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CONVERSION OF CELLULOSE TO LEVULINIC ACID AND LACTIC ACID IN HOT COMPRESSED WATER

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งานวิจัยนี้ได้ทำการศึกษาการเปลี่ยนของเซลลูโลสเป็นกรดเลวูลินิกและกรดแลกติก เซลลูโลสในชีวมวลถูกพิจารณาเป็นพลังงานคาร์บอนใหม่เพราะการลดลงของเชื้อเพลิงซากดึกดำบรรพ์ในโลก โดยได้ทำการศึกษาผลกระทบของกระบวนการน้ำร้อนอัดความดันกับก๊าซคาร์บอนไดออกไซด์สำหรับการเปลี่ยนเซลลูโลสเป็นกรดเลวูลิกและยังคงศึกษาผลกระทบของการใช้โลหะออกไซด์เป็นตัวเร่งปฏิกิริยาสำหรับการเปลี่ยนของเซลลูโลสเป็นกรดแลกติก ยิ่งไปกว่านั้นในงานวิจัยนี้ยังสนใจศึกษาภาวะที่เหมาะสม ปริมาณของตัวเร่งปฏิกิริยา ชนิดของตัวเร่งปฏิกิริยาและการนำกลับมาใช้ใหม่ของตัวเร่งปฏิกิริยา ผลจากการทดลองของงานวิจัยนี้ถูกแบ่งออกเป็น 3 ส่วน ดังนี้ ส่วนที่ 1 เป็นการแสดงผลของการใช้น้ำร้อนอัดความดันกับก๊าซคาร์บอนไดออกไซด์ ผลจากการทดลองแสดงให้เห็นว่าวิธีการนี้สามารถเปลี่ยนเซลลูโลสเป็นกรดเลวูลินิกได้โดยตรงแต่ผลผลิตของกรดเลวูลินิกมีความแตกต่างเพียงเล็กน้อยเมื่อมีการเพิ่มก๊าซคาร์บอนไดออกไซด์ลงในปฏิกิริยา ดังนั้นจากผลการทดลองจึงสรุปว่าได้ว่าการใช้การใช้น้ำร้อนอัดความดันกับก๊าซคาร์บอนไดออกไซด์ยังไม่เพียงพอสำหรับการเปลี่ยนของเซลลูโลสเป็นกรดเลวูลินิก ส่วนที่ 2 ได้ทำการศึกษาผลของโลหะออกไซด์และภาวะที่เหมาะสม โลหะออกไซด์หลายชนิดถูกนำมาศึกษา โดยผลจากทดลองแสดงให้เห็นว่าเซอร์โคเนียมออกไซด์ให้ผลผลิตของกรดแลกติกสูง จากการศึกษาได้รับผลผลิต 21.2% ของกรดแลกติกโดยการใช้เซอร์โคเนียมเป็นตัวเร่งปฏิกิริยา ภาวะที่เหมาะสมสำหรับกระบวนการเปลี่ยนเซลลูโลสคืออุณหภูมิ 473 เคลวิน เวลาในการทำปฏิกิริยา 6 ชั่วโมง เซอร์โคเนียมออกไซด์หลายชนิดถูกนำไปวิเคราะห์เพื่อเข้าใจความสัมพันธ์ระหว่างร้อยละผลผลิตของกรดแลกติกและสมบัติของตัวเร่งปฏิกิริยา ผลจากการวิเคราะห์พบว่าจำนวนกรดและเบสของตัวเร่งปฏิกิริยาแสดงถึงความมีบทบาทที่สำคัญสำหรับการเปลี่ยนเซลลูโลสเป็นกรดแลกติก จากการศึกษาการนำกลับมาใช้ใหม่พบว่าผลผลิตของกรดแลกติกลดลงเล็กน้อยหลักจากตัวเร่งปฏิกิริยาถูกนำใช้มาใช้ครั้งที่สอง ส่วนที่ 3 ได้ทำการศึกษาผลของการผสมโลหะออกไซด์ โลหะออกไซด์หลายชนิดถูกนำมาใช้ในปฏิกิริยา จากผลการทดลองพบว่า 10%เซอร์โคเนียมออกไซด์-อลูมิน่าออกไซด์ ให้ผลผลิต 25.3% ของกรดแลกติก

ภาควิชา	เคมีเทคนิค	ลายมือชื่อนิสิต	....
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5772826023 : MAJOR CHEMICAL TECHNOLOGY
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PANYA WATTANAPAPHAWONG: CONVERSION OF CELLULOSE TO LEVULINIC ACID AND LACTIC ACID IN HOT COMPRESSED WATER. ADVISOR: ASSOC. PROF. PRASERT REUBROYCHAROEN, Ph.D., CO-ADVISOR: ARITOMO YAMAGUCHI, Ph.D., 115 pp.

In this research, I studied cellulose conversion into levulinic acid and lactic acid. Cellulose in biomass is considered as a renewable carbon source because of decreasing of fossil fuel in the world. I studied the effect of hot compressed water with carbon dioxide process on cellulose conversion into levulinic acid and I also studied the effect of metal oxides as a catalyst on cellulose conversion into lactic acid. Moreover, the optimum condition, amount of catalyst, the type of catalyst, and reusability of catalyst were investigated. The results are divided as three parts. First part, I reported that the use of hot compressed water with carbon dioxide could be directly converted cellulose to levulinic acid and that the yield of levulinic acid slightly differed when carbon dioxide is added into reaction. Thus, I concluded that the use of hot compressed water with carbon dioxide was not enough for cellulose conversion into levulinic acid. Second part, I studied the effect of metal oxides on cellulose conversion into lactic acid. The result showed that ZrO_2 gave the high yield of lactic acid. I obtained 21.2% yield of lactic acid by using ZrO_2 as a catalyst. The optimum condition for cellulose conversion was reaction temperature 473 K, reaction time 6 h. Many ZrO_2 was characterized to understand correlation between the yield of lactic acid and properties of catalyst. I found that the amount of acid site and base site of catalyst played an important role for cellulose conversion into lactic acid. The result of reusability of catalyst showed that the yield of lactic acid slightly decreased after the first reaction. Third part, I studied the effect of mixed metal oxides on cellulose conversion into lactic acid. Various mixed metal oxide were used in reaction. The results showed that 10%ZrO_2-Al_2O_3 gave the 25.3 % yield of lactic acid.

Department:	Chemical Technology	Student's Signature	
Field of Study:	Chemical Technology	Advisor's Signature	
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CHAPTER I

GENERAL BACKGROUND

1.1 Introduction

Biomass from plant is considered as one of the renewable carbon source and becomes an increasing important option for replacing fossil fuels. Most of food, such as rice, wheat, and also meat, are biomass. Biomass does compete with food. The utilization of non-edible biomass is important. Biomass is abundant, cheap and it has widespread worldwide availability. Biomass can be converted into heat, power and value-added chemical products. Biomass is consisted of three main structure units, including cellulose, hemicellulose and lignin. It can be found in the cell walls of plants. Cellulose is composed of glucose through a **β**–1, 4–glucosidic bond, and conversion of cellulose via glucose into chemicals is reported for the production of many chemicals such as 5-hydroxymethylfurfural, sorbitol, levulinic acid, and lactic acid [1-4]. The main pathway for conversion of biomass to renewable fuels and value-added chemical products has two major routes. Thermal processing and aqueous phase processing. The thermal processing is known for the production of fuels while aqueous phase processing is effective in order to produce value-added chemical products. The intermediate substances can be subsequently upgraded to value-added chemical and fuels for transportation sector [5, 6].

Levulinic acid also represented as 4-oxopentanoic acid, is considered as one of the most promising platform chemical for fuels and chemical products. Levulinic acid is produced as versatile building block containing ketone, and acidic carbonyl group. Levulinic acid is an intermediate substance for preparation of various high-value chemical products such as polymer, resin, animal feed, food, as well as component of flavoring, textile dyes, plasticizers, flavor substances [7-9]. Esterification of levulinic acid with alcohols produced levulinic ester for using as diesel additive [10]. Levulinic acid can produce γ-valerolactone (GVL) by hydrogenation reaction and GVL is used for blending with gasoline as well as a precursor of polymers [11]. The process of cellulose conversion to levulinic acid is carried out by using dilute sulfuric acid for the pretreated cellulose to C_6 sugars such as glucose and fructose. The dilute sulfuric acid is an acid-catalyst which causes a serious corrosion with the equipment in the process, which is harsh operating condition. The cellulose was performed for conversion to levulinic acid. Although some methods can solve the problem, the other problems (e.g. low selectivity) still exist [12-14].

Lactic acid is used in many industries such as cosmetic, and pharmaceutical, especially, for polylactic acid production [15-18]. Moreover, lactic acid is classified as an intermediate chemical, which can be converted into other chemicals such as acrylic acid and propylene glycol [16, 19]. The lactic acid was commercially produced via a fermentation process using saccharides from edible food as a reactant and the demand of lactic acid is growing [15, 16, 20]. The conventional fermentation process has some disadvantages; (i) lactic bacteria have the optimum productivity in the pH range from 5 to 7, resulting in the requirement of neutralization and purification, (ii) production rate is low, and (iii) edible carbohydrates are conventionally used as a starting material [20]. Currently, the homogeneous and heterogeneous acidic catalysts are usually used in the reaction for cellulose conversion. Homogeneous catalysts are used for cellulose conversion such as HCl, H_2SO_4. The heterogeneous catalysts are studied about the different metals (e.g., Pd, Pt, Ru, Au) supported on metal oxides (TiO_2, SiO_2, Activated carbon and ZrO_2). The catalytic production of lactic acid from inedible cellulose has been studied for using instead of the fermentation process. Homogeneous catalysts provide high yield of lactic acid form cellulose (lactic acid yield 68% by $PbCl_2$ [21] and 91% by $ErCl_3$ [22]); however, use of homogeneous catalysts is compromised by difficulties associated with product separation from the catalysts and recyclability of the catalysts. Heterogeneous catalysts for cellulose conversion into lactic acid are highly desired because they can be easily separated from product. A few heterogeneous catalysts have been reported for the cellulose conversion into lactic acid. Yang et al. obtained 24% yield of lactic acid from cellulose using $LaCoO_3$ perovskite metal oxide [23]. Chambon et al. used AlW as a solid catalyst and obtained 28% yield of lactic acid from cellulose [24]. $NbF_5–AlF_3$ was reported to be active for cellulose conversion into lactic acid (27% yield) by Coman et al. [25]. However, the stability of these solid catalysts have limitation. The limitation of these solid catalysts are leaching of metal species into solution. $LaCoO_3$ leached into solution as follows: 2.4% of Co and 1.5% of La [23]. AlW leached into solution 1.5% of W [24]. Moreover, the preparation cost of these solid catalysts makes the industrial use difficult. Previous results showed that ZrO_2 and TiO_2 was stable solid in hot compressed water [26, 27].

1.2 Scope of this work

In this work, cellulose conversion was investigated to produce levulinic acid and lactic acid. The effects of reaction temperature, CO_2 pressure, reaction time, amount of catalyst, and type of metal oxide were investigated. Many metal oxides such as ZrO_2, TiO_2, and mixed metal oxides were used in reaction to enhance cellulose conversion into levulinic acid and lactic acid. This research work was scoped as follows:

1) To study the effect of carbon dioxide on cellulose conversion.
2) To study the effect of the difference of metal oxides.
3) To study the effect of the difference of mixed metal oxides
4) To study catalytic performance of the difference of type of zirconium oxide.
5) To understand the different properties of zirconium oxide.
6) To understand the effect of the different properties of zirconium oxide to Lactic acid yield.
7) To understand the reaction pathway of cellulose conversion into lactic acid.
8) To understand of the role of acid sites and base sites.

1.3 Objectives

1) To find the optimum condition for cellulose conversion into levulinic acid using hot compressed water with carbon dioxide.

2) To find simple metal oxides to obtain high yield of lactic acid from cellulose conversion.
3) To study the effect of mixed metal oxides on cellulose conversion into lactic acid.
4) To understand the difference properties of metal oxides and mixed metal oxide.
5) To understand mechanism of cellulose conversion to lactic acid.

CHAPTER II
THEORY AND LITERATURE REVIEWS

2.1 Biomass

Biomass is the other name of plants and including some materials. Lignocellulosic biomass is a special name for some biomass, which could not be used as food or feed. Biomass is a mixture of complex of polysaccharides. The main composition of biomass are cellulose, hemicellulose, and lignin. The rigid structure of the cell wall is caused by the interaction between cellulose fiber, hemicellulose and lignin. Biomass does compete with food. The utilization of non-edible biomass is important because it can solve the problem of agricultural and forestry waste use, and environmentally benign technology [28, 29]. In term of industry, biomass is used to produce energy by burning of wood, and it is converted to other organic substances. Biomass can directly be converted to energy source by combustion method to heat production but biomass cannot directly be converted to form of biofuel. Biomass can be converted to biofuel by many methods such as thermal, chemical, and biochemical methods. The burning of biomass also generates pollution such as carbon monoxide and carbon dioxide to atmosphere. The pollution from biomass combustion has higher than burning coal. However, biomass has also been classed as a new energy source in the world because biomass is abundant, cheap and it has widespread worldwide availability. Moreover, biomass has become popular for using in coal power stations. Thus, biomass can be converted into heat, power and value-added chemical products. The structure of biomass in the cell walls of plants was shown in Figure. 2.1 [28, 30-32].

