N*-acetyl-D-glucosamine obtained from chitin by hydrolysis reaction, and *N*-acetyl-D-glucosamine was converted to D-glucosamine by deacetylation reaction. However, chitosan can obtain from chitin by deacetylation reaction, and then the chitosan is converted to D-glucosamine by hydrolysis reaction. D-glucose is obtained from D-glucosamine (previous step) by deamination reaction, and D-glucose could be convert to fructose and ammonia gas.
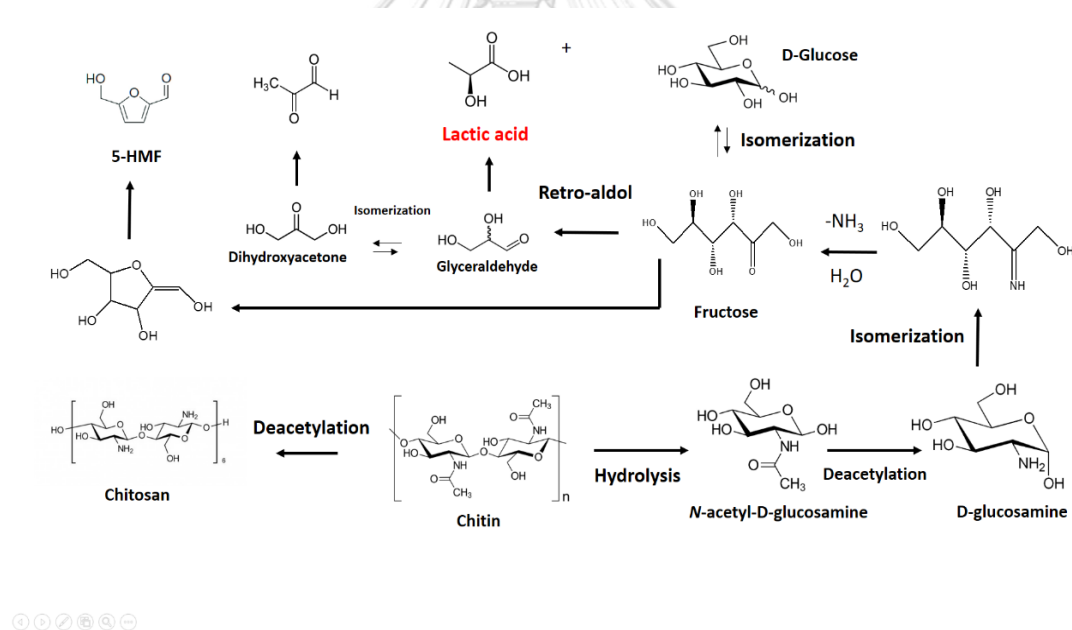
Figure 4.8 Proposed reaction mechanism for chitin conversion to lactic acid. [32]

Tube for detect nitrogen species was used to analyzed gas product. Before

using the tube showed yellow color, and after used to identify the gas product, tube

color became to pink. This result showed that ammonia gas was composition of gas

product. However, NO_x was not found in gas product. (**Figure 4.9**). Ammonia gas was

found in gas product, confirm deamination step in reaction mechanism. From

previous research indicated that D-glucosamine was converted to imine by

isomerization reaction, and then the imine was converted to D-glucose by

deamination reaction [118]. However, we cannot detected imine in our product

because imine may not stable in our system.

(a)

After

Before

(b)

After

Before

Figure 4.9 Tubes for detect nitrogen species (a) NH_3 and (b) NO_x [32]

In addition, *N*-acetyl-D-glucosamine, D-glucosamine, and D-glucose were investigated in conversion reaction by using MgO catalyst. (**Table 4.13**) Lactic acid yield of chitin and *N*-acetyl-D-glucosamine showed almost similar, but D-glucosamine and D-glucose showed higher lactic acid yield. From the result indicated that chitin conversion reaction to lactic acid produce D-glucosamine and D-glucose in reaction pathway.

Table 4.13 The effect of N-acetyl-D-glucosamine conversion, D-glucosamine conversion, and D-glucose conversion (0.5 g in 50 g of water 533 K for 6 h) without MgO (0.5 g) and with MgO [99].

		Yield / %	
Reactant	Catalyst	Acetic acid	Lactic acid
N-Acetyl-D-glucosamine	None	14.6	0.5
N-Acetyl-D-glucosamine	MgO	14.8	7.7
D-Glucosamine	None	–	2.0
D-Glucosamine	MgO	–	23.3
D-Glucose	No	–	7.0
D-Glucose	MgO	–	35.6
Chitin	MgO	13.5	10.8

Reaction conditions: 0.5 g ball-milled chitin, 50 g water, 533 K reaction temperature 0.5 g MgO.

From literature reported that D-glucose was isomerized to fructose by using base catalyst [119-121]. In addition, $Mg(OH)_2$ increased the isomerization reaction [103].In chitin conversion system, we used MgO and $Mg(OH)_2$ (MgO is hydrolyzed to $Mg(OH)_2$) could be increase isomerization reaction. In next step, glyceraldehyde and dihydroxyacetone were obtained from fructose by retro-aldol reaction, which enhanced by base catalyst [103, 122]. From previous research lactic acid could be converted from dihydroxyacetone and glyceraldehyde in water solvent [31].

Figure 4.10 Tubes for detect nitrogen species (a) NH_3 and (b) NO_x [32]

Table 4.14 Reuse of the MgO-1 catalyst (0.5 g) for conversion of aqueous chitin (0.5 g in 50 g of water) to lactic acid at 533 K for 6 h [99].

Recycle time	TOC (%)	Yield / %	
		Acetic acid	Lactic acid
1st use	57.4	13.5	10.8
2nd use	59.3	13.7	10.4
3rd use	62.9	14.1	10.1

Reaction conditions: Chitin reagent from Wako Co. Ltd. 0.5 g ball-milled chitin, 50 g water, 533 K reaction temperature 0.5 g catalyst weight.

Reusability of MgO catalyst was studied. After chitin conversion reaction, mixed liquid from the reaction was filtered to separate in two fraction (liquid fraction and solid fraction) and then solid fraction or solid residue was dried at 373 K overnight and then the solid residue was used to be catalyst for recycle process. (**Table 4.14**). From recycle reaction, lactic acid yield in second and third times was not different with first times. Inductively coupled plasma analysis was used to analyze amount of Mg leaching in liquid product. In first reaction (**Table 4.14**) showed amount of Mg 15% was leached from MgO catalyst. In addition, amount of Mg was checked in 0.5 g MgO mixed with 50 g water at 533 K for 6 h. The result showed amount of Mg only 4.8%. From result indicated that leaching of Mg was not affected to product yield (lactic acid or acetic acid) because amount of MgO had little effect to lactic acid yield and acetic acid yield.

CHAPTER V

RESULT AND DISCUSSION

5.1 The effect of mall milled pre-treatment

In this section, we investigated effect of ball milled pretreatment on conversion of chitin by using hot compressed water. I found that ball milling pretreatment could increase conversion of chitin. Ball milled chitin at 24 h and 48 h obtained conversion of chitin 55.0 and 56.6 % respectably which higher conversion than chitin without ball milled pretreatment (49%). From the result indicated that the crystallinity of the chitin had been reduced by the ball milling pretreatment. This method could destroy the crystallinity by breaking hydrogen bonds in chitin.

5.2 Chitin conversion into lactic acid by hot compressed water without catalyst

In this part, I applied hot compressed water method for chitin conversion. I found that this method could directly convert chitin to other chemical such as acetic acid, 5-Hydroxymethylfurfural and lactic acid at temperature 533 K for 16h. However, the yield of lactic acid from water solvent without catalyst show a low percent yield. Thus, the result of this result showed that using only hot compressed water was not enough for chitin conversion into lactic acid because the reaction should be used catalyst to increase selectivity of lactic acid.

5.3 Chitin conversion into lactic acid by hot compressed water by using catalyst

I have successfully converted chitin into lactic acid using simple metal oxide as a catalyst. MgO had higher catalytic performance for chitin conversion into lactic acid than other metal oxide. The optimal condition of chitin conversion into lactic acid from MgO was carried out at reaction temperature 533 K, reaction time 6 h, amount of catalyst 1 %wt., 50 mL of water solvent, and 0.5 g ball milled chitin. All metal oxides were also measure pH before and after reaction. The result show that MgO showed highest pH before and after reaction. The correlation of lactic acid yield and catalysts depended on basicity of the catalysts.

5.4 Reaction mechanism of chitin conversion by using hot compressed water

In this part, we investigated reaction mechanism of chitin conversion by using hot compressed water. Reaction mechanism depend on strongly basic of MgO. Thus, conversion of D-glucose to fructose was increased by using MgO or $Mg(OH)_2$. Conversion of fructose to glyceraldehyde and dihydroxyacetone was enhanced by using MgO or $Mg(OH)_2$. Ammonia gas could be confirmed occurring in the system by tube detection. D-glucosamine or D-glucose were produced in chitin conversion reaction to obtain lactic acid. MgO catalyst showed good resistibility which high lactic acid yield in 3 recycle times.

5.5 Suggestion and Recommendation

Some aspects of chitin conversion into lactic acid need futher investigated as the following:

5.5.1 The effect of mall milled pre-treatment

However, the use of ball milled pretreatment could increase chitin conversion but I studied only one method for pretreatment of chitin. Therefore, exploration of other method or new method is required for further study.

5.5.2 Chitin conversion into lactic acid by hot compressed

The catalytic process for chitin conversion into lactic acid is very importance because the process can directly convert non-edible chitin into lactic acid. The result of experimental showed that the yield of lactic acid depended on base sites of catalyst. Therefore, the future work should find the new preparation method for synthesis MgO or mixed MgO with other catalyst, and method for characterization to more understand active site and reaction mechanism.

REFERENCES

[1] S.T. Pham, M.B. Nguyen, G.H. Le, T.D. Nguyen, C.D. Pham, T.S. Le, T.A. Vu, Influence of brønsted and lewis acidity of the modified Al-MCM-4 1 solid acid on cellulose conversion and 5-hydroxylmethylfurfuran selectivity, Chemosphere, 265 (2021) 129062.

[2] K. Kumar, V. Khatri, S. Upadhyayula, H.K. Kashyap, Cellulose conversion to biofuel precursors using conjugated ionic liquid catalyst: An experimental and DFT study†, Applied Catalysis A: General, 610 (2021) 117951.

[3] L. Zhang, Y. Tian, Y. Wang, L. Dai, Enhanced conversion of a-cellulose to 5-HMF in aqueous biphasic system catalyzed by FeCl3-CuCl2, Chinese Chemical Letters, (2021).

[4] N. Rey-Raap, L.S. Ribeiro, J.J.d.M. Órfão, J.L. Figueiredo, M.F.R. Pereira, Catalytic conversion of cellulose to sorbitol over Ru supported on biomass-derived carbon-based materials, Applied Catalysis B: Environmental, 256 (2019) 117826.

[5] H. Kobayashi, H. Ohta, A. Fukuoka, Conversion of lignocellulose into renewable chemicals by heterogeneous catalysis, Catalysis Science & Technology, 2 (2012) 869-883.

[6] I. Agirrezabal-Telleria, I. Gandarias, P.L. Arias, Heterogeneous acid-catalysts for the production of furan-derived compounds (furfural and hydroxymethylfurfural) from renewable carbohydrates: A review, Catalysis Today, 234 (2014) 42-58.

[7] A. Yamaguchi, N. Mimura, M. Shirai, O. Sato, One-pot conversion from lignocellulosic biomass to iosorbide, Journal of the Japan Petroleum Institute, 59 (2016) 155-159.

[8] A. Yamaguchi, O. Sato, N. Mimura, M. Shirai, One-pot conversion of cellulose to isosorbide using supported metal catalysts and ion-exchange resin, Catalysis Communications, 67 (2015) 59-63.

[9] H. Chen, X. Fu, Industrial technologies for bioethanol production from lignocellulosic biomass, Renewable and Sustainable Energy Reviews, 57 (2016) 468-478.

[10] I. Hamed, F. Özogul, J.M. Regenstein, Industrial applications of crustacean by-products (chitin, chitosan, and chitooligosaccharides): A review, Trends in Food Science & Technology, 48 (2016) 40-50.

[11] H. El Knidri, R. Belaabed, A. Addaou, A. Laajeb, A. Lahsini, Extraction, chemical modification and characterization of chitin and chitosan, International Journal of

Biological Macromolecules, 120 (2018) 1181-1189.

[12] N. Yan, X. Chen, Sustainability: Don't waste seafood waste, Nature, 524 (2015) 155-157.

[13] X. Chen, H. Yang, N. Yan, Shell Biorefinery: Dream or Reality?, Chemistry – A European Journal, 22 (2016) 13402-13421.

[14] F.M. Kerton, Y. Liu, K.W. Omari, K. Hawboldt, Green chemistry and the ocean-based biorefinery, Green Chemistry, 15 (2013) 860-871.

[15] X. Chen, N. Yan, Novel Catalytic systems to convert chitin and lignin into valuable chemicals, Catalysis Surveys from Asia, 18 (2014) 164-176.

[16] J.-K. Chen, C.-R. Shen, C.-H. Yeh, B.-S. Fang, T.-L. Huang, C.-L. Liu, *N*-acetyl glucosamine obtained from chitin by chitin degrading factors in chitinbacter tainanesis, Int J Mol Sci, 12 (2011) 1187-1195.

[17] J. Zhang, N. Yan, Production of glucosamine from chitin by co-solvent promoted hydrolysis and deacetylation, ChemCatChem, 9 (2017) 2790-2796.

[18] W. Hou, L. Liu, H. Shen, Selective conversion of chitosan to levulinic acid catalysed by acidic ionic liquid: Intriguing NH_2 effect in comparison with cellulose, Carbohydrate Polymers, 195 (2018) 267-274.

[19] H.S. Kim, M.-R. Park, S.-K. Kim, G.-T. Jeong, Valorization of chitosan into levulinic acid by hydrothermal catalytic conversion with methanesulfonic acid, Korean Journal of Chemical Engineering, 35 (2018) 1290-1296.

[20] M.R. Park, H.S. Kim, S.K. Kim, G.T. Jeong, Production of levulinic acid from glucosamine using solid acid catalyst, Korean Chemical Engineering Research, 56 (2018) 61-65.

[21] Á. Szabolcs, M. Molnár, G. Dibó, L.T. Mika, Microwave-assisted conversion of carbohydrates to levulinic acid: an essential step in biomass conversion, Green Chemistry, 15 (2013) 439-445.

[22] M.R. Park, S.K. Kim, G.T. Jeong, Production of levulinic acid from glucosamine using zirconium oxychloride, Journal of Industrial and Engineering Chemistry, 61 (2018) 119-123.

[23]J. Vijayakumar, V. Thangavelu, A. Rajendran, Recent trends in the production, purification and application of lactic acid, Chemical & Biochemical Engineering Quarterly (cabeq@pbf.hr); Vol.22 No.2, 22 (2008).

[24] H. Jang, S.-H. Kim, D. Lee, S.E. Shim, S.-H. Baeck, B.S. Kim, T.S. Chang, Hydrogenation

of lactic acid to propylene glycol over a carbon-supported ruthenium catalyst, Journal of Molecular Catalysis A: Chemical, 380 (2013) 57-60.

[25] T.M. Aida, A. Ikarashi, Y. Saito, M. Watanabe, R.L. Smith, K. Arai, Dehydration of lactic acid to acrylic acid in high temperature water at high pressures, The Journal of Supercritical Fluids, 50 (2009) 257-264.

[26] A. Komesu, J.A.R.d. Oliveira, L.H.d.S. Martins, M.R. Wolf Maciel, R. Maciel Filho, Lactic acid production to purification: A review, BioResources; Vol 12, No 2 (2017), (2017).

[27] A.N. Vaidya, R.A. Pandey, S. Mudliar, M.S. Kumar, T. Chakrabarti, S. Devotta, Production and recovery of lactic acid for polylactide—An overview, Critical Reviews in Environmental Science and Technology, 35 (2005) 429-467.

[28] D. Zhou, D. Shen, W. Lu, T. Song, M. Wang, H. Feng, J. Shentu, Y. Long, Production of 5-Hydroxymethylfurfural from Chitin Biomass: A Review, Molecules, 25 (2020) 541.

[29] R. Auras, Poly(lactic acid), Encyclopedia of Polymer Science and Technology.

[30] S. Tanodekaew, M. Prasitsilp, S. Swasdison, B. Thavornyutikarn, T. Pothsree, R. Pateepasen, Preparation of acrylic grafted chitin for wound dressing application, Biomaterials, 25 (2004) 1453-1460.

[31] P. Wattanapaphawong, P. Reubroycharoen, A. Yamaguchi, Conversion of cellulose into lactic acid using zirconium oxide catalysts, RSC Adv., 7 (2017) 18561-18568.

[32] K. Kun-asa, P. Reubroycharoen, K. Yamazaki, N. Mimura, O. Sato, A. Yamaguchi, Magnesium oxide-catalyzed conversion of chitin to lactic acid, ChemistryOpen, 10 (2021) 307-307.

[33] J. Goldemberg, S. Teixeira Coelho, Renewable energy—traditional biomass vs. modern biomass, Energy Policy, 32 (2004) 711-714.

[34] S.R. Bull, Renewable energy today and tomorrow, Proceedings of the IEEE, 89 (2001) 1216-1226.

[35] I. Dincer, Renewable energy and sustainable development: a crucial review, Renewable and Sustainable Energy Reviews, 4 (2000) 157-175.

[36] M.S. Umar, T. Urmee, P. Jennings, A policy framework and industry roadmap model for sustainable oil palm biomass electricity generation in Malaysia, Renewable Energy, 128 (2018) 275-284.

[37] M.A. Nasution, T. Herawan, M. Rivani, Analysis of Palm Biomass as Electricity from

Palm Oil Mills in North Sumatera, Energy Procedia, 47 (2014) 166-172.

[38] A. Evans, V. Strezov, T.J. Evans, Sustainability considerations for electricity generation from biomass, Renewable and Sustainable Energy Reviews, 14 (2010) 1419-1427.

[39] D. Mohan, C.U. Pittman, P.H. Steele, Pyrolysis of wood/biomass for bio-oil: A critical review, Energy & Fuels, 20 (2006) 848-889.