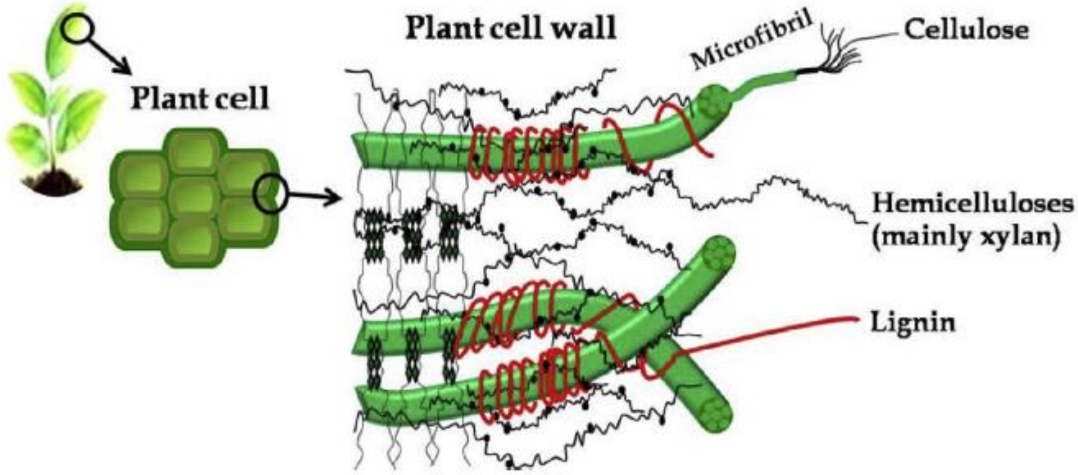


Figure 2.1 Lignocellulose biomass composition in plants [28]

2.1.1 The processing for biomass conversion

Pathway for biomass conversion to renewable energy source such as fuels and high value-added chemical products has many routes such as thermal processing, and aqueous phase processing as shown in Figure. 2.2 [29]. The thermal processing is well-known for the production of fuels while aqueous phase processing is effective in order to produce high value-added chemical products. In addition to the both processing, chemical and biochemical processing is also a routes for conversion of biomass. The intermediate substances can be subsequently upgraded to high value-added chemical and fuels for transportation sector [5, 6].

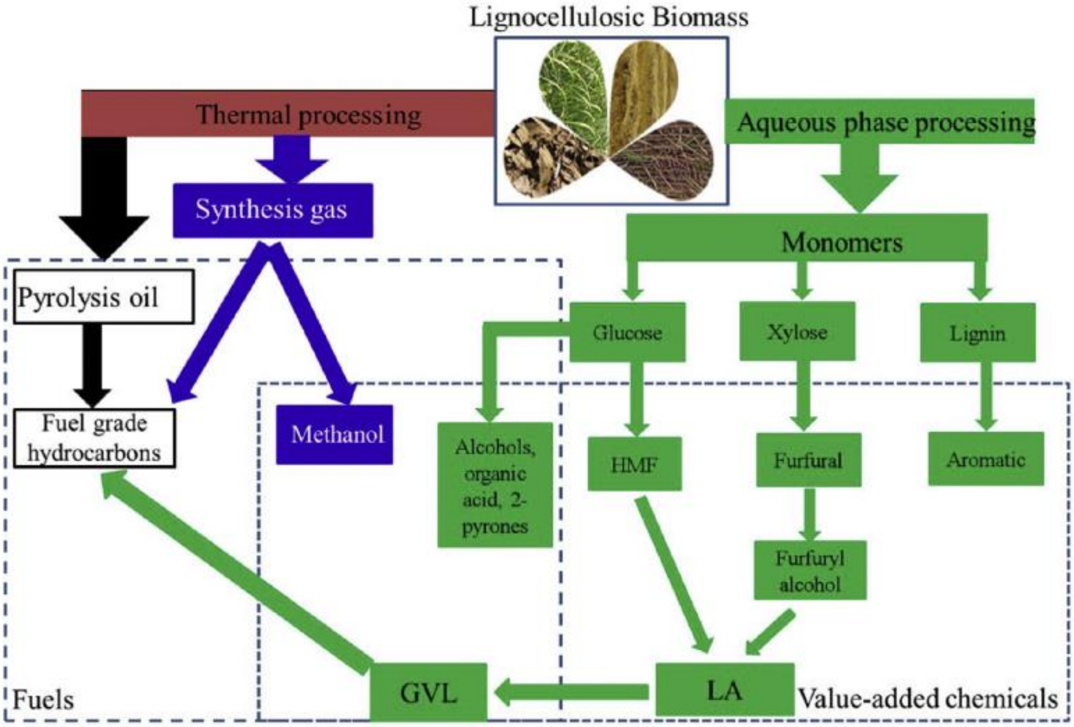


Figure 2.2 Diagram of the conversion of lignocellulosic biomass through thermochemical and aqueous phase processing to fuels and value-added chemicals [5].

2.1.1.1 Thermal processing

Thermal processing is a process for biomass conversion into energy source such as fuel. This process is widely used in many industries for conversion of biomass. The other name of this process is thermal oil heating or etc. The process of this method is operated with the closed loop system. Pyrolysis method is classified as a part of thermal processing because this method uses only heat for conversion of biomass. However, Gasification method uses heat in system but this method converts biomass to products by chemical reactions, which are controlled by temperature and pressure. Many countries and many industries use thermal processing to produce energy by burning of biomass. However, thermal processing is also limited because the amount of moisture content in biomass is not same. The moisture content in biomass is the big problem for thermal processing. Thermal processing has also been developed for overcoming this problem. Furthermore, thermal processing via combustion also converts biomass into heat and power, which is called as the combination of energy. This method is carried out to produce heat and electric. The electric is a major product and heat is a by-product. By-product is released via cooling tower. However, some waste heat can be recovered into system.

2.1.1.2 Aqueous processing

Aqueous processing or liquid phase processing is the conversion method of biomass into high value-added chemicals. 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 the liquid phase. For comparison of gas phase, the operation of liquid phase has higher efficiencies than gas phase. The advantage of this process is that the catalysts such as homogeneous and heterogeneous catalysts can be used in this process in order to increase the yield of products without the problem and that the use of this process and catalyst help to decrease temperature of reaction. The disadvantage of this process is that this process is needed to carry out under high pressure and high temperature without catalyst. Therefore, the use of this method depends on reactant and operating condition.

2.1.1.3 Chemical processing

Chemical processing is a process for conversion of biomass into energy or conversion of chemical substances into other chemicals. Chemical processing is caused by chemical reactions in the process. Chemical reactions in the process depend on chemical reactants and products. This process is used in many parts such as methanol production, Fischer-Tropsch synthesis, olefins, especially, gasification process. The products of chemical processing are fuel, which is used for transportation. Each part of chemical process has the difference of chemical reaction. Oxidation reaction, reduction reaction, acid-base reaction, and etc. are the chemical reactions within chemical processing. The difference of chemical reactions can be used to combine in chemical process in order to receive the target product. Solid, liquid, and gas can be used as a reactant in this process. For example, Fischer-Tropsch synthesis is the process to produce liquid hydrocarbon from mixed gas. Gasification process is the process for conversion biomass or fossil fuel to syngas. Gasification of biomass can be operated under at atmospheric pressure via combustion to produce a syngas. Syngas is a mixed gas of carbon monoxide, carbon dioxide, hydrogen, and methane. This gas can be used in other process. Therefore, chemical processing is an interesting method of biomass conversion.

2.1.1.4 Biochemical processing

Biochemical processing is used in many industries for biomass or other reactants to products. The fermentation method is classified as a part in biochemical process. The other method such as anaerobic digestion and composting are also classified as a part of biochemical. Conversion of biomass or other reactants is carried out by enzymes of bacteria for cleavage the molecule of biomass or reactants to liquid fuel or chemicals. The advantage of biochemical process is that this process can produce a high yield of product. However, the disadvantage of this process is a long time for conversion and enzymes recovery.

However, the processing for biomass conversion has also many disadvantage such as the pollution from thermal processing, the low yield of products in aqueous processing, the hash operation from chemical processing, and the treatment of water from biochemical processing. Furthermore, thermal processing also generates the black carbon into atmosphere from the conversion of biofuel, and biomass. This is a reason for increasing of global warming. Thus, these processing have been developed. The use of biomass as a reactant for conversion into fuel. It also generates air pollution such as carbon dioxide, carbon monoxide, nitrogen oxide (NO_x), volatile organic compound, and etc. The benefits of conversion biomass into fuel are the decreasing of using fossil fuel. Previous studies reported that the advantage of using biomass as a biofuel is that biomass will release the pollution into atmosphere less than the use of fossil fuel. The conversion of biomass into chemical is also a way for decreasing of using fossil fuel. Moreover, the use of biomass instead of fossil fuel is an alternative for production fuel and chemicals in the future. Recently, Biomass is brought to use as a reactant to produce electric in plant industries. The use of biomass in power plant is help to decrease the use of the fossil fuel. Decreasing of using fossil fuel has effect on plant economics. However, the increasing of demand to using biomass has the effect on biomass cost in the world.

2.2 Cellulose

Cellulose is a major composition of plant and non-edible lignocellulosic biomass. It is used as a raw material for the paper, textile, and chemical industries. In the future, cellulose is predicted as clean energy because cellulose is abundant in biomass and it is too much in the world. At first, Anselme Payen [33] can separate cellulose from timber where they separated cellulose by using nitric acid and sodium hydroxide solution. Cellulose is a polysaccharide made up of glucose monomers joined through β-1,4-linked linear polymer of glucose units. The properties of cellulose are insoluble in water, dilute acidic solutions, and dilute alkaline solutions at normal temperatures. The component of cellulose contains carbon, hydrogen, and oxygen. Cellulose consists of pure dehydrated repeating units of D-glucoses. The formula of cellulose is $(C_6H_{10}O_5)_n$. n is the degree of polymerization. The structure of cellulose is the linking of D-glucose molecule by the component of cellulose has glucose as a composition only. The structure of cellulose showed in Figure. 2.3. The linking of two molecules of D-glucose is called cellobiose. The structure of cellubiose showed in Figure 2.3. In addition, some animals and some bacteria also have cellulose as a composition but the low content of cellulose is found in these species [34-36].

Cellulose can be divided to three types by using the different concentration of NaOH and the difference of temperature. First type is α-cellulose. This type can be dissolved in 16.5 % NaOH at temperature 293 K. Second type is β-cellulose. This type is obtained from the remaining of the acid and the alkaline solution. Third type is and γ-cellulose. This cellulose type can be dissolved in the water. Some cellulose can be dissolved in NaOH but some cellulose can be dissolved in water because the different of degree of polymerization in cellulose. Thus, the degree of polymerization in cellulose is a key factor of the solubility of cellulose [34].

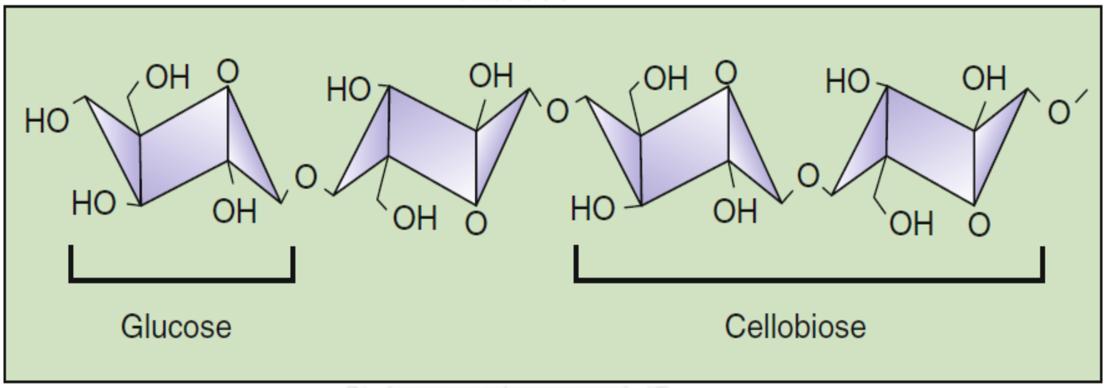


Figure 2.3 Molecular chain structure of cellulose [34].

2.2.1 The properties of cellulose

The properties of cellulose is no taste, no smell, and white color. Cellulose is hydrophilic and it has the contact angle of 20–30 degrees [37]. It cannot be dissolved in water and organic solvents and it is biodegradable. Moreover, cellulose can be melt at 740 K. Cellulose is decomposed to glucose units when it is treated by the high concentration of mineral acids at high temperature [38]. Cellulose is created from the linking of many D-glucose units, which link through β(1,4)-glycosidic bonds. However, the linkage of α(1,4)-glycosidic bonds is not same with β-glycosidic bonds. The difference of linkage of α-glycosidic bonds and β-glycosidic bonds is shown in Figure 2.4. Cellulose has properties of a straight chain polymer. It does not have branching chain in structure of same starch. The molecules of cellulose can be extended and it has hardness in structure. The reason of this properties is the formation of the D-glucose. The high tensile strength of cellulose structure comes from the linkage bonds of hydroxyl groups on the glucose unit link with one chain of hydrogen bonds in oxygen atoms of the next glucose unit or on a neighbor glucose unit. This linkage bond is the reason of the strong of microfibrils in cellulose. This linkage bonds of hydroxyl group have the effect on the hardness of cell wall of cellulose by microficrils formed to polysaccharide matrix. The result of comparison of crystalline of cellulose with starch shows that cellulose has higher crystalline that starch. The high crystalline has effect on melting point of cellulose. Strach, which has a low of crystalline, is melted at temperature 333-343 K in water while cellulose, which has high crystalline, is melt at temperature 593 K and pressure 25 MPa in water [39]. The difference of crystalline structure of cellulose depends on the position of linkage of hydrogen bond within fiber of cellulose. Normally, cellulose has two types of structures as follow: I_α and I_β. However, many plants consist mainly I_β but some plants have enriched I_α such as algae [40]. The fibers of cellulose can be divided into two types: cellulose I and cellulose II. Cellulose II has high stability than cellulose I. Currently, cellulose III and cellulose IV can be produced by using chemical treatments. Thus, the properties of cellulose depend on the chain length and degree of polymerization (the number of glucose units).

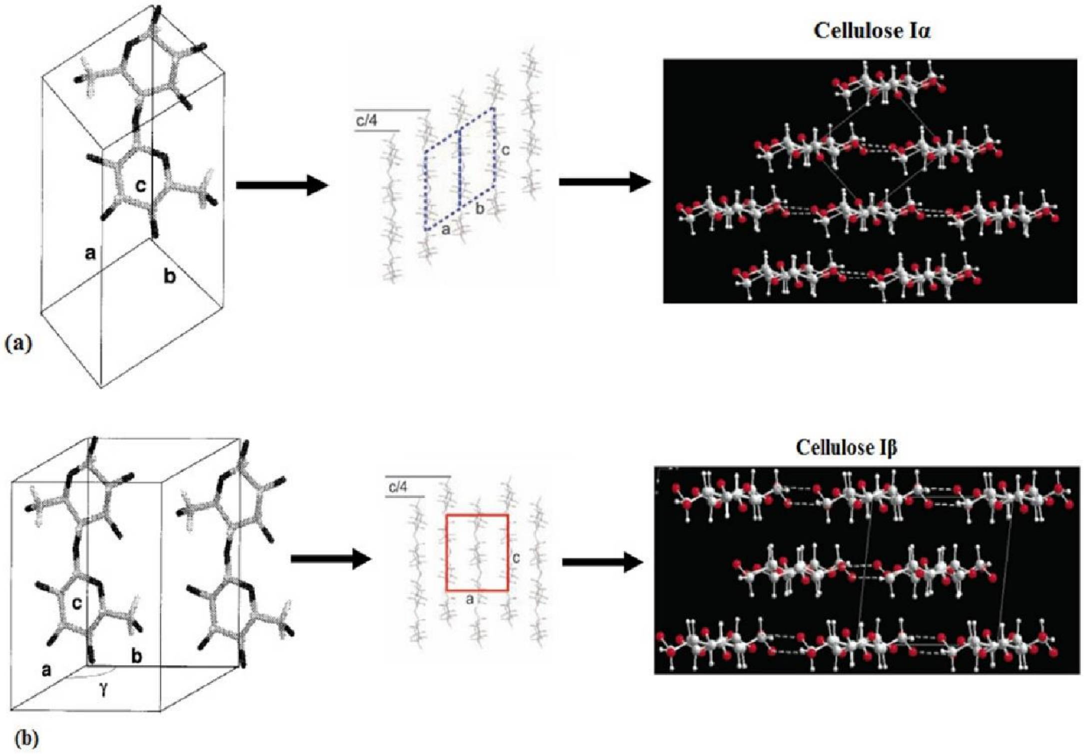


Figure 2.4 The linkage of glycosidic bonds (a) I_α, and (b) I_β [40].

The different types of plants have effect on the properties of chain length in cellulose such as wood pulp chain lengths between 300 and 1700 units while cotton and other fiber plants have chain lengths in range 800 to 10,000 units. The solubility of cellulose depends on the chain length. Cellulose with a small chain length cannot be dissolved in water. On the other hand, cellulose with a large chain length can be dissolved in water and organic solvents. The difference of plant and bacterial is that the component of plant, cellulose and hemicellulose while the component of much water content in structure and higher tensile strength due to higher chain lengths. Some researchers [41] produce reagent to dissolve cellulose such as Schweizer's reagent, cupriethylenediamine, cadmiumethylenediamine, N-methylmorpholine N-oxide, and lithium chloride / dimethylacetamide. These reagents are used to regenerate cellulose from dissolving pulp. Cellulose is also soluble in many kinds of ionic liquids [42]. In generally, the structure of cellulose consists of crystalline and amorphous. Some researchers [43-45] found that the treatment cellulose by strong acid was created by nanocrystilline cellulose. It is caused from amorphous regions can break up [46]. Nanocrystalline cellulose is mixed with polymer to produce nanocomposites in order to increase mechanical and thermal properties [47].

2.3 Hemicllulose

Hemicellulose is also main component in lignocellulosic biomass. Aspinall [48] reported that hemicellulose is derived from hetropolymers or matrix of polysaccharides. Hemicellulose consists most of the D-pentose sugars. The composition of hemicellulose consists of sugar monomers such as D-xylose, D-mannose, D-glucose, or D-galactose and etc. These sugar monomers are branched chains with linkage to form as hemicellulose (as shown in Figure 2.5). Almost all plants contain xylan as a major component in structure of hemicellulose. The main chain of homopolymer is liked by D-xylosyls with each other. Xylan is a group of hemicellulose and it consists of unit of xylose (a pentose sugar). Moreover, xylan has combination between glucan with 1,4-**β**-D-xylopyranose and with branch chains of 4-oxymethylglucuronic acid. However, the structure and the content of hemicellulose in plants are different. Previous studies found that the structure of cellulose was depended on the composition of main and branch chain in hemicellulose [34].

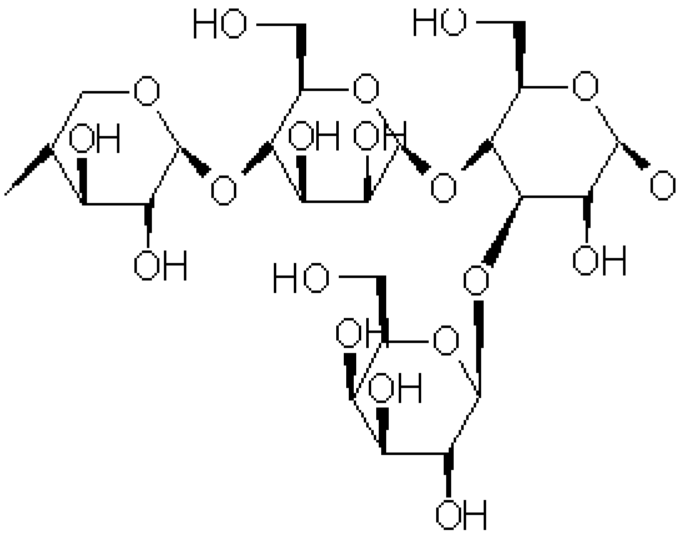


Figure 2.5 The structure of hemicellulose [49].
(D-xylose, D-mannose, D-glucose, D-galactose)

2.3.1 The difference of structure between cellulose and hemicellulose

- Hemicellulose is the mixture of sugar such as xylose, mannose, glucose, and galactose but cellulose is only glucose as a composition.
- Hemicellulose consists of the branch chain in structure but cellulose does not have branch chain in structure.
- Cellulose has a high degree of polymerization but hemicellulose has a low molecular weight polymers.
- Hemicellulose has many types of sugar groups such as C_5 or C_6 of carbon atoms.
- Hemicellulose can be dissolved in water more than cellulose.

Table 2.1 The different properties between cellulose and hemicellulose

	Cellulose	**Hemicellulose**
Monomer	Pure glucose	Mixed of C_5 and C_6 sugars
Chain length	Long	Short
Molecular Weight	High	Low
Structure of Polymer	Linear	Branch
Morphology	Crystalline + amorphous	Amorphous
Solubility	Low	High
Reactivity	low reactive	high reactive

2.4 Lignin

Lignin is classified as complex organic polymers. It is also as a main structure of plants. Lignin is the important composition of cell wall because linin has a hardness and it is difficult to degradation. Lignin is the most part in biomass, which is generated from linkage of phenolic polymer. The structure of lignin is a very complicated because the structure of lignin consists of phenylpropane units and three main monomers are coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The main monomers are showed in Figure 2.6. The difference of monomers of lignin can be divided as three types as follows: guaiacyl lignin, guaiacyl-syringyl lignin, guaiacyl-syringyl-hydroxy-phenyl [34, 50].

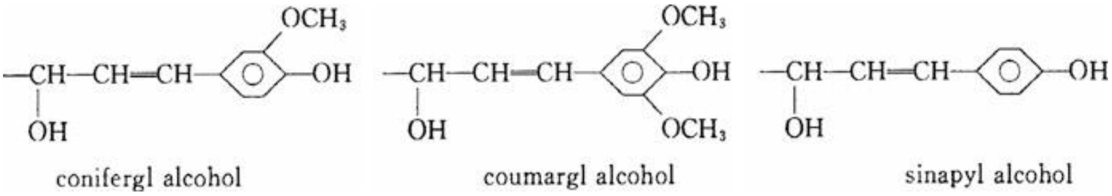


Figure 2.6 Basic structural unit of lignin [34].

Lignin consists of three-dimensional network, which is a complicated amorphous polymer. Lignin consists of the linkage of phenylpropane units by the irregular coupling of C–C and C–O. The basic structure of lignin consists of three monomers: first, p-phenyl monomer is derived from coumaryl alcohol. Second, guaiacyl monomer is derived from coniferyl alcohol. Last, syringyl monomer is derived from sinapyl alcohol (Fig. 2.6). The composition of lignin carbon, hydrogen, ash, and oxygen. Previous studies [51] reported that the formula of lignin was $(C_{31}H_{34}O_{11})_n$. However, this formula may be incorrect because it different from the primary structure. The strength of wood comes from the function of xylem cell and lignified sclerenchyma fiber [52]. The small segment of lignin is showed in Figure 2.7.

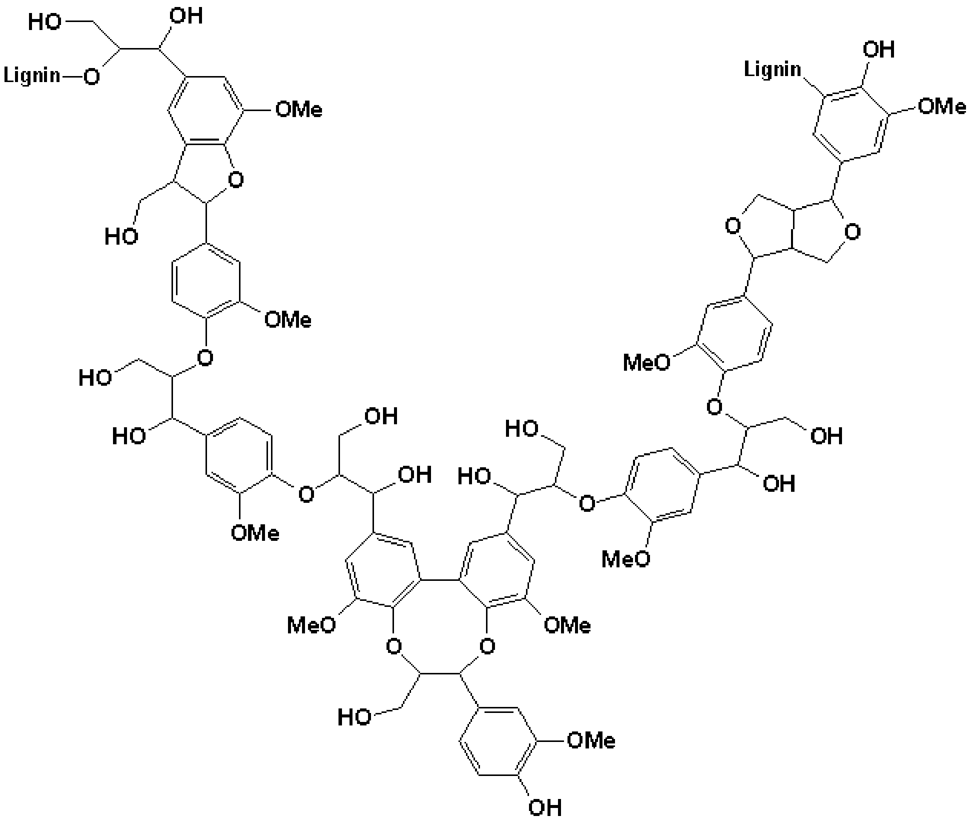


Figure 2.7 A small segment of lignin [53]

2.5 Hot compressed water with carbon dioxide

2.5.1 Hot compressed water

Hot compressed water has many properties and it can be used in different reactions. The properties of hot compressed water depend on the conditions of temperature and pressure. Hot compressed water has the different properties and it has influence to chemical reactions. However, the role of water in each reactions is difficult to indicate. Although the reaction of hot compressed water is complicates, it is better than the degradation reaction. Many researchers studied the properties of water at sub- or super-critical temperature in order to use the advantage of ionic product. Kruse and Dinjus [54] studied the microscopic properties of hot compressed water to understand the reaction mechanisms in hot compressed water. It is carried out at different conditions. They studied the properties of hot compressed water by using interesting microscopic. Many researcher studied the chemical reactions of water in this medium. Hot compressed water can be adjusted for reactions as medium condition. It can be used as a solvent meanwhile it also used as a catalyst and reactant. The role of water depends on the reaction conditions. The result of microscopic experiment showed that the polar of molecules was a very important to reaction and the purification of water as well. However, a lot of researchers still study to understand chemical reactions in hot compressed water [55].