[40] L. Dai, N. Zhou, H. Li, W. Deng, Y. Cheng, Y. Wang, Y. Liu, K. Cobb, H. Lei, P. Chen, R. Ruan, Recent advances in improving lignocellulosic biomass-based bio-oil production, Journal of Analytical and Applied Pyrolysis, 149 (2020) 104845.

[41] J. Laurijssen, M. Marsidi, A. Westenbroek, E. Worrell, A. Faaij, Paper and biomass for energy?: The impact of paper recycling on energy and CO_2 emissions, Resources, Conservation and Recycling, 54 (2010) 1208-1218.

[42] H.H. Khoo, Review of bio-conversion pathways of lignocellulose-to-ethanol: Sustainability assessment based on land footprint projections, Renewable and Sustainable Energy Reviews, 46 (2015) 100-119.

[43] M.J. Hülsey, Shell biorefinery: A comprehensive introduction, Green Energy & Environment, 3 (2018) 318-327.

[44] H. Zabed, S. Akter, J. Yun, G. Zhang, F. Awad, X. Qi, J. Sahu, Recent advances in biological pretreatment of microalgae and lignocellulosic biomass for biofuel production, Renewable and Sustainable Energy Reviews, 105 (2019) 105-128.

[45] T. Nussbaumer, Combustion and co-combustion of biomass: fundamentals, technologies, and primary measures for emission reduction, Energy & Fuels, 17 (2003) 1510-1521.

[46] A. Molino, S. Chianese, D. Musmarra, Biomass gasification technology: The state of the art overview, Journal of Energy Chemistry, 25 (2016) 10-25.

[47] X. Hu, M. Gholizadeh, Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialisation stage, Journal of Energy Chemistry, 39 (2019) 109-143.

[48] H. Yang, R. Yan, H. Chen, D.H. Lee, D.T. Liang, C. Zheng, Pyrolysis of palm oil wastes for enhanced production of hydrogen rich gases, Fuel Processing Technology, 87 (2006) 935-942.

[49] A. Demirbas, G. Arin, An Overview of biomass pyrolysis, Energy Sources, 24 (2002) 471-482.

[50] S. Behera, R. Singh, R. Arora, N.K. Sharma, M. Shukla, S. Kumar, Scope of algae as third generation biofuels, Frontiers in Bioengineering and Biotechnology, 2 (2015).

[51] F. Abnisa, A. Arami-Niya, W.M.A.W. Daud, J.N. Sahu, Characterization of Bio-oil and bio-char from pyrolysis of palm oil wastes, BioEnergy Research, 6 (2013) 830-840.

[52] H. Jiang, L. Song, Z. Cheng, J. Chen, L. Zhang, M. Zhang, M. Hu, J. Li, J. Li, Influence of pyrolysis condition and transition metal salt on the product yield and characterization via Huadian oil shale pyrolysis, Journal of Analytical and Applied Pyrolysis, 112 (2015) 230-236.

[53] Y.H. Chan, S. Yusup, A.T. Quitain, Y. Uemura, M. Sasaki, Bio-oil production from oil palm biomass via subcritical and supercritical hydrothermal liquefaction, The Journal of Supercritical Fluids, 95 (2014) 407-412.

[54] F. Xu, A. Khalaf, J. Sheets, X. Ge, H. Keener, Y. Li, Chapter three - phosphorus removal and recovery from anaerobic digestion residues, in: Y. Li, X. Ge (Eds.) Advances in Bioenergy, Elsevier2018, pp. 77-136.

[55] J.-L. Zheng, M.-Q. Zhu, J.-L. Wen, R.-c. Sun, Gasification of bio-oil: Effects of equivalence ratio and gasifying agents on product distribution and gasification efficiency, Bioresource Technology, 211 (2016) 164-172.

[56] M.H. Waldner, F. Vogel, Renewable production of methane from woody biomass by catalytic hydrothermal gasification, Industrial & Engineering Chemistry Research, 44 (2005) 4543-4551.

[57] Y. Rao, J. Wan, Y. Liu, I. Angelidaki, S. Zhang, Y. Zhang, G. Luo, A novel process for volatile fatty acids production from syngas by integrating with mesophilic alkaline fermentation of waste activated sludge, Water Research, 139 (2018) 372-380.

[58] C. Wang, J. Zhang, G. Qin, L. Wang, E. Zuidema, Q. Yang, S. Dang, C. Yang, J. Xiao, X. Meng, C. Mesters, F.-S. Xiao, Direct conversion of syngas to ethanol within zeolite crystals, Chem, 6 (2020) 646-657.

[59] Y. Lu, B. Cao, F. Yu, J. Liu, Z. Bao, J. Gao, High selectivity higher alcohols synthesis from syngas over three-dimensionally ordered macroporous Cu-Fe catalysts, ChemCatChem, 6 (2014) 473-478.

[60] J.R. Rostrup-Nielsen, Syngas in perspective, Catalysis Today, 71 (2002) 243-247.

[61] F.R. Amin, H. Khalid, H. Zhang, S.u. Rahman, R. Zhang, G. Liu, C. Chen, Pretreatment methods of lignocellulosic biomass for anaerobic digestion, AMB Express, 7 (2017) 72.

[62] M.A. Amezcua-Allieri, T. Sánchez Durán, J. Aburto, Study of chemical and enzymatic hydrolysis of cellulosic material to obtain fermentable sugars, Journal of Chemistry, 2017 (2017) 5680105.

[63] R. Naveed, M. Athar, S. Begum, S. Ahmed, S. Naveed, Simulation of circulating fluidized bed gasification for characteristic study of pakistani coal, Polish Journal of Chemical Technology, 17 (2015) 66.

[64] S. Farzad, M.A. Mandegari, J.F. Görgens, A critical review on biomass gasification, co-gasification, and their environmental assessments, Biofuel Research Journal, 3 (2016) 483-495.

[65] O.A. Alekseev, M.É. Shamsutdinov, F.K. Kutyshev, A.V. Kostochko, Combustion and heat properties of lignin–containing fuels, combustion, Explosion and Shock Waves, 37 (2001) 67-71.

[66] A. Gani, I. Naruse, Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass, Renewable Energy, 32 (2007) 649-661.

[67] G. Dorez, L. Ferry, R. Sonnier, A. Taguet, J.M. Lopez-Cuesta, Effect of cellulose, hemicellulose and lignin contents on pyrolysis and combustion of natural fibers, Journal of Analytical and Applied Pyrolysis, 107 (2014) 323-331.

[68] S. Brethauer, M.H. Studer, Biochemical conversion processes of lignocellulosic biomass to fuels and chemicals; A Review, CHIMIA International Journal for Chemistry, 69 (2015) 572-581.

[69] U. Bornscheuer, K. Buchholz, J. Seibel, Enzymatic degradation of (ligno) cellulose, angewandte chemie International Edition, 53 (2014) 10876-10893.

[70] G.P. Van Der Laan, A.A.C.M. Beenackers, Kinetics and selectivity of the fischer–tropsch synthesis: A Literature Review, Catalysis Reviews, 41 (1999) 255-318.

[71] R.P. Chandra, R. Bura, W.E. Mabee, A. Berlin, X. Pan, J.N. Saddler, Substrate pretreatment: The key to effective enzymatic hydrolysis of lignocellulosics?, in: L. Olsson (Ed.) Biofuels, Springer Berlin Heidelberg, Berlin, Heidelberg, 2007, pp. 67-93.

[72] S. Sun, S. Sun, X. Cao, R. Sun, The role of pretreatment in improving the enzymatic hydrolysis of lignocellulosic materials, Bioresource Technology, 199 (2016) 49-58.

[73] P. Kumar, D.M. Barrett, M.J. Delwiche, P. Stroeve, Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production, Industrial & Engineering Chemistry Research, 48 (2009) 3713-3729.

[74] Y. Sun, J. Cheng, Hydrolysis of lignocellulosic materials for ethanol production: a review, Bioresource Technology, 83 (2002) 1-11.

[75] E. Takács, L. Wojnárovits, C. Földváry, P. Hargittai, J. Borsa, I. Sajó, Effect of combined gamma-irradiation and alkali treatment on cotton–cellulose, Radiation Physics and Chemistry, 57 (2000) 399-403.

[76] S. Sasmal, K. Mohanty, Pretreatment of lignocellulosic biomass toward biofuel production, in: S. Kumar, R.K. Sani (Eds.) biorefining of biomass to biofuels: opportunities and perception, Springer International Publishing, Cham, 2018, pp. 203-221.

[77] C. Schmitz, L. González Auza, D. Koberidze, S. Rasche, R. Fischer, L. Bortesi, conversion of chitin to defined chitosan oligomers: current status and future prospects, Mar Drugs, 17 (2019).

[78] M. Rinaudo, Chitin and chitosan: Properties and applications, Progress in Polymer Science, 31 (2006) 603-632.

[79] R. Bloch, M.M. Burger, Purification of wheat germ agglutinin using affinity chromatography on chitin, Biochem Biophys Res Commun, 58 (1974) 13-19.

[80] F.J. Wolman, G.J. Copello, A.M. Mebert, A.M. Targovnik, M.V. Miranda, A.A. Navarro del Cañizo, L.E. Díaz, O. Cascone, Egg white lysozyme purification with a chitin-silica-based affinity chromatographic matrix, Eur Food Res Technol, 231 (2010) 181-188.