2.5.2 Carbon dioxide

The behavior of carbon dioxide is that carbon dioxide properties is gas in air at standard temperature and pressure. When carbon dioxide was freeze, carbon dioxide was changed from gas to solid. This solid is called dry ice. We know that the behavior of carbon dioxide when carbon dioxide has temperature higher than 304.25 K and pressure higher than 7.39 MPa. This condition is classified as supercritical fluid. Supercritical carbon dioxide is becoming an important for industry because it can be used as solvent in chemical extraction. In addition to carbon dioxide has low toxicity and environmental friendly. Carbon dioxide has stability at low temperature. However, carbon dioxide has the benefit in extraction industry but some chemicals can be dissolved in carbon dioxide.

2.5.3 The combination of hot compressed water and carbon dioxide.

The process for using hot compressed water and carbon dioxide is expected to be highly reactive for the cellulose conversion. Hot compressed water is known as a promising solvent for acid-catalyzed or base-catalyzed reaction because the water can decompose to ionization at high temperature. The addition of carbon dioxide will increase the proton concentration of liquid water because carbon dioxide is dissolves in water to form carbonic acid (as shown in equation (2)). Carbonic acid is classified as weak as and can be applied to acid reactions. The advantage of combination between water and carbon dioxide is environmentally-friendly because the added carbon dioxide can be separated easily by depressurization after reaction [56, 57].

$$H_2O \longrightarrow H^+ + OH^- \quad (1)$$

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-} \quad (2)$$

2.6 Metal oxides

Currently, metal oxides are widely used in many fields such as chemical industries. Metal oxides are very important because it is used as a catalyst and also used as a support. The properties of metal oxides make many function. Some metal oxides have the properties as acid–base function but some metal oxides show a redox properties. Metal oxides are classified as a heterogeneous catalyst [58]. Metals and metal oxides are used in many reactions for synthesis or conversion of chemical. Transition metal and noble metal group of oxides have the effect on activity for reaction. The difference of activity is studied and used in industries [59, 60].

2.6.1 Single metal oxides

Single metal oxides are the combination of metal species and oxygen atom in the form of oxide. This combination is called metal oxide. The formula of metal oxide is written by depending on the composition of metal species and oxide. Normally, the symbol of metal species is written first and then it is write the symbol oxidation number. Last, the symbol of oxygen O is written. The symbol of metal oxide can be written as follows: M–OH, M–O–M, and M=O (M means metal species, and O means oxygen vacancy). At room temperature, metal oxides has properties as a solid and crystalline but some phases of metal oxide also is amorphous phase. Metal oxide catalysts are used in many industries because it has a performance for increasing conversion and synthesis rate. Moreover, the price of metal oxide is cheap for production and it is easily to separate, including regeneration. The different types of metal oxides has effect on organic reactions such as oxidation, dehydration, dehydrogenation and isomerization [61, 62].

Metal oxides can be found in nature and it has properties as a solid at room temperature. In general, metal oxides cannot be dissolved in water and can be changed to salts in the acid. Example the reaction of zinc oxide is dissolved in hydrochloric acid to form zinc chloride

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$

In case of hydrothermal reaction, some researchers reported that a few simple metal oxides such as ZrO_2 and TiO_2 have been found to be stable solid catalysts in hot compressed water [26, 27].

2.6.1.1 Zirconium oxide

Zirconium oxide, zirconium(IV) oxide or zirconia is wildly used in many industries such as ceramic, coating, and etc. and also used as a solid catalyst. Zirconium oxide can be divided into three phase structures as follows: monoclinic, tetragonal, and cubic. The chemical properties of zirconium oxide is unreactive. In hydrofluoric acid and sulfuric acid, zirconium oxide is slowly dissolved. When zirconium oxide react with carbon under heating, zirconium oxide is converted to zirconium carbide. When zirconium oxide is heated in the presence of chlorine, zirconium oxide converts to zirconium tetrachloride. This is an example of the conversion of zirconium oxide. The properties of zirconium oxide is a while color and non-flamable. Neuman et al. [63] applied Zr species as a one part in ceramic. The result showed that ZrB_2-B_4C could increase hardness and fracture toughness of ceramics. Qin et al. [64] studied the removal of phosphate and cesium using zirconium oxide from green water treatment. The result showed that they could remove phosphate and cesium by a simple thermal treatment. Bhowmick et al. [65] developed nanocomposite between zirconium oxide nanoparticle and organic-inorganic hybrid composites. The result showed that this composite was the greatest mechanical strength, porosity, antimicrobial property and suitable water absorption capacity and compatibility with human pH and blood.

2.6.1.2 Alumina

Aluminium oxide or aluminum oxide has been used in many fields such as filler, glass, purification of gas stream, and composite fiber. Aluminium oxide is composite between aluminium and oxygen. Auluminum oxide was used as a catalyst support and also used as a catalyst. This is largely because it is relatively low cost as well as high surface areas. Aluminium oxide is found in of form corundum in natural. This form has the stability in thermaldynamically [9]. Aluminium oxide has crystral structure as trigonal where oxygen ions form a hexagonal nearly structure and aluminium is fill in the hole of the octahedral. In a part of crystalline, condurum is the structure as a trigonal lattice. The original cell of aluminum oxide has two formula. In addition aluminaium oxides also have other phase. The cubic phase has α, and η. The monoclinic has θ phase, the hexagonal has χ phase, and the orthorhombic has κ and the δ phase. This phase is tetragonal or orthorhombic. Cubic γ-Al_2O_3 is a phase for using in many industries. Melting temperature of aluminium oxide is 2,345 K and boiling point of aluminium oxide is 3,250 K. The density of aluminium close to melting point is 2.93 g/cm^3. Osorio-Vargas et al. [66] used γ-Al_2O_3 as a catalyst support for ethanol steam-reforming reaction. The result showed that this catalyst had a good selectivity to H_2, no presence of C_2 intermediates and stable up to 48 h of time-on-stream at 773 K. Liu et al. [67] studied the effect of low-density polyethylene nanocomposites which contained Al_2O_3 nanoparticles.

2.6.1.3 Silica

Silica is used in many fields such as whitewear, glass, and ceramics. Silica is known as a composition of silicon dioxide. Silicon dioxide consists of silica metal with oxygen atom. The chemical formula of silicon dioxide is SiO_2. It is used in many fields. Silica, which is found much in nature, is a metal oxide in many compounds such as in plants, and humans. [68]. Silica is a composition of sand. It spreads all the world. Silica is also the major composition of materials such as glass, rock, and concrete. In addition, silica is also used as catalyst and catalyst support. Moreover, silica is applied to materials and is used in electronics industries and food industries. Currently, silica can be obtained from purification of quartz. Quartz is a compound, which has silica as composition. It is much in the earth. Quartz is also used in chemical processing because it has thermal stability for some industries. Melting temperature of silica is 1,986 K and boiling point of silica is 3,220 K. Normally, silica cannot be dissolved in water but the solubility depends on the crystalline form of silica. These properties were obtained from the study of single crystals silica in thermal processing. The pure quartz is a source for using in electronic applications. Silica is classified as a nontoxic. Bej et al. [69] studied the performance of Ni/SiO_2 for cellulose conversion. The result showed that the activity of catalyst depended on the active species and size. The nanoparticles of Ni has a size in range 9–15 nm. It was found that this catalyst had efficiency for steam reforming of methane. Moreover, the structure of SiO_2 like SBA-15 and MCM-41 was mesoporous with large surface areas. They reported that this catalyst was suitable for steam reforming of ethanol reaction.

2.6.2 Mixed metal oxides

Mixed metal oxides or composition oxides consist of two or more different kinds of metals with oxygen atom. Mixed metal oxides are the combination of two metal species, three metal species, or four metal species. The mixed metal oxide is used in many industries. In addition, mixed metal oxides is used as a catalyst. The figure of mixed metal oxide is shown in Figure 2.8 [70, 71].

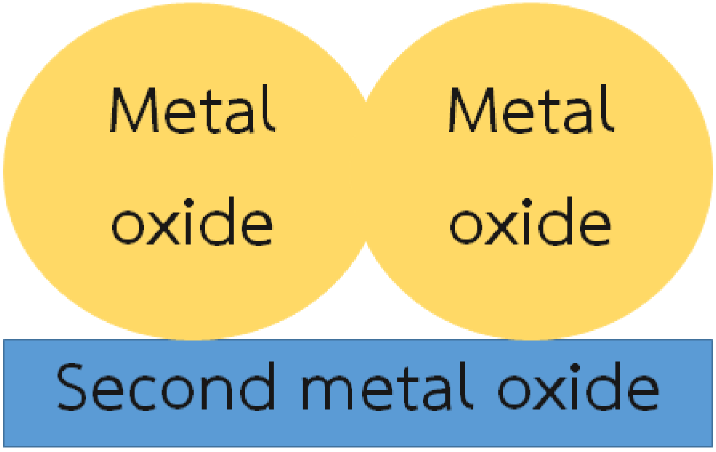


Figure 2.8 Mixed metal oxides

Mixed metal oxides are important in the studies and uses in industries. In field of research, mixed metal oxide have an acid–base and redox properties. Mixed metal oxides can apply to use in many reactions for destructive oxidation of $(CH_3)_2S_2$ [72].

The advantage of metal oxides and mixed metal oxides is easily to separate after reaction, decrease corrosion problems of reactor, control cost effectiveness, and reuse the catalyst.

2.7 Levulinic acid

Levulinic acid also represented as 4-oxopentanoic acid, is considered as one of the most promising platform chemicals for fuels and chemical products. Levulinic acid is produced as versatile building block containing a ketone, and acidic carbonyl group. Levulinic acid is an intermediate substance for preparation of various high-value chemical products such as polymer, resin, animal feed, food, as well as component of flavoring, textile dyes, plasticizers, flavor substances and fuels additive [7-9]. Esterification of levulinic acid with alcohols produced levulinic ester for using as diesel additive [10]. Levulinic acid can produce γ-valerolactone (GVL) by hydrogenation reaction and GVL is used for blending with gasoline as well as a precursor of polymers [11]. Recently, the conventional process of cellulose conversion to levulinic acid has been carried out by using dilute sulfuric acid for the pretreated cellulose to C_6 sugars such as glucose and fructose. The dilute sulfuric acid is an acid-catalyst which causes a serious corrosion with the equipment in the process, which is harsh operating condition. Mechanism of cellulose conversion into levulinic acid was shown in Figure 2.9. Although some methods can solve the problem, the other problems (e.g. low selectivity) still exist [12-14, 73, 74].