[81] M.M.T. Namboodiri, K. Pakshirajan, Chapter 10 - Valorization of waste biomass for chitin and chitosan production, in: T. Bhaskar, A. Pandey, E.R. Rene, D.C.W. Tsang (Eds.) Waste Biorefinery, Elsevier2020, pp. 241-266.

[82] K. Rufato, J. Galdino, K. Ody, A. Pereira, E. Corradini, A. Martins, A. Paulino, A. Fajardo, F. Aouada, F. Porta, A. Rubira, E. Muniz, Hydrogels Based on chitosan and chitosan derivatives for biomedical applications, 2018, pp. 1-40.

[83] T. Chandy, C.P. Sharma, Chitosan-as a biomaterial, biomaterials, Artificial Cells and Artificial Organs, 18 (1990) 1-24.

[84] L.J. Min, T.Y.S. Edgar, Z. Zicheng, Y.W. Yee, Chapter 6 - Biomaterials for Bioprinting, in: L.G. Zhang, J.P. Fisher, K.W. Leong (Eds.) 3D Bioprinting and Nanotechnology in Tissue Engineering and Regenerative Medicine, Academic Press2015, pp. 129-148.

[85] M.H. Mohammed, P.A. Williams, O. Tverezovskaya, Extraction of chitin from prawn shells and conversion to low molecular mass chitosan, Food Hydrocolloids, 31 (2013) 166-171.

[86] X. Gao, X. Chen, J. Zhang, W. Guo, F. Jin, N. Yan, Transformation of chitin and waste shrimp shells into acetic acid and pyrrole, ACS Sustainable Chemistry & Engineering, 4 (2016).

[87] W. Hou, Q. Zhao, L. Liu, Selective conversion of chitin to levulinic acid catalyzed by ionic liquids: distinctive effect of N-acetyl groups, Green Chemistry, (2019).

[88] Y. Wang, W. Deng, B. Wang, Q. Zhang, X. Wan, Z. Tang, Y. Wang, C. Zhu, Z. Cao, G. Wang, H. Wan, Chemical synthesis of lactic acid from cellulose catalysed by lead(II) ions in water, Nature Communications, 4 (2013) 2141.

[89] Y. Hou, Z. Lin, M. Niu, S. Ren, W. Wu, Conversion of cellulose into formic acid by Iron(III)-catalyzed oxidation with O_2 in acidic aqueous solutions, ACS Omega, 3 (2018) 14910-14917.

[90] S. Yu, H. Zang, S. Chen, Y. Jiang, B. Yan, B. Cheng, Efficient conversion of chitin biomass into 5-hydroxymethylfurfural over metal salts catalysts in dimethyl sulfoxide - water mixture under hydrothermal conditions, Polymer Degradation and Stability, 134 (2016) 105-114.

[91] F.D. Bobbink, J. Zhang, Y. Pierson, X. Chen, N. Yan, Conversion of chitin derived N-acetyl-d-glucosamine (NAG) into polyols over transition metal catalysts and hydrogen in water, Green Chemistry, 17 (2015) 1024-1031.

[92] Y. Pierson, X. Chen, F.D. Bobbink, J. Zhang, N. Yan, Acid-catalyzed chitin liquefaction in ethylene glycol, ACS Sustainable Chemistry & Engineering, 2 (2014) 2081-2089.

[93] T. Minowa, F. Zhen, T. Ogi, Cellulose decomposition in hot-compressed water with alkali or nickel catalyst, The Journal of Supercritical Fluids, 13 (1998) 253-259.

[94] T. Minowa, Z. Fang, T. Ogi, aacute, G. rhegyi, aacute, bor, Decomposition of Cellulose and Glucose in Hot-Compressed Water under Catalyst-Free Conditions,

JOURNAL OF CHEMICAL ENGINEERING OF JAPAN, 31 (1998) 131-134.

[95] Y. Yu, H. Wu, Effect of ball milling on the hydrolysis of microcrystalline cellulose in hot-compressed water, AIChE Journal, 57 (2011) 793-800.

[96] A. Kruse, E. Dinjus, Hot compressed water as reaction medium and reactant: Properties and synthesis reactions, The Journal of Supercritical Fluids, 39 (2007) 362-380.

[97] E.A. Elkhalifa, H.B. Friedrich, Magnesium oxide as a catalyst for the dehydrogenation of n-octane, Arabian Journal of Chemistry, 11 (2018) 1154-1159.

[98] L. Grenet, Injection de spins dans les semi-conducteurs, (2010).

[99] R. Ochoa, H. Van Woert, W.H. Lee, R. Subramanian, E. Kugler, P.C. Eklund, Catalytic degradation of medium density polyethylene over silica-alumina supports, Fuel Processing Technology, 49 (1996) 119-136.

[100] Y. Uemichi, M. Hattori, T. Itoh, J. Nakamura, M. Sugioka, Deactivation behaviors of zeolite and silica–alumina catalysts in the degradation of polyethylene, Industrial & Engineering Chemistry Research, 37 (1998) 867-872.

[101] J. Sepulveda, S. Teixeira, U. Schuchardt, Alumina-catalyzed epoxidation of unsaturated fatty esters with hydrogen peroxide, Applied Catalysis A: General, 318 (2007) 213-217.

[102] T. Hano, H. Takanashi, M. Hirata, K. Urano, S. Eto, Removal of phosphorus from wastewater by activated alumina adsorbent, Water Science and Technology, 35 (1997) 39-46.

[103] M. Gu, Z. Shen, W. Zhang, M. Xia, J. Jiang, W. Dong, X. Zhou, Y. Zhang, Hydrogenolysis of glucose into propylene glycol over Pt/SiO_2 @$Mg(OH)_2$ Catalyst, ChemCatChem, 12 (2020) 3447-3452.

[104] P. McKendry, Energy production from biomass (part 1): overview of biomass, Bioresource Technology, 83 (2002) 37-46.

[105] R. Abdullah, K. Ueda, S. Saka, Hydrothermal decomposition of various crystalline celluloses as treated by semi-flow hot-compressed water, Journal of Wood Science, 60 (2014) 278-286.

[106] J.M.R. Gallo, D.M. Alonso, M.A. Mellmer, J.A. Dumesic, Production and upgrading of 5-hydroxymethylfurfural using heterogeneous catalysts and biomass-derived solvents, Green Chemistry, 15 (2013) 85-90.

[107] T. Zhong, M.P. Wolcott, H. Liu, N. Glandon, J. Wang, The influence of pre-fibrillation via planetary ball milling on the extraction and properties of chitin nanofibers, Cellulose, 27 (2020) 6205-6216.

[108] M.-K. Jang, B.-G. Kong, Y.-I. Jeong, C.H. Lee, J.-W. Nah, Physicochemical characterization of **α**-chitin, **β**-chitin, and **γ**-chitin separated from natural resources, J. Polym. Sci. A. Polym. Chem., 42 (2004) 3423-3432.

[109] M.-K. Jang, B.-G. Kong, Y.-I. Jeong, C.H. Lee, J.-W. Nah, Physicochemical characterization of **α**-chitin, **β**-chitin, and **γ**-chitin separated from natural resources, Journal of Polymer Science Part A: Polymer Chemistry, 42 (2004) 3423-3432.

[110] H. Zhao, J.H. Kwak, Y. Wang, J.A. Franz, J.M. White, J.E. Holladay, Effects of crystallinity on dilute acid hydrolysis of cellulose by cellulose ball-Milling study, Energy Fuels, 20 (2006) 807-811.

[111] A. Yamaguchi, N. Hiyoshi, O. Sato, K.K. Bando, M. Shirai, Gaseous fuel production from nonrecyclable paper wastes using supported metal catalysts in high-temperature liquid water, ChemSusChem, 3 (2010) 737-741.

[112] R.S.C.M. de Queiroz Antonino, B.R.P. Lia Fook, V.A. de Oliveira Lima, R.Í. de Farias Rached, E.P.N. Lima, R.J. da Silva Lima, C.A. Peniche Covas, M.V. Lia Fook, Preparation and characterization of chitosan obtained from shells of shrimp (Litopenaeus vannamei Boone), Mar Drugs, 15 (2017) 141.

[113] J. Zhang, N. Yan, Production of Glucosamine from Chitin by Co-solvent promoted hydrolysis and deacetylation, ChemCatChem, 9 (2017) 2790-2796.

[114] M. Yabushita, H. Kobayashi, K. Kuroki, S. Ito, A. Fukuoka, Catalytic depolymerization of chitin with retention of *N*-Acetyl group, ChemSusChem, 8 (2015) 3760-3763.

[115] M. Lusardi, T. Struble, A.R. Teixeira, K.F. Jensen, Identifying the roles of acid–base sites in formation pathways of tolualdehydes from acetaldehyde over MgO-based catalysts, Catalysis Science & Technology, 10 (2020) 536-548.

[116] I.F. Mironyuk, V.M. Gun'ko, M.O. Povazhnyak, V.I. Zarko, V.M. Chelyadin, R. Leboda, J. Skubiszewska-Zieba, W. Janusz, Magnesia formed on calcination of $Mg(OH)_2$ prepared from natural bischofite, Appl. Surf. Sci., 252 (2006) 4071-4082.