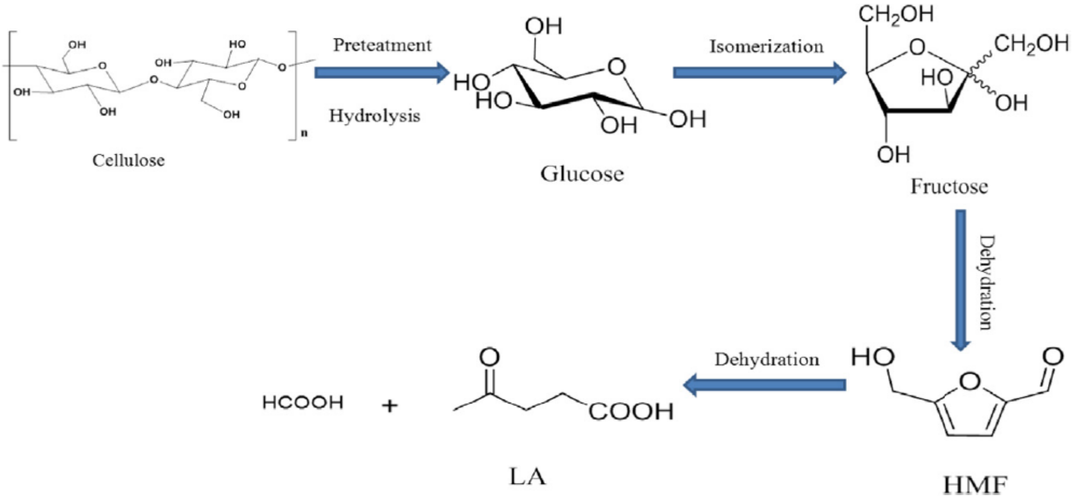


Figure 2.9 Mechanism of cellulose conversion into levulinic acid [14, 73-74].

2.8 Lactic acid

Lactic acid is one of the promising platform chemicals produced from cellulose because it is widely used in the food, cosmetic, pharmaceutical, and chemical industries [15, 16]. Moreover, lactic acid is used as a reactant for polylactic acid production [17, 18] and can be converted into a wide range of chemicals such as propylene glycol and acrylic acid [16, 19]. The lactic acid was commercially produced via fermentation process using saccharides from edible food as a reactant and the demand of lactic acid is growing [15, 16, 20]. However, the conventional fermentation process has some disadvantages: the fact that (i) the optimum pH range for production by lactic bacteria is 5–7 results in a requirement for neutralization and purification, (ii) the production rate is low, and (iii) edible carbohydrates are conventionally used as a starting material [20]. The step of fermentation process was showed in Figure 2.10.

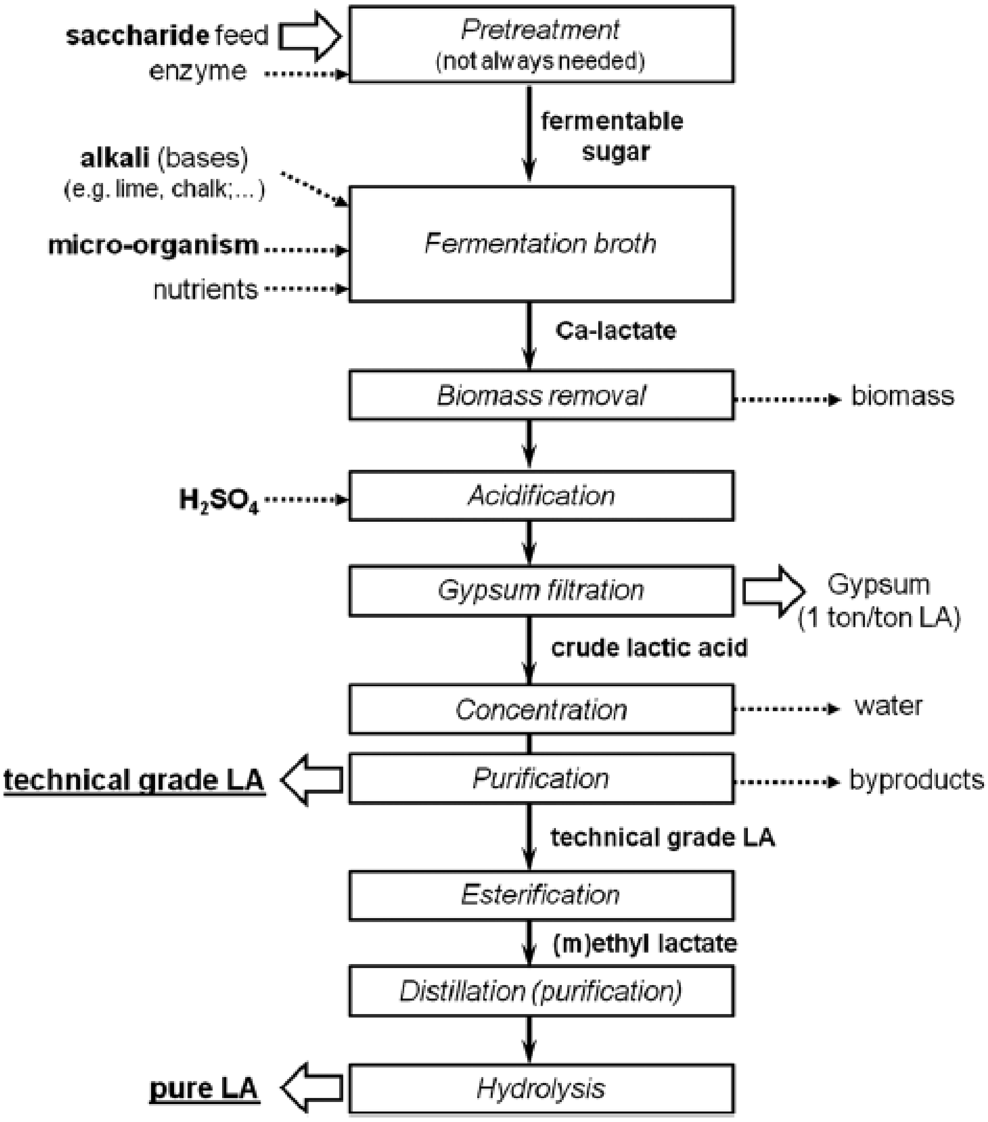


Figure 2.10 Block scheme of the fermentative production of lactic acid [75].

2.8.1 Reaction mechanism

The reaction mechanism of cellulose conversion into lactic acid has been discussed in the literatures. Mechanism is presented in Figure 2.11 by Dusselier et al [75]. They described mechanism of cellulose conversion into lactic acid as follows: cellulose was hydrolyzed by water to glucose and then glucose was converted to fructose. Next, fructose was converted to dihydroxyacetone and glyceraldehyde.

Dihydroxyacetone and glyceraldehyde were converted to pyruvaldehyde by dehydration reaction. Finally, pyruvaldehyde was converted to lactic acid

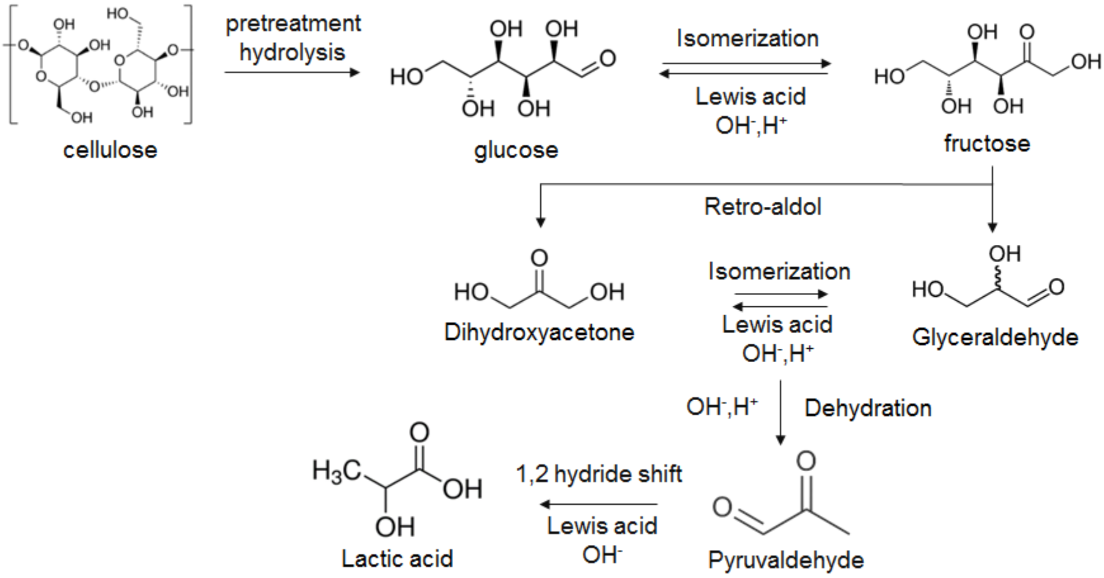


Figure 2.11 Mechanism of cellulose conversion into lactic acid [75].

2.9 Literature reviews

Daorattanachai et al. [76] studied the effect of kraft lignin on hydrolysis and dehydration by using sugars, cellulose, hemicellulose and biomass as a reactant under hot compressed water (HCW) with phosphoric acid. The results showed that lignin was retarded the hydrolysis of cellulose, hemicellulose to sugar but the admixed lignin into reaction promoted the isomerization reaction of glucose to fructose and also promoted dehydration reaction of fructose to HMF. The yield of HMF increased from 16.9% to 24.0% after the addition of H_3PO_4. The amount of acid (H_3PO_4) has the effect to the hydrolysis and dehydration reaction of biomass. Moreover, the high of products increased when the amount of H_3PO_4 was increased. They also suggested that hot compressed water promoted isomerization reaction of fructose to HMF. Lignin was decomposed to organic acids such as acetic acid, formic acid, glycolic acid and lactic acid by it decomposed from side-chain from phenyl propane unit but it was not from aromatic of lignin.

Sato et al. [77] studied continuous dehydration of 1,4-butanediol in flowing liquid water with carbon dioxide. They found that the dehydration reaction increased after carbon dioxide was added into reaction. The increasing of dehydration reaction has the effect to the conversion of 1,4-butanediol (1,4-BDO) to tetrahydrofuran (THF) in hot compressed water because the concentration of proton increased. They reported that carbonic acid caused the dissolution of carbon dioxide in water and the addition of carbon dioxide was not change the equilibrium constant (K). The optimum condition for the dehydration of 1,4-butanediol was temperature 573 K, pressure 40 MPa, retention time 60 min by THF was obtained 83%.

Yamaguchi et al. [78] studied the conversion wood ships to sugar alcohols using supported platinum catalysts in water without acid catalyst. The experiment was divided two processes as follows: hydrolysis of cellulose and hemicellulose to soluble sugars by hot compressed water, and hydrogenation of sugars to sugar alcohol by platinum over activated carbon and hydrogen gas. They found that the Pt loading and catalyst amounts increased the yield of sugar alcohol from wood chips. The total yield of sugar alcohol increased from 40.6% to 53.8% when the amount of 2%Pt/C catalyst increased from 0.2 to 0.3 g. However, the total yield of sugar alcohol decreased after using 0.1 g of 4%Pt/C catalyst. They obtained a maximum yield of sugar alcohol from 0.3 g of 4% Pt/C with 62.0%. This result showed the yield of product yield based on sugar content and lignin could not convert to product but cellulose and hemicellulose could convert under this reaction.

Yamaguchi et al. [79] studied the cyclization of alkanediols in high-temperature liquid water high-pressure carbon dioxide. They used three types of reactant as follows: 1,4- butanediol (1,4-BDO), 2R,5R-hexanediol (2R,5R-HDO), 2,5-dimethyl-2,5-hexanediol (2,5-DM-2,5-HDO) as a reactant. These reactant was converted to tetrahydrofuran (THF), 2,5-dimethyltetrahydrofuran (2,5-DMTHF), and to 2,2,5,5-tetramethyltetrahydrofuran (2,2,5,5-TMTHF), respectively. The results showed that increasing of dehydration reaction when carbon dioxide was added in to reaction come from increasing of proton concentration increased by the formation of carbonic acid. The order of dehydration rate of 1,4-BDO less than. Moreover, the dehydration rate of 2R,5RHDO showed lower than 2,5-DM-2,5-HDO. Thus, the addition of carbon dioxide into reaction increased the dehydration reaction. This method is also environmentally benign because after reaction water and carbon dioxide was easily to separate after the reaction.

Krogrll et al. [80] studied the extraction of hemicellulose from wood under high-temperature pH measuring. The result showed that the conventional glass pH electrodes are not suitable for pH detection at high temperatures because at high temperature caused losing of sensitive ion by the degradation of hydro gen ion in membrane. The potential measurement was used to study the stability of Zr/ZrO_2 electrode. The results calibration of pH was made from phthalate and phosphate buffers. The result showed that an yttria stabilized Zr/ZrO_2 pH electrode could use in condition (high temperature). The electrode could use under condition (pH ranged 0.35 of acid and base at temperature 443 K).

Yamaguchi et al. [81] studied hydrogen production from woody biomass over supported metal catalysts in supercritical water. The results showed that lignin could convert to hydrogen and methane under supercritical water over metal on supported catalysts. They reported that the yields of gaseous products increased when the metal on supported catalysts were added into reaction. They also suggested that these catalysts had performance for gasification of lignin under supercritical water. The order of metal for gasification of lignin as follows: Ru > Rh > Pt > Pd > Ni over activated carbon. However, the order of hydrogen production was Pd > Ru > Pt > Rh > Ni over activated carbon. In supercritical water, gasification of lignin has performance when titania and activated carbon were used as supports of metal catalysts.