[117] J.M. Hanlon, L.B. Diaz, G. Balducci, B.A. Stobbs, M. Bielewski, P. Chung, I. MacLaren, D.H. Gregory, Rapid surfactant-free synthesis of Mg(OH)$_2$ nanoplates and pseudomorphic dehydration to MgO, CrystEngComm, 17 (2015) 5672-5679.

[118] K.W. Omari, J.E. Besaw, F.M. Kerton, Hydrolysis of chitosan to yield levulinic acid and 5-hydroxymethylfurfural in water under microwave irradiation, Green Chem., 14 (2012) 1480-1487.

[119] C. Liu, J.M. Carraher, J.L. Swedberg, C.R. Herndon, C.N. Fleitman, J.-P. Tessonnier, Selective Base-catalyzed isomerization of glucose to fructose, ACS Catal., 4 (2014) 4295-4298.

[120] J.M. Carraher, C.N. Fleitman, J.-P. Tessonnier, Kinetic and mechanistic study of glucose isomerization using homogeneous organic brønsted base catalysts in water, ACS Catal., 5 (2015) 3162-3173.

[121] Q. Yang, M. Sherbahn, T. Runge, Basic amino acids as green catalysts for Isomerization of glucose to fructose in water, ACS Sustainable Chem. Eng., 4 (2016) 3526-3534.

[122] P. Yazdani, B. Wang, F. Gao, S. Kawi, A. Borgna, Role of the strong lewis base sites on glucose hydrogenolysis, ChemCatChem, 10 (2018) 3845-3853.
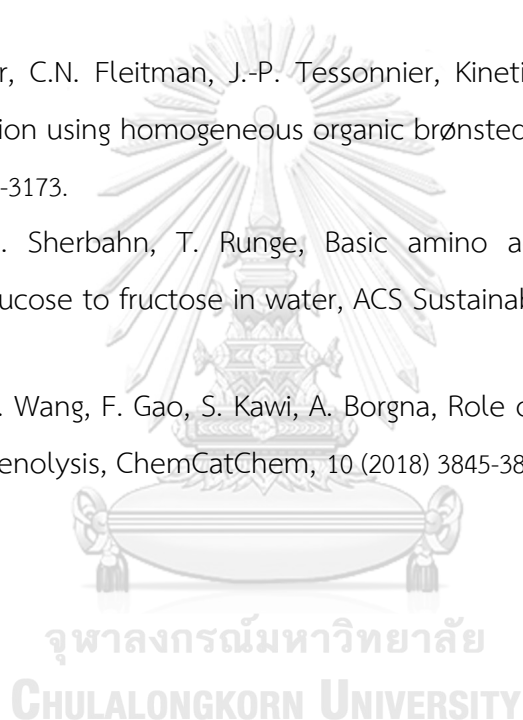
จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

APPENDIX

APPENDIX A

CHITIN CONVERSION

Table 1A.1 The data of experimental

Temperature (K)	Weight of reactant (g)	Weight of catalyst (g)	Weight solid residue (g)
473	0.5049	0.5065	0.7826
493	0.5018	0.5004	0.7563
513	0.5054	0.4935	0.7431
533	0.5057	0.5014	0.6290
553	0.5037	0.5000	0.5949

The chitin conversion was calculates by using equation (1)

$$\text{Conversion (\%)} = \left(1 - \frac{\text{Weight of solid residue}}{\text{Weight of initial substrate}}\right) \times 100 \qquad (1)$$

Calculation of reaction, temperature 473 K

Weight solid residue = 0.8900 g

Weight of solid catalyst = 0.5065 g

Weight of reactant = 0.5049 g

Water content = 9.53 %

Dry chitin (g) = $\left(\frac{(100)-(9.35)}{100}\right) \times 0.5049$ = 0.4577

Chitin conversion (%) = $\left(1 - \frac{(0.7826)-(0.5065)}{(0.4577)}\right) \times 100$

Therefore,

Chitin conversion = 39.68 %

APPENDIX B

CALCULATION OF PRODUCT YIELD

1.1 Example of product yield calculation

Table 1B.1 The data experimental

Temperature (K)	Weight of solvent (g)	Flask Weight (g)	Recovered Flask Weight (g)	Liquid for recovery (g)	Water in TOC (g)
473	50.46	72.8927	120.7813	47.8886	5.1485
493	50.32	71.8931	119.944	48.0509	5.155
513	50.07	72.8884	121.6115	48.7231	5.1325
533	50.21	62.2003	110.5367	48.3364	5.3815
553	50.21	66.3225	113.5382	47.2157	5.3815

Table 1B.1 (Continue) The data experimental

Temperature (K)	TC	IC	TOC (mg/L)	TOC (%)	C total (mol)
473	1723	102.3	1615.852	37.11	0.0064
493	2233	168.3	2058.845	47.74	0.0082
513	2459	179	2274.868	53.10	0.0092
533	2890	297.9	2586.619	59.86	0.0104
553	2606	410.3	3010.619	68.33	0.0118

Temperature (K)	5-HMF	N-Acetyl-D-glucosamine	D-Glucosamine	Levulinic acid	Lactic acid	Acetic acid
473	0	0	0	0	120872	201317
493	2359	0	0	0	174168	306229
513	0	0	0	0	193441	318117
533	0	0	0	0	176346	380726
553	0	0	0	0	125082	414369

Table 1B.1 (Continue) The data experimental

The product yield was calculated by using equation (1)

$$\text{Product yield (\%)} = \left(\frac{\text{moles of C in product}}{\text{moles of C in initial reactant}} \right) \times 100 \qquad (1)$$

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

1) Calculation of product yield from High performance liquid chromatography (HPLC)

In this case, we calculated the yield of Lactic acid at reaction temperature 473 K
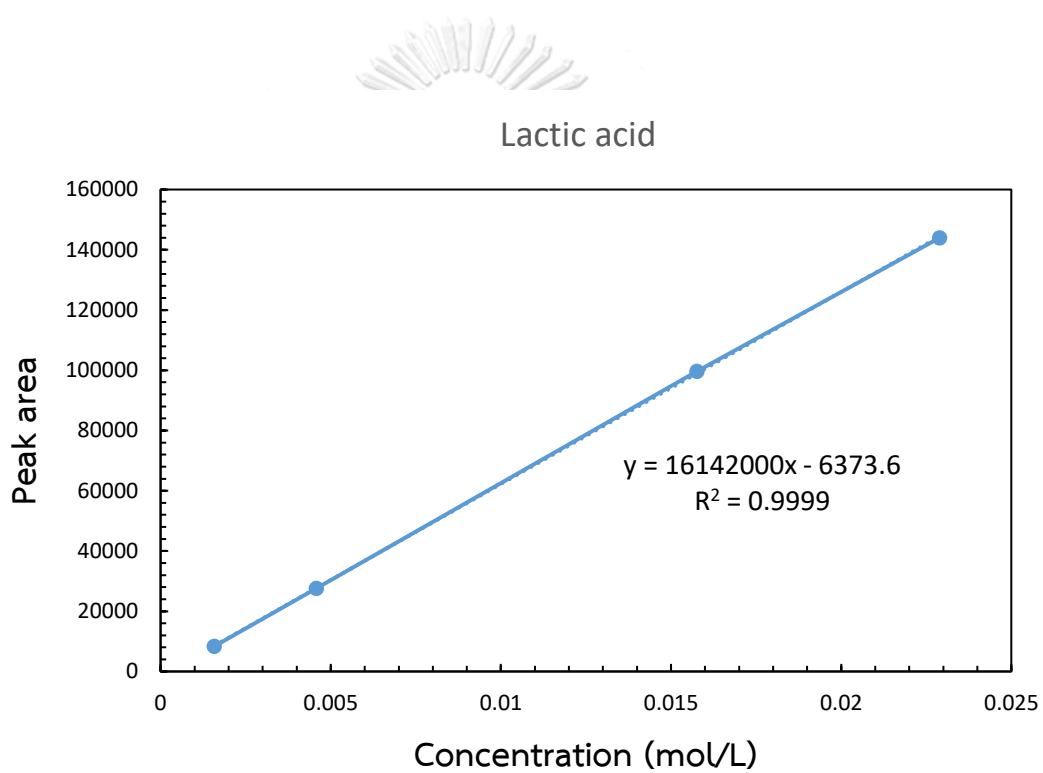
1.1 Calibration curve of standard sample

Lactic acid

$y = 16142000x - 6373.6$
$R^2 = 0.9999$

Figure 1B.1 Calibration curve of lactic acid

Concentration of lactic acid was calculate by equation (2)

y = 16142000x - 6373.6   (2)

x = Concentration of lactic acid (mol/L)

y = Peak area of lactic acid

<u>The data from experiment</u>

Peak area of lactic acid at temperature 473 K = 120,872

120872 = 16142000x - 6373.6

X = 0.007883 mol/L

1.2 Calculation of mole of carbon atom in product

Mole of carbon atom in product =

$$\left(\frac{(\text{Concentration of lactic acid}) \times (\text{Weight of liquid recovery})}{1000}\right) \times$$

Amount of carbon atom in product

<u>The data from experiment</u>

Weight of liquid recovery = 47.8886 g

Mole of carbon atom in product = $\left(\dfrac{(0.007883) \times (47.8886)}{1000}\right) \times 3$

Therefore,

Mole of carbon atom in product = 0.001132502

1.4) Product yield was calculated in equation (1)

Mole of carbon atom in chitin = **0.017377**

Therefore, From equation (1)

Product yield (%) = $\left(\dfrac{(0.001132502)}{0.017377} \right) \times 100$

Therefore,

Product yield of lactic acid = 6.52 %
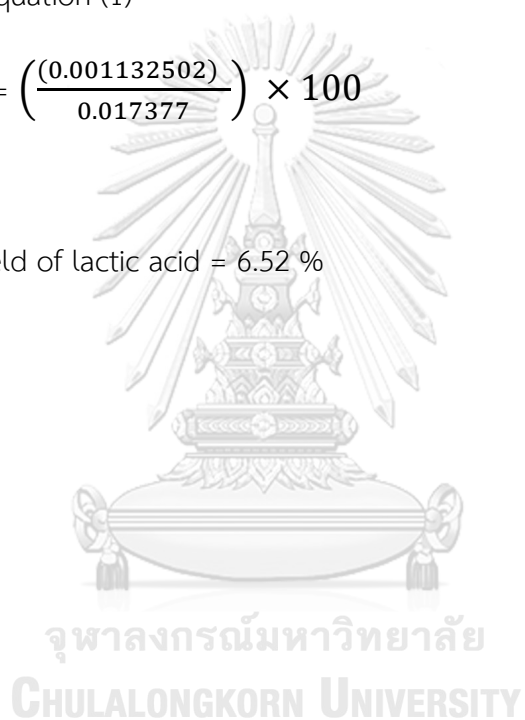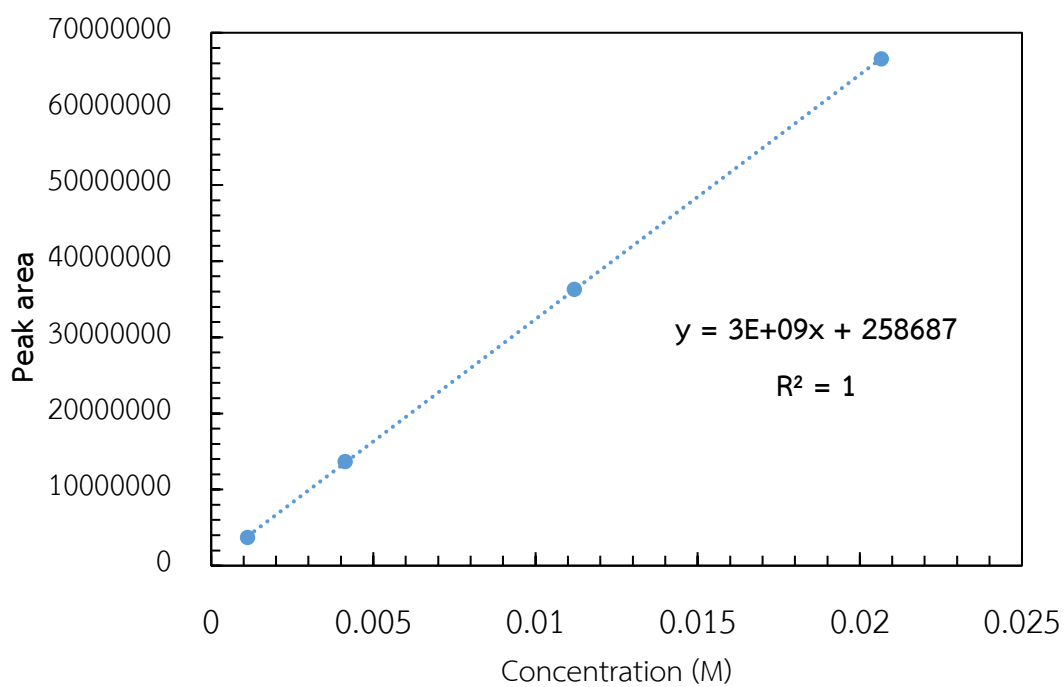
Figure 1B.2 Calibration curve of 5-HMF

Figure.1B.2 show HPLC calibration curve of 5-HMF. The calibration curve

show R^2 equal to 1. This calibration curve can use to measure amount of 5-HMF.

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY
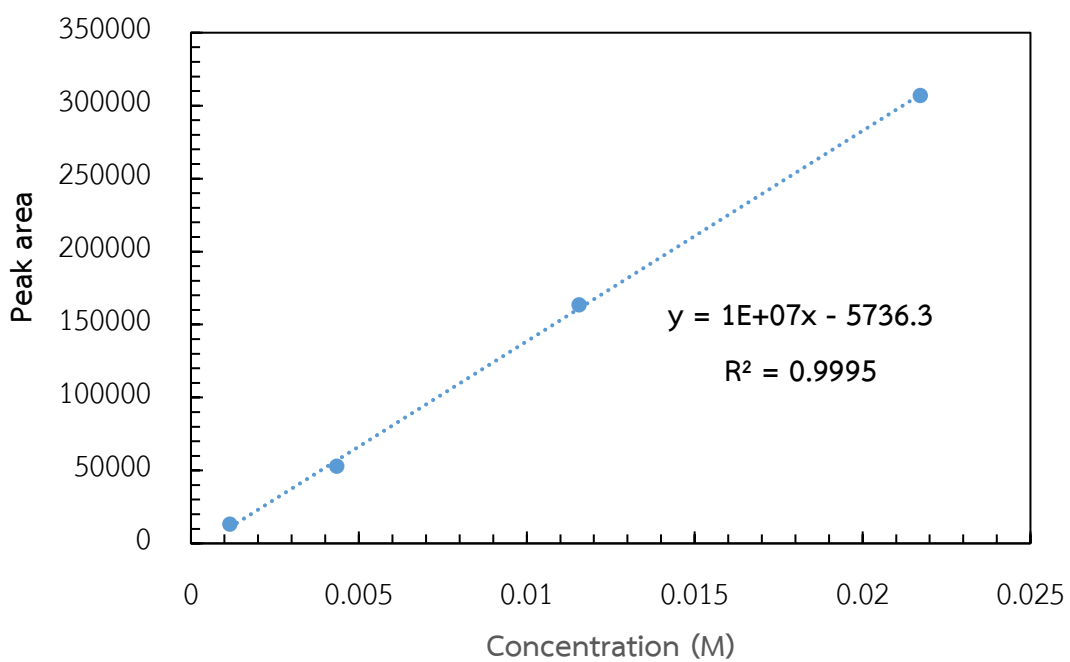
Figure 1B.3 Calibration curve of levulinic acid

Figure.1B.3 show HPLC calibration curve of levulinic acid. The calibration curve show R^2 equal to 0.9995. This calibration curve can use to measure amount of levulinic acid.

Figure 1B.4 Calibration curve of acetic acid

Figure.1B.4 show HPLC calibration curve of acetic acid. The calibration curve

show R^2 equal to 0.998. This calibration curve can use to measure amount of acetic

acid
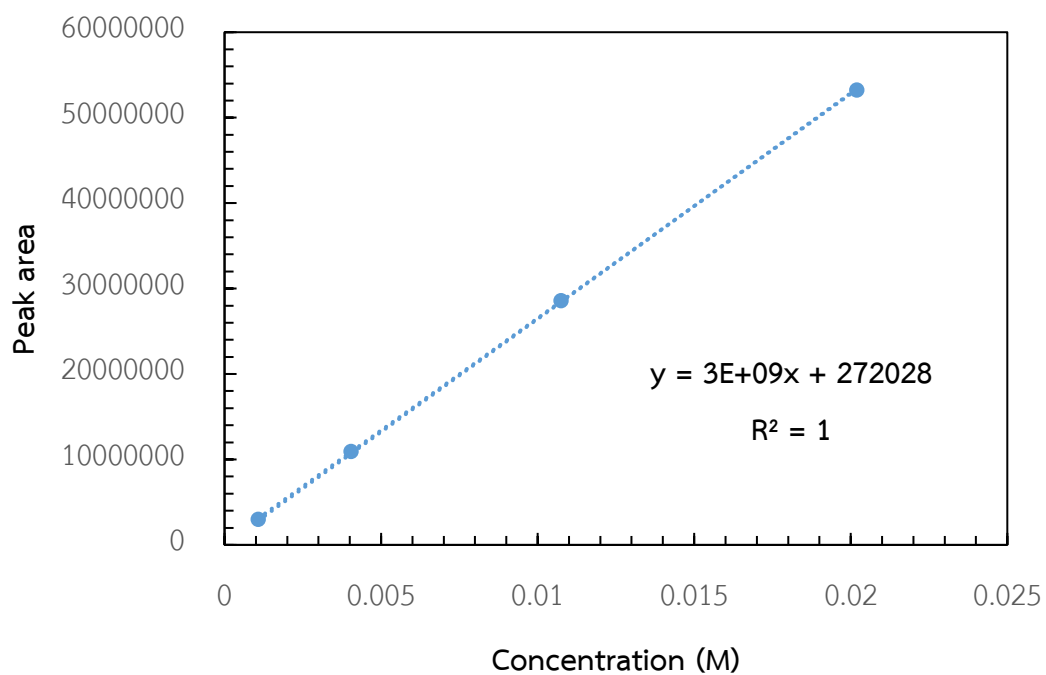
Figure 1B.5 Calibration curve of *N*-actyl-D-glucosamine