Shirai et al. [82] reported hydrogenation rate of benzaldehyde and dehydration rate of sorbitol in water increased when carbon dioxide was added into reaction. The result showed that the optimum condition of hydrogenation reaction of benzaldehyde over a charcoal-supported palladium catalyst water was 313 K. Moreover, the hydrogenation rate increased when carbon dioxide pressure equaled to 5 MPa. The optimum condition of dehydration reaction of sorbitol conducted was 500 K by the dehydration rate was added into 30 MPa of carbon dioxide.

Yamaguchi et al. [83] studied the dehydration in intramolecular of mannitol under high-temperature liquid water without acid catalysts. They found that mannitol could convert to product. They obtained anhydromannitol and 1,4-anhydromannitol as a product from mannitol. On the other hand, they obtained only 1,4-anhydrosorbitol as a product from sorbitol. The difference of 1,4-anhydroarabitol and 2,5-anhydroarabitol was the difference of structure. The position of hydroxyl groups of cyclic ethers formed at position cis- and trans- . Trans-form caused the hydroxyl groups at the difference positions of carbon in sorbitol by the dehydration reaction was promoted sorbitol to 1,4-AHSO as a major product. Contrary, Cis-form caused the hydroxyl groups at the C-2 and C-3 positions of mannitol by the dehydration reaction of mannitol to 1,4-AHMA as a product. Thus, the structural of reactant has the effect to the reaction pathway of conversion of sorbitol and manitol into 1,4-AHMA.

Sheikhdavoodi et al. [84] studied sugarcane bagasse gasification in supercritical water. The result showed that KOH catalysts gave the maximum yield of hydrogen production. They found that reaction temperature was a major reason of the high yield of hydrogen production. The optimum condition of sugarcane bagasse gasification was temperature 800 °C with the presence of KOH catalyst. They also studied the effect of other alkali salts. The result showed that the order of performance of catalyst for hydrogen production was KOH > NaOH > K_2CO_3 > $KHCO_3$ > $NaHCO_3$ > activated carbon. They reported that the efficiency of gasification can obtain 100%. They obtained the highest hydrogen production with 75.6 mol kg^{-1}.

Jin and Enomoto [85] studied hydrothermal conversion of biomass into acetic acid and lactic acid. The results showed that biomass could convert biomass into products under hydrothermal reaction. The mainly product was acetic acid and lactic acid from biomasses by using alkali as a catalyst under hydrothermal reaction. Glycerin could convert to lactic acid f by using alkali catalyst under hydrothermal reaction. The result showed that hydrothermal reaction could easily converted biomass into acetic acid and lactic acid by alkali catalyst promoted some reaction of biomass into acetic acid and lactic acid. Moreover, alkali catalyst also a major reason for biomass conversion into acetic acid and lactic acid product. They reported that hydrothermal process had a high potential for conversion of biomass into chemical.

Deng and Wang [86] studies the C-C cleavage of biomass for the conversion of biomass into high value chemicals. They reported that organic acids such as ethylene glycol and lactic acid were interesting. The results showed that the selective of C-C cleavage bonds in cellulose has effect to conversion of reactant into high-value chemicals. The cellulose could directly convertor to product such as levulinic and lactic acids under inert atmosphere. They reported that the addition of hydrogen gas into reaction was converted cellulose into ethylene and propylene glycols. On the other hand, the addition of O_2 gas into reaction showed that cellulose was converted to malonic, glyconic acetic and formic acids as a product. In addition to the presence of catalyst in system could converted cellulose into other chemicals. Thus, they suggested that the different atmospheres has effect to C–C cleavage bonds of cellulose.

Bicker et al. [87] found that addition of metal ions such as Co(II), Ni(II), Cu(II) and Zn(II) into reaction have the effect to the yield of lactic acid. They obtained 42% yield of lactic acid from using sucrose as a reactant. On the other hand, 86% yield of lactic obtained using dihydroxyacetone as a reactant. The optimum condition of this method is temperature 573 K and 25 MPa. The result showed that the presence of metal ion promoted the conversion of triose sugar to lactic acid. The use of Zn(II) as a catalyst could convert sugar to the highest yield of lactic acid.

Wang et al. [88] studied glucose conversion using copper oxide as a catalyst under hydrothermal reaction. They used a batch reactor and continuous reactor in order to comparison the product. The result showed that the use of copper oxide increased the yields of lactic acid and acetic acid from glucose. The highest of selective lactic acid and acetic acid production is 59% and 32%, respectively. The optimum condition of this reaction was temperature 573 K, and reaction 1 min. The addition of CuO has the effect to the production of lactic acid and acetic acid in NaOH. The mechanism of glucose into lactic acid and acetic acid were that glucose was converted into lactic acid by though glyceraldehyde and pyruvaldehyde while fructose was oxidized into acetic acid. Thus, they reported that the addition of CuO has effect to the conversion of glucose to lactic acid.

Dong et al. [89] studied that the use of mixed metal catalyst (Zn-Sn-Beta) for cellulose conversion into lactic acid. This metal oxide was prepared via ion exchange promoted. The process of cellulose conversion was carried out in water. The result showed that the conversion of sucrose was 99% with 54% of lactic acid yield. The optimum condition was temperature 463 K, and reaction time 2 h under air pressure. They studied the properties of acid and of the Zn-Sn over Beta zeolite. The suggested that Zn into the Sn-Beta zeolite enhanced the Lewis acid and base sites of catalyst. Increasing of the base sites inhibited a dehydration reaction of fructose to 5-hydroxymethylfurfural and other decomposition. They reported that the increasing of Lewis acid promoted the reaction of sucrose into lactic acid and the base sites inhibit the conversion of fructose into 5-HMF. The sequence caused the Brønsted acid.

Yan et al. [90] reported that NaOH and $Ca(OH)_2$ could promote the reaction of glucose into lactic acid under hydrothermal reaction. They obtained 27% yield of lactic acid from conversion of glucose with the presence of 2.5 M NaOH. Contrary, 20% yield of lactic acid obtained from conversion of glucose with 0.32M $Ca(OH)_2$. The optimum condition was temperature 573 K reaction time 60 s. They suggested the mechanisms of glucose conversion into lactic acid as follows: glucose was converted to fructose and then fructose converted to lactic acid. lactic acid was formed via the aldose of three carbon atoms. The result showed that lactic acid was generated though formaldehyde or glycolaldehyde. Moreover, retrol-aldol condensation reaction was the key step of conversion of hexose to C_3 sugar.

Wang et al. [91] studied conversion of cellulose to lactic acid using erbium-exchanged montmorillonite K10 as a catalyst. These catalysts were evaluated under hydrothermal condition for conversion of cellulose into lactic acid. The optimum condition of cellulose conversion was operated at condition 0.3 g cellulose, 0.1 g catalyst, 30 mL water at temperature 240 °C under 2 MPa of N_2, and reaction time 30 min. The reusability of catalyst showed that the yield of lactic acid decreased in the first recycle. Second recycle, the yield of lactic acid also decreased. They reported that lactic acid yield decreased because the leaching of erbium species in solution. Moreover, some carbon was covered on the surface of catalyst. However, they purposed that erbium over montmorillonite K10 has performance for cellulose conversion into lactic acid.

Tang et al. [92] studied the conversion of cellulose and carbohydrates into chemical. They report that vanadium oxide (VO^{2+}) accelerated cellulose conversion and also accelerated glucose into lactic acid and formic acid. They suggested that VO^{2+} promoted the isomerization reaction of glucose into fructose via the retro-aldol condensation reaction. This reaction accelerated fructose to C_3 sugar and the isomerization of C_3 sugar, which leads to the formation of lactic acid. The oxidative C-C cleavage bonds of the intermediates. This sequence caused by the redox reaction of $VO^{2\ +}/VO^{2+}$. The result of this step obtained formic acid and CO_2 as a product. They reported that the addition of alcohol into reaction has the effect to the formation of CO_2 but it enhances the formic acid yield.

CHAPTER III

EXPERIMENTAL

3.1 Materials and reagents

Materials used in the study are listed in Table 3.1.

Table 3.1 List of chemicals and catalyst

Chemicals	**Source**
Microcrystalline cellulose	Merck
Titanium oxide (Anatase-phase)	Kanto Chemical
Titanium oxide (Rutile-phase)	
Cerium oxide	
Cerium oxide	Nippon Yttrium
Thulium oxide	
Yttrium oxide	
Zirconium oxide	Wako Pure Chemical Industries
Hafnium oxide	
Gallium oxide	
Zirconyl chloride	
28% Ammonia solution	
DL-Glyceraldehyde	
Lactic acid	
D(+)-Glucose	
D(-)-Fructose	

Table 3.1 (Continue) List of chemicals and catalyst

Chemicals	**Source**
Magnesium oxide	Ube Industries
Hydroxymethylfurfural	Sigma-Aldrich
Furfural	
Aluminum oxide	
Iron(III) oxide	
Lanthanum oxide	
Zirconium oxide	
Levulinic acid	TCL Company
Pyruvaldehyde	MP Biomedicals
Dihydroxyactone	
Niobium oxide	Koso Chemical
Tantalum oxide	Nacalai Tesque
Zirconium oxide	
Vanadium oxide	Rare Metallic
Zirconium oxide	Hosokawa Micron Co.
Zirconium oxide (ZRO-6)	Daiichi Kigenso Kagaku Kogyo
Zirconium oxide (ZRO-7)	
Zirconium oxide (ZRO-8)	
Zirconium oxide (ZRO-9)	
10%WO_3-ZrO_2	
9%LA_2O_3-ZrO_2	

Table 3.1 (Continue) List of chemicals and catalyst

Chemicals	Source
5%CeO_2-ZrO_2	Daiichi Kigenso Kagaku Kogyo
30%TiO_2-ZrO_2	
10%SiO_2-ZrO_2	
14%Y_2O_3-ZrO_2	
5%ZrO_2-Al_2O_3	
10%ZrO_2-Al_2O_3	
20%ZrO_2-Al_2O_3	
2%CaO-ZrO_2	

3.2 Preparation of zirconium oxide

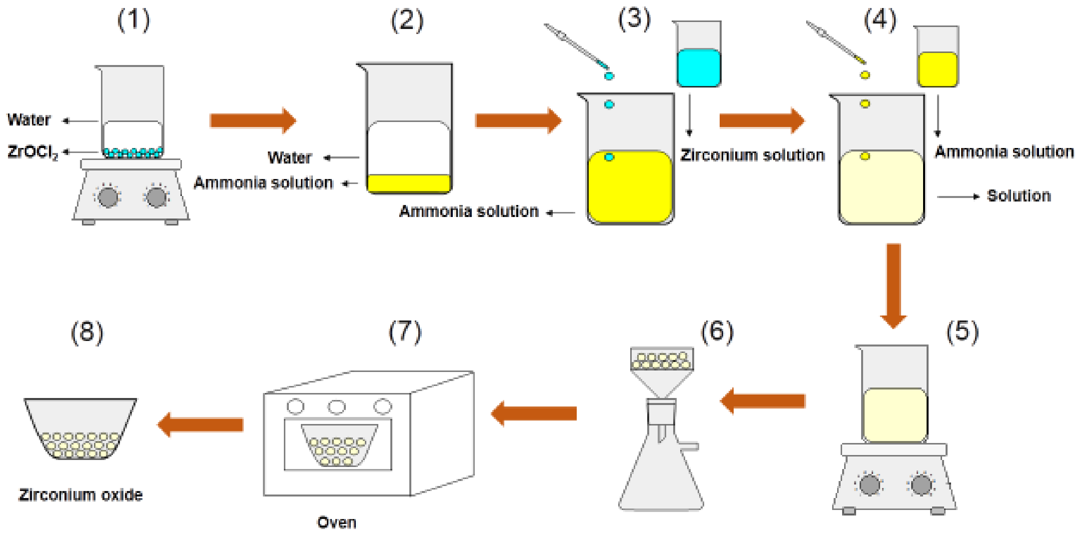


Figure 3.1 Preparation of zirconium oxide

Zirconium oxide was prepared by a precipitation method as follows [93]; 13.07 g of zirconyl chloride ($ZrOCl_2$•$8H_2O$) was dissolved in 500 cm^3 of water. 6.1 g of 28% ammonia solution was added into 1 L of distillate water for preparation 0.1 M aqueous ammonia. The aqueous solution of $ZrOCl_2$•$8H_2O$ was gradually dropped into 300 cm^3 of a 0.1 M of aqueous ammonia with stirring. 0.1 M ammonia solution was added until the pH of the obtained suspension reached 10. This suspension was stirred for 1 h and then aged for 24 h. The precipitate was separated from the aqueous solution by filtration, washed several times with distilled water. The precipitate was dried at 393 K overnight and then the samples were calcined at temperatures of 773, 873, 973, and 1073 K in air for 4 h. These calcined samples are denoted as ZrO_2-X (X = calcination temperature).