Fig.1B.5 show HPLC calibration curve of *N*-acetylglucosamine. The calibration curve show R^2 equal to 1. This calibration curve can use to measure amount of *N*-acetyl-D-glucosamine.
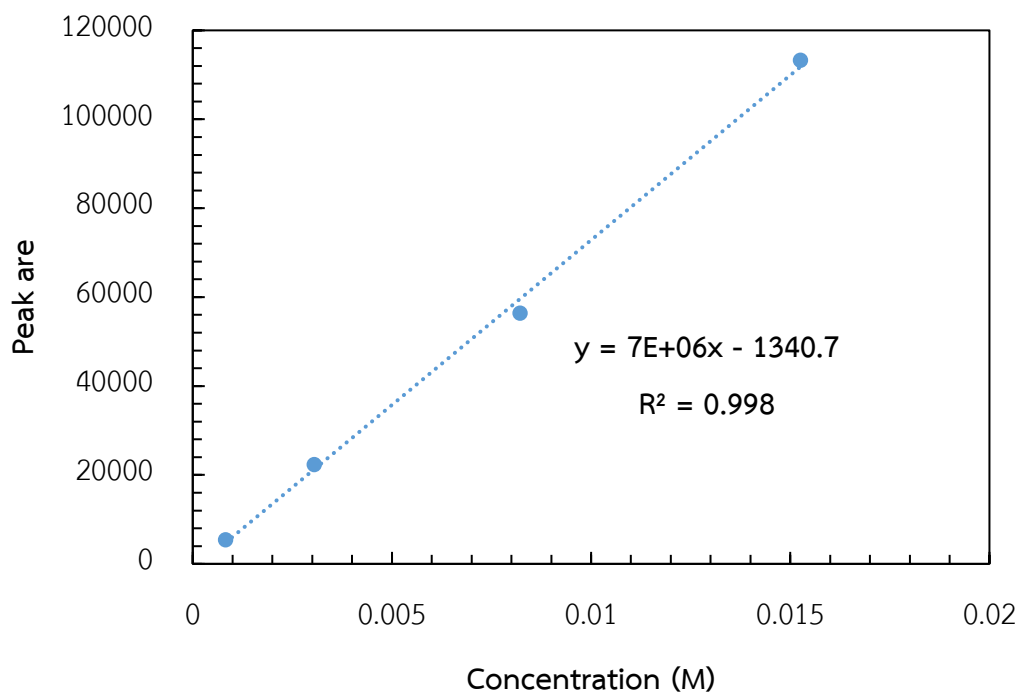
APPENDIX C

CALCULATION OF PRODUCT YIELD

Table 1C.1 The effect of ball milled pre-treatment

Ball milled time (hr)	Conversion (%)	TOC (%)	Product yield (%)				
			N-acetyl-glucosamine	Levulinic acid	5-HMF	Acetic acid	Lactic acid
0	14.9	10.4	-	-	0.9	2.1	0.8
24	55.0	30	-	-	0.9	3.6	1.1
48	56.6	36.9	-	-	1.6	8.7	1.3

Reaction conditions: 50 g water, 473 K reaction temperature, 16 h reaction time.

Type 1 = Chitin reagent from Wako Co. Ltd.

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

Table 1C.2 The effect of chitin type

Ball milled time (hr)	Conversion (%)	TOC (%)	Product yield (%)				
			N-acetyl-glucosamine	Levulinic acid	5-HMF	Acetic acid	Lactic acid
Type 1	14.89	10.4	-	-	0.86	2.06	0.78
Type 2	19.83	9.62	-	-	0.71	0.88	0.63
Type 3	17.06	9.82	-	-	0.49	0.67	0.58

Reaction conditions: 0.5 g ball-milled chitin, 50 g water, 473 K reaction temperature,

16 h reaction time. Type 1 = Chitin reagent from Wako Co. Ltd.

Type 1 = Chitin reagent from Wako Co. Ltd.

Type 2 = Chitin unbleached from MP Biomedicals

Type 3 = Chitin Pratical Grade Toronto research chemicals inc.

Table 1C.3 The effect of reaction temperature

Temperature (K)	Conversion (%)	TOC (%)	Product yield (%)				
			N-acetyl-glucosamine	Levulinic acid	5-HMF	Acetic acid	Lactic acid
473	50.18	31.7	-	-	1.3	6.4	1.1
483	48.63	28.1	-	-	0.9	10.2	3.0
493	60.56	43.1	-	-	0.8	10.2	2.5
503	74.68	36.5	-	-	0.7	13.6	3.1
513	79.83	44.1	-	-	0.7	13.9	3.3
533	84.79	49.5	-	-	0	14.6	1.5
553	84.56	45.9	-	-	0	14.4	0.9

Reaction conditions: 0.5 g ball-milled chitin, 50 g water, 16 h reaction time. Type 1

= Chitin reagent from Wako Co. Ltd.

Table 1C.4 The effect of reaction time

Reaction time (h)	Conversion (%)	TOC (%)	Product yield (%)				
			N-acetyl-glucosamine	Levulinic acid	5-HMF	Acetic acid	Lactic acid
2	20.3	30.2	-	-	0.4	0.2	0.4
4	30.6	36.5	-	-	0.2	0.5	0.5
6	67.0	55.3	-	-	1	9.3	3.1
16	73.0	54.4	-	-	0.5	12.2	3.0
24	81.6	39.4	-	-	0	13.8	3.2

Reaction conditions: Chitin reagent from Wako Co. Ltd. 0.5 g ball-milled chitin, 50 g

water, 533 K reaction temperature.

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

Table 1C.5 The effect of oxide catalyst

Catalyst	Conversion (%)	TOC (%)	Yield (%)				
			N-acetyl-glucosamine	Levulinic acid	5-HMF	Acetic acid	Lactic acid
None	89.8	49.5	-	-	-	14.6	1.5
Al_2O_3	53.1	51.9	-	-	-	14.5	6.2
ZrO_2	98	53.1	-	-	-	14.3	3.9
ZnO	99	50.5	-	-	-	13.9	3.4
CeO_2	99	53.2	-	-	-	14.1	0.7
TiO_2	99	46.4	-	-	-	13.1	0.4
SiO_2	99	47.6	-	-	-	13.1	1.4
MgO-1	70.3	57.4	-	-	-	13.5	10.8

Reaction conditions: Chitin reagent from Wako Co. Ltd. 0.5 g ball-milled chitin, 50 g water, 533 K reaction temperature, catalyst 0.5 g

Table 1C.6 The effect of other catalyst

Catalyst	TOC (%)	Yield (%)				
		N-acetyl-glucosamine	Levulinic acid	5-HMF	Acetic acid	Lactic acid
$Ca(OH)_2$	73.2	-	-	-	13.2	18.0
Na_2CO_3	80.9	-	-	-	14.6	16.0
Hydrotalcite	55.1	-	-	-	12.9	6.7
$CaCO_3$	63.8	-	-	-	13.1	15.5
$Mg(OH)_2$	57.2	-	-	-	13.8	8.2

Reaction conditions: Chitin reagent from Wako Co. Ltd. 0.5 g ball-milled chitin, 50 g

water, 533 K reaction temperature, catalyst 0.5 g

Table 1C.7 The effect of gardes of chitin and chitosan on conversion of chitin

Reactant	Conversion (%)	TOC (%)	Yield (%)				
			N-acetyl-glucosamine	Levulinic acid	Acetic acid	Lactic acid	5-HMF
1st grade (FUJIFILM Wako Pure Chemical)	70.3	57.4	-	-	13.5	10.8	0.0
Practical grade (Toronto Research Chemicals)	71.8	56.0	-	-	12.7	8.4	0.0
Unbleached grade (MP Biomedicals)	69.2	56.1	-	-	13.2	10.5	0.0
Chitosan (Sigma-Aldrich)	63.4	51.1	-	-	5.5	9.5	0.0

Reaction conditions: 0.5 g ball-milled chitin, 50 g water, 533 K reaction temperature, catalyst 0.5 g

Table 1C.8 The effect of type of chitin and chitosan

Reactant	Catalyst	Conversion (%)	TOC (%)
N-Acetyl-D-glucosamine	None	92.4	42.0
N-Acetyl-D-glucosamine	MgO	71.0	55.0
D-Glucosamine	None	94.4	78.3
D-Glucosamine	MgO	98.0	71.6
D-Glucose	No	98.0	72.6
D-Glucose	MgO	74.8	67.2

Reaction conditions: 0.5 g starting material, 50 g water, 533 K reaction temperature,

catalyst 0.5 g

Table 1C.8 The effect of type of chitin and chitosan (continue)

Reactant	Catalyst	Yield (%)			
		N-acetyl-glucosamine	Levulinic acid	Acetic acid	Lactic acid
N-Acetyl-D-glucosamine	None	-	-	14.6	0.5
N-Acetyl-D-glucosamine	MgO	-	-	14.8	7.7
D-Glucosamine	None	-	-	–	2.0
D-Glucosamine	MgO	-	-	–	23.3
D-Glucose	No	-	-	–	7.0
D-Glucose	MgO	-	-	–	35.6
Chitin	MgO	-	-	13.5	10.8

Reaction conditions: 0.5 g starting material, 50 g water, 533 K reaction temperature,

catalyst 0.5 g

จุฬาลงกรณ์มหาวิทยาลัย

CHULALONGKORN UNIVERSITY

APPENDIX D

REACTION MECHANISM
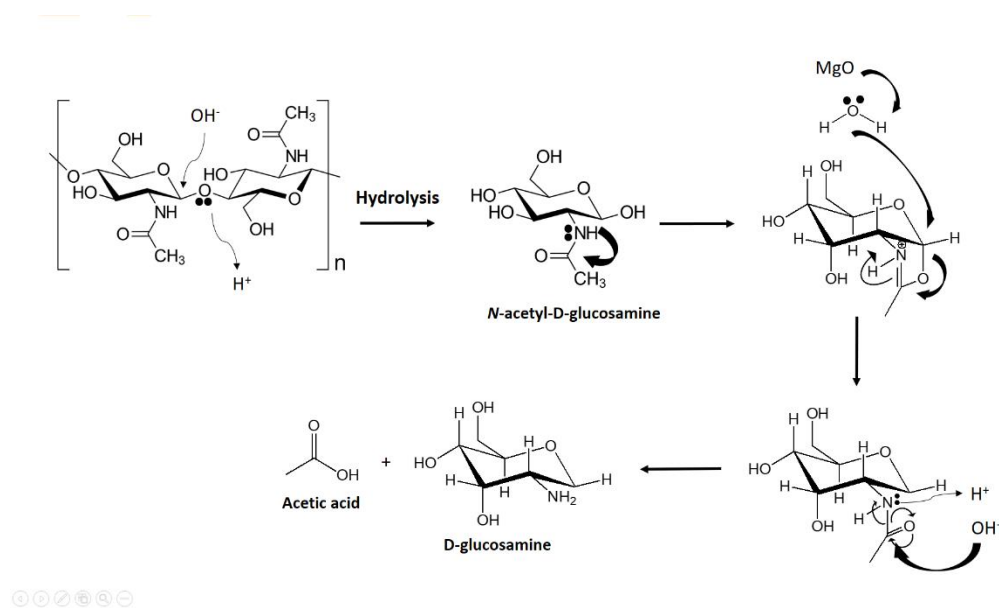
Reaction mechanism of chitin conversion to lactic acid

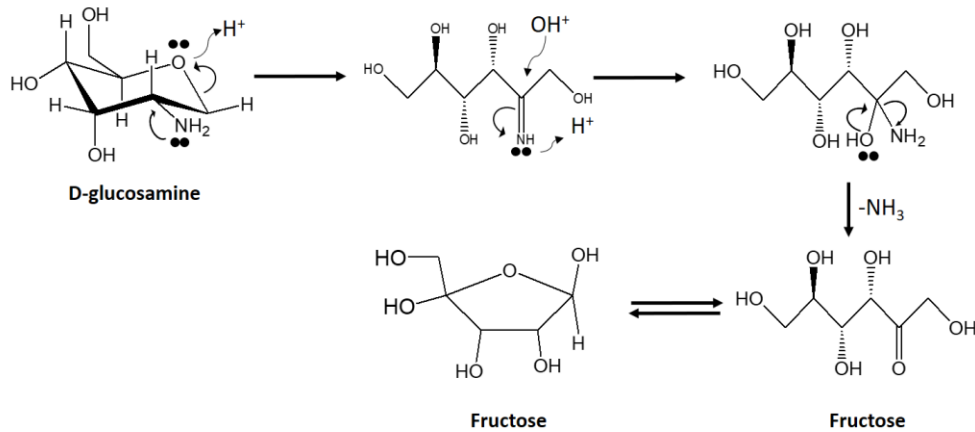**Figure 1D.1** Reaction mechanism of chitin to D-glucosamine

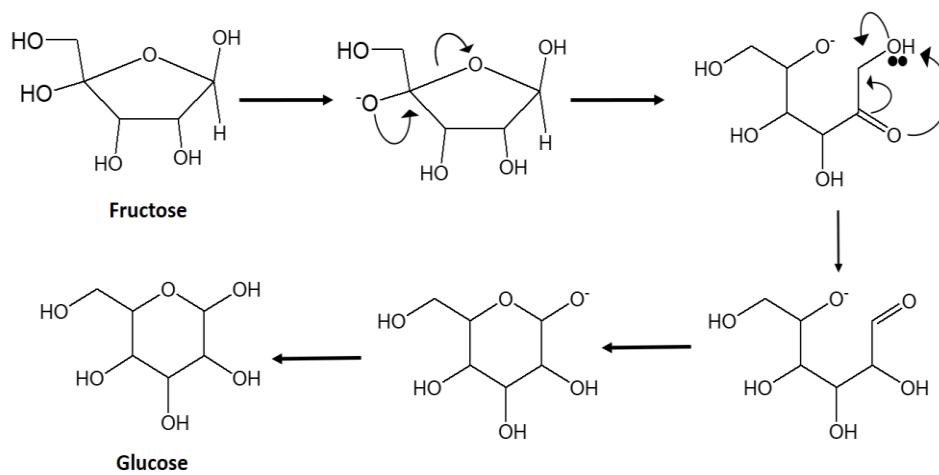**Figure 1D.2** Reaction mechanism of D-glucosamine to fructose

Figure 1D.3 Reaction mechanism of fructose to glucose
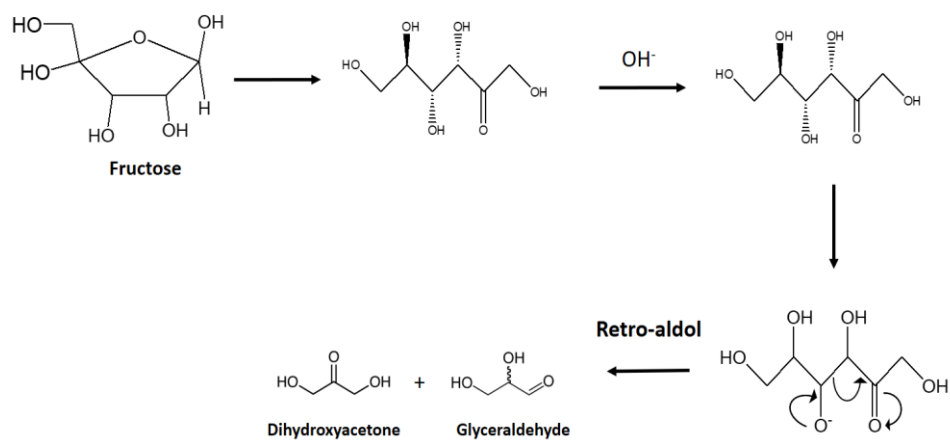
Figure 1D.4 Reaction mechanism of fructose to dihydroxyacetone and glyceraldyhyde
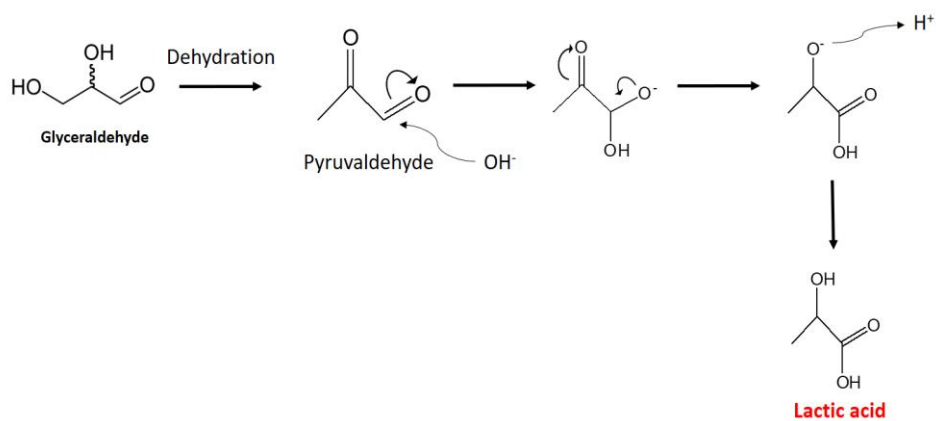

Figure 1D.5 Reaction mechanism of glyceraldehyde to lactic acid

VITA

NAME   Kodchakon Kun-asa

DATE OF BIRTH   13 April 1992

PLACE OF BIRTH   Bangkok

INSTITUTIONS ATTENDED   Bachelor's degree of science, majoring in Chemistry, Faculty of Science, Ubonratchathani university in 2013 and Master,s degree of science, majoring in Chemical Technology, Chulalongkorn University in 2016. Present she has been graduate student in Department of Chrmical Technology, Faculty of Science, Chulalongkorn University, Bangkok, Thailand since 2016 and finished her study in 2021.

HOME ADDRESS   35 Pitaksantirat road, Muang Mukdahan Sub-district, Muang District, Mukdahan, 49000

PUBLICATION   K. Kun-asa, P. Reubroycharoen, K. Yamazaki, N. Mimura, O. Sato, A. Yamaguchi, Magnesium Oxide-Catalyzed Conversion of Chitin to Lactic Acid, ChemistryOpen, 10 (2021) 307-307.

AWARD RECEIVED   Poster presentation: Catalytic conversion of chitin to useful chemicals, The 51st Autumn Meeting of The Society of Chemical Engineers, Japan, for September 24 to 26 at Iwate University