3.3 Reaction test

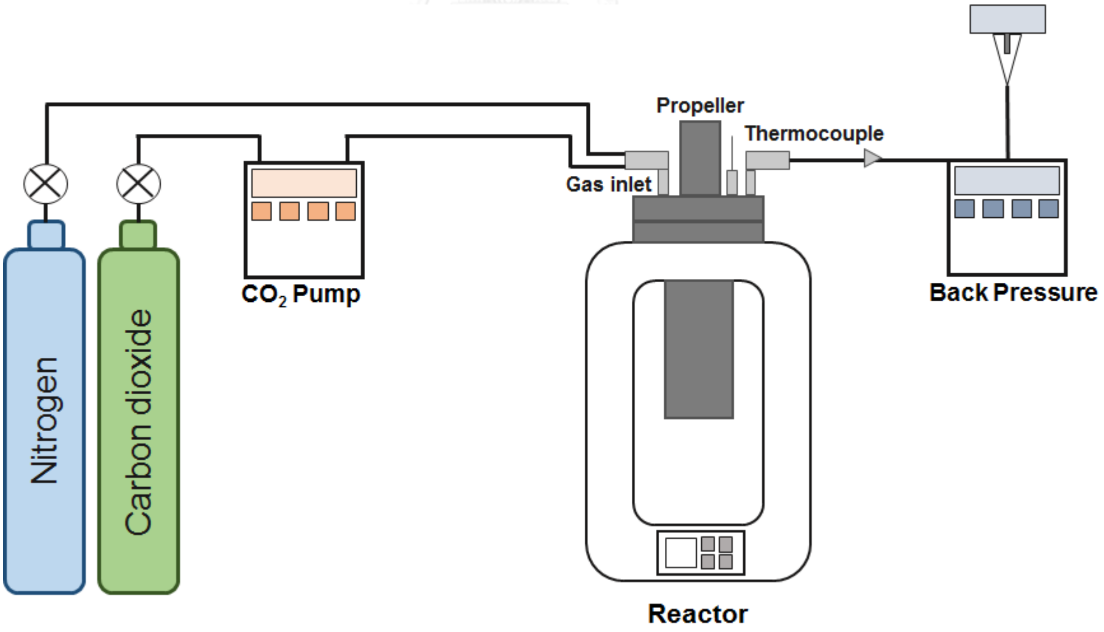


Figure 3.2 Reactor system for cellulose conversion

3.3.1 Ball milling pretreatment

In this work, for all of experiments I used ball milled cellulose as a reactant. Cellulose (Merck Ltd., microcrystalline cellulose) 10 g was added into ball milling pot. Zirconium balls were added into ball milling pot, then ball milling pot was set on ball milling roll. After that, ball milled cellulose was kept.

3.3.2 Cellulose conversion into levulinic acid by hot compressed water and carbon dioxide

The conversion of cellulose was carried out in a stainless steel batch reactor (OM Lab-Tech, MMJ-100) with an inner volume of 100 cm^3. Ball-milled cellulose (Merck Ltd., microcrystalline cellulose) (0.5 g), water (50 g) were loaded into the reactor after that the reactor was heated to 323 K. When temperature increased to 323 K, the reactor was purged with carbon dioxide after that carbon dioxide was loaded into the reactor (10.2 MPa). Carbon dioxide gas was added in to reactor by using CO_2 pump (Jasco Company, Model: PU-2080-CO_2 plus). The reactor was heated to 473 K and maintained at that temperature for 6 h with screw stirring. After the reaction, the reactor was cooled down until temperature decreased to 323 K. Carbon dioxide gas was gradually released by using Back pressure regulator (Jasco Company, Model: BP-2080-M plus). A mixture of liquid and solid was recovered and filtered to separate the solid materials from the liquid fraction. The solid residue was dried overnight at 333 K, and the weight of the dry solid residue was recorded.

3.3.3 Cellulose conversion into lactic acid by using metal oxides and mixed metal oxide as a catalyst

Cellulose conversion was carried out in a stainless steel batch reactor (OM Lab-Tech, MMJ-100) with an inner volume of 100 cm^3. Ball-milled cellulose (Merck Ltd., microcrystalline cellulose) (0.5 g), water (50 g), and the reactor was purged with nitrogen gas (0.1 MPa). The reactor was heated to 473 K and maintained at that temperature for 6 h with screw stirring. After the reaction, the reactor was cooled down at room temperature. A mixture of liquid and solid was recovered and filtered to separate the solid materials from the liquid fraction. The solid residue was dried overnight at 333 K, and the weight of the dry solid residue was recorded.

Quantitative analyses of water-soluble chemicals such as lactic acid, levulinic acid, 5-hydroxymethylfurfural (HMF), and furfural in the liquid fraction were performed by gas chromatography (GC). Quantitative analyses of sugars such as glucose were conducted by high-performance liquid chromatography (HPLC). The amount of total organic carbon (TOC) in the liquid fraction was determined using a total organic carbon analyzer (TOC). The conversion and product yields were calculated based on the dry weight and moles of carbon by equation (1) and (2), respectively.

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

$$\text{Product yield (\%)} = \left(\frac{\text{mole of carbon atom in product}}{\text{mole of carbon atom in cellulose}}\right) \times 100 \qquad (2)$$

3.4 Product analysis and Characterization

3.4.1 Gas chromatography (GC)

Gas chromatography (Shimadzu, GC-2014) with a flame ionization detector and an InertCap capillary column (GL Sciences Inc.); 1-butanol was used as the internal standard. I used gas chromatography to identify the products in solution such as lactic acid, levulinic acid, 5-hydroxymethylfurfural (HMF), and furfural. The result from gas chromatography was used to calculate the amount of product in equation (2).

3.4.2 High-performance liquid chromatography (HPLC)

High-performance liquid chromatography (Shimadzu, HPLC) with a refractive index detector (Shimadzu, RID-10A) and a UV-Vis detector (Shimadzu, SPD- 20AV) equipped with a Rezex RPM-Monosaccharide Pb+2 column (Phenomenex). I used high-performance liquid chromatography to identify sugars such as glucose and fructose. The result from high-performance liquid chromatography was used to calculate the amount of product in equation (2).

3.4.3 Total organic carbon analyzer (TOC)

Total organic carbon analyzer (Shimadzu, TOC-V_{CSN}). I used total organic carbon analyzer to calculate the amount of organic carbon in solution.

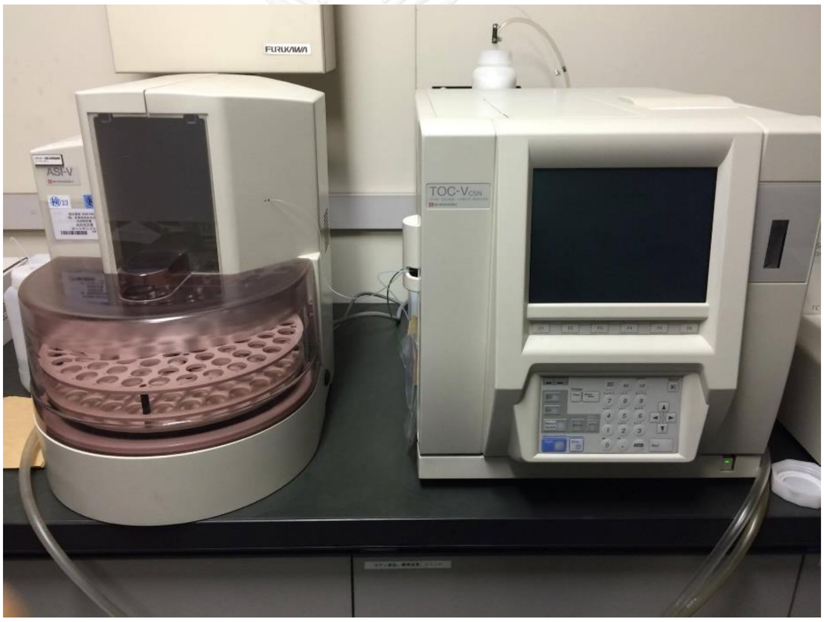


Figure 3.3 Picture of total organic carbon analyzer (Shimadzu)

3.4.4 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of the catalysts were recorded using a Rigaku SmartLab with Cu Kα radiation (λ = 0.15406 nm) under 30 mA current and 40 kV voltages in the 2θ range of 5–90° with a 2θ step size of 0.02°.

3.4.5 N_2-adsorption

Nitrogen adsorption and desorption measurements at 77 K were carried out on a Micromeritics 3FLEX 3500 chemisorption analyzer for samples degassed at 573 K for 4 h. The specific surface areas of the catalysts were determined by the Brunauer–Emmett–Teller (BET) method.

3.4.6 NH_3-Temperature-programmed desorption (NH_3-TPD)

Temperature-programmed desorption of ammonia (NH_3-TPD) was carried out with a TPD-1-AT instrument (Bel Japan, Inc.). The sample (ca. 0.05 g) was loaded in a quartz tube and pretreated at 773 K in flowing helium for 1 h. After cooling in flowing helium to 373 K, the sample was saturated in 5% ammonia diluted with helium (0.5 cm^3 s^{-1}) for 30 min, after which the flowing gas was switched to helium at a flow rate of 0.83 cm^3 s^{-1} for 1 h. Finally, the sample was heated at a constant rate of 10 K min^{-1} to 953 K. The ammonia signal was analyzed with an online quadrupole mass spectrometer.

Figure 3.4 Picture of NH_3-Temperature-programmed desorption (Bel Japan, Inc.)

3.4.7 CO_2-Temperature-programmed desorption (CO_2-TPD)

Temperature-programmed desorption of carbon dioxide (CO_2-TPD) was carried out on a Micromeritics 3FLEX 3500 chemisorption analyzer with an online quadrupole mass spectrometer. The sample (ca. 0.2 g) was loaded into a quartz tube and pretreated at 773 K in flowing helium for 1 h. After cooling in flowing helium to 323 K, the sample was saturated in a CO_2 flow (0.5 cm^3 s^{-1}) for 30 min. The flowing gas was switched to helium (0.83 cm^3 s^{-1}) for 1 h, and then the sample was heated at a constant rate of 10 K min^{-1} to 953 K.

3.4.8 Atomic emission spectrometer

The concentration of zirconium species in liquid solution was determined using an inductively coupled plasma (ICP) atomic emission spectrometer (SPS4000, SII NanoTechnology Inc.).

CHAPTER IV

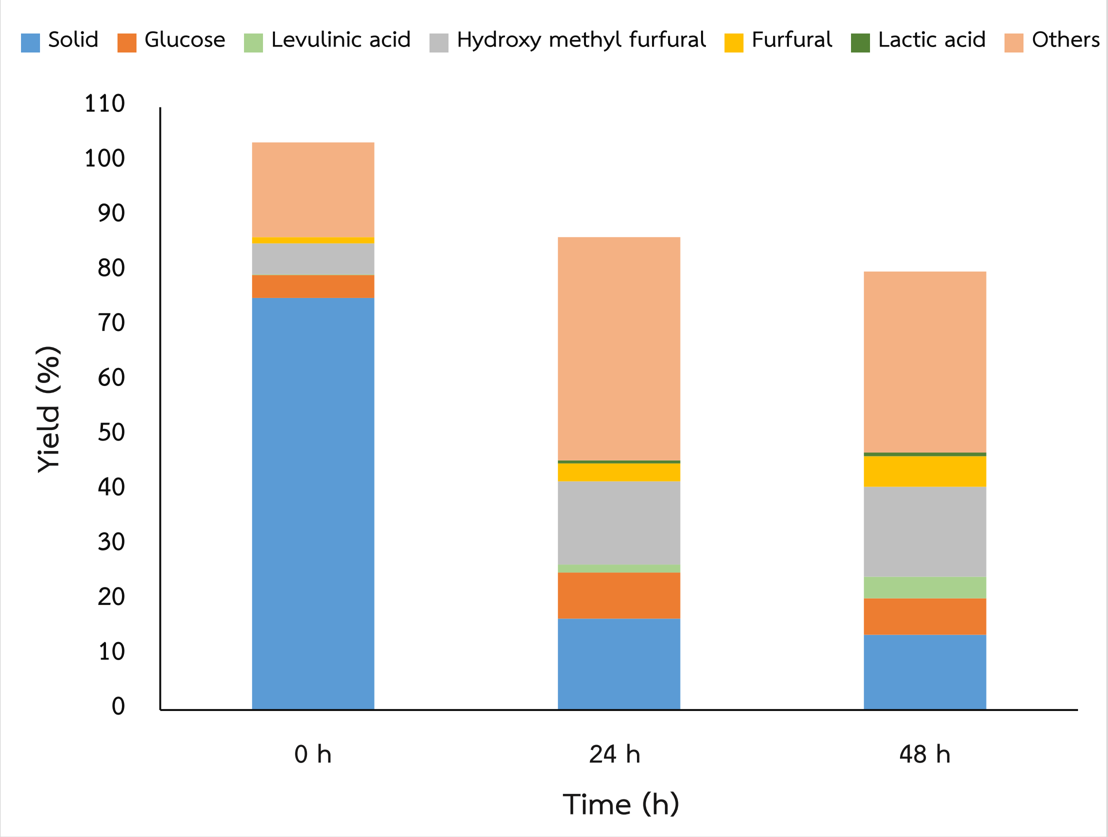
RESULTS AND DISCUSSION

The study in this chapter is divided into three parts. The first part is the investigation for the effect of carbon dioxide pressure for cellulose conversion. The second part studies the use of metal oxides as a catalyst and characterization of metal oxides were investigated in third part. The effects of reaction temperature, reaction time, amount of catalyst, and reusability of catalyst as well as the reaction path way were investigated. The catalytic performance of metal oxide catalyst was compared with non-catalyst in reaction. The third part studies the effect of mixed metal oxide. The different properties between metal oxide and mixed metal oxide were investigated.

4.1 Cellulose conversion into levulinic acid by hot compressed water and carbon dioxide method.

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

4.1.1 The effect of ball milled pre-treatment



(**Condition**; Temperature 473 K, reaction time 6 h, deionized water 50 mL, and 0.5 g of reactant)

Figure 4.1 The effect of ball milled pretreatment on cellulose conversion in water without catalyst

First, we studied the effect of ball milled pretreatment. Microcrystalline cellulose was milled at 24 h and 48 h. Ball milled pretreatment at 48 h of cellulose could convert cellulose more than using cellulose without ball milled pretreatment. The result showed that ball milled pretreatment could destroy the crystallinity by breaking hydrogen bonds in cellulose. After cellulose was treated by ball milling pretreatment. Ball milled cellulose was analyzed by X-ray diffraction. The result of XRD was shown in Figure 4.2. Figure 4.1 showed the product yields of solid phase and liquid phase. This figure was not showed the yield of gas phase. Therefore, the yield of product was not equaled 100%. Liquid phase was detected in order to find the product after reaction. After the characterization, we found glucose, levulinic acid, hydroxy methyl furfural, furfural, and lactic acid in solution but we could not also found unknown chemical in solution. Unknown chemicals were recorded as other in Figure 4.1. Other products might be the intermediate chemical of levulinic acid and lactic acid such as hexose sugar, sugar alcohol, glyceraldehyde, dihydroxyacetone, pyruvaldehyde, and etc.

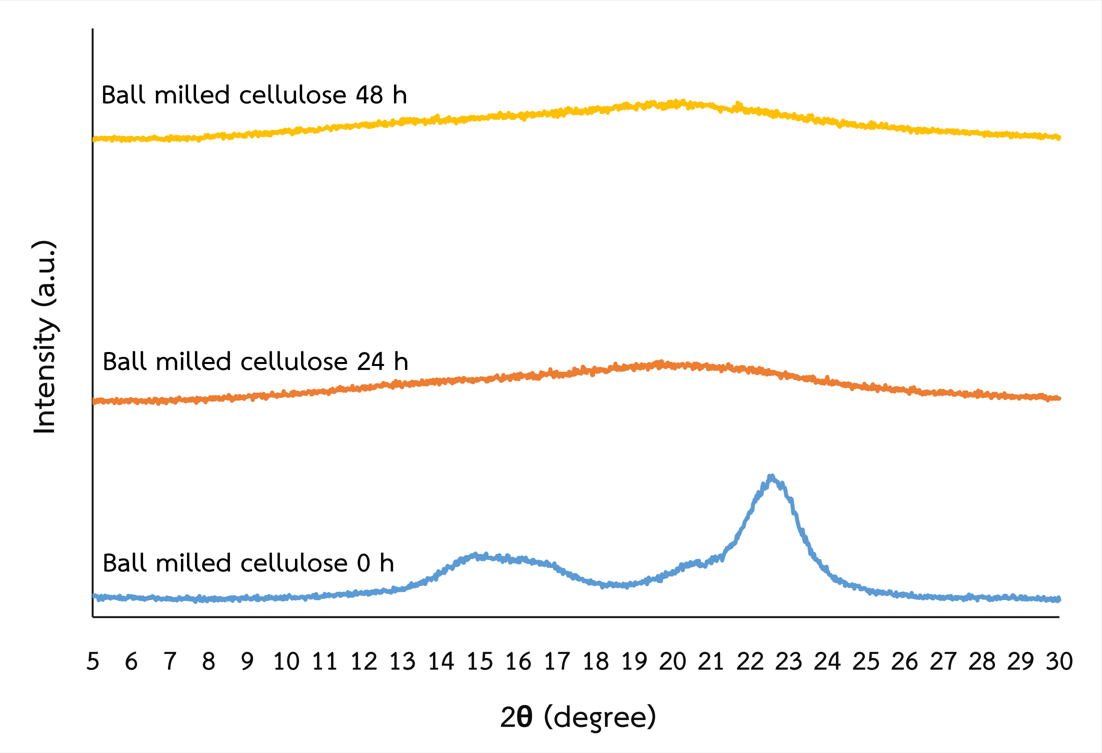
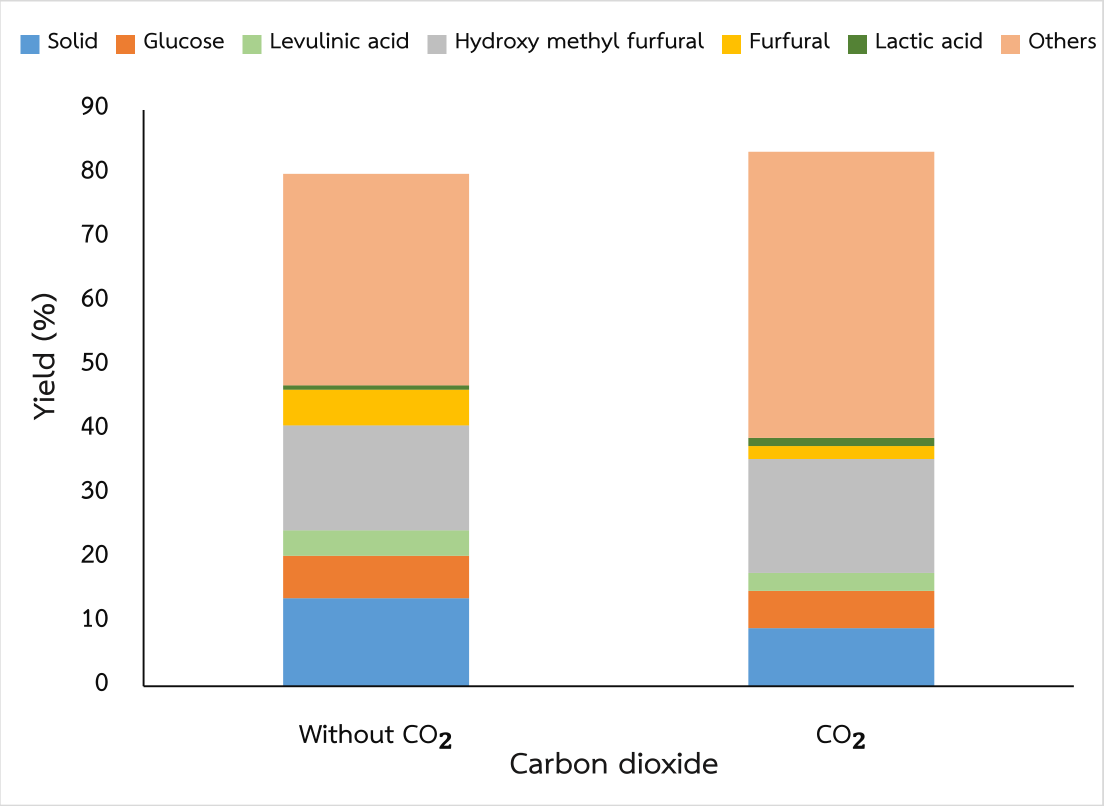


Figure 4.2 XRD patterns of ball milled cellulose

The result of XRD showed crystalline peak of cellulose at 2θ = 22.6° [94]. The intensity of crystalline peak of cellulose decreased when ball milling time of cellulose increased.

4.1.2 The effect of addition of carbon dioxide

Figure 4.3 showed the result of addition of carbon dioxide. 4.0% yield of levulinic acid obtained from cellulose conversion in case of without carbon dioxide. When carbon dioxide was added into reaction, cellulose could convert to levulinic acid with 2.8%. The result showed that the yield of levulinic acid slightly differed in condition with or without carbon dioxide. Thus, the use of carbon dioxide was not enough for cellulose conversion into levulinic acid.

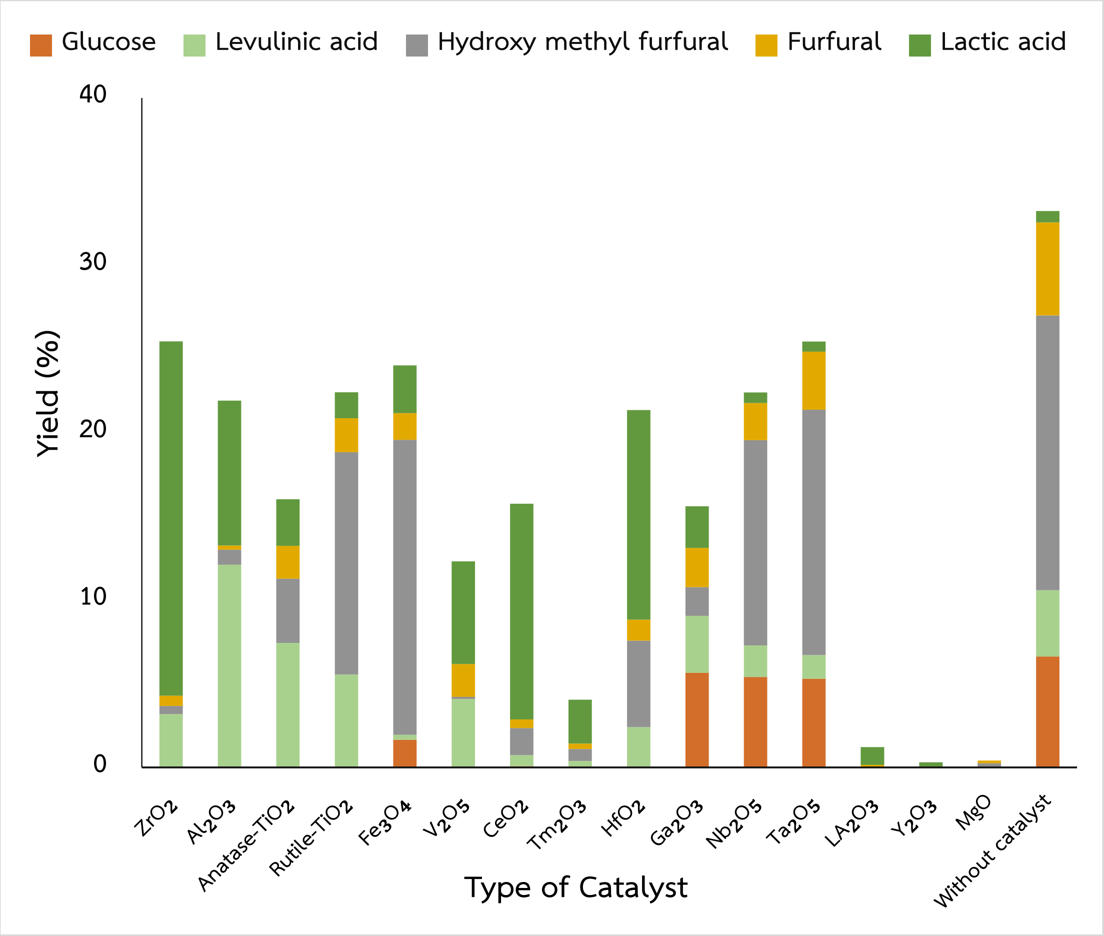


(**Condition**; Temperature 473 K, reaction time 6 h, 15 MPa of carbon dioxide, deionized water 50 mL, and 0.5 g of reactant.)

Figure 4.3 The effect of addition of carbon dioxide on cellulose conversion without catalyst.

4.2 Cellulose conversion into lactic acid by using metal oxides as a catalyst

4.2.1 Catalyst Screening



(**Condition**; Temperature 473 K, deionized water 50 mL, amount of catalyst 1 g (HfO_2 and Ga_2O_3 0.5 g), reaction time 6 h, and 0.5 g of ball-milled cellulose.)

Figure 4.4 Catalyst screening for cellulose conversion into lactic acid

Catalyst screening of cellulose was carried out in condition (473 K, 6 h) using various transition metal oxides such as ZrO_2 (ZRO-7), Al_2O_3, A-TiO_2, R-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 as a catalyst. The conversion of cellulose without solid catalysts was carried out for reference. In case of without catalyst, cellulose could convert to chemical with 86.3% in water. However, cellulose was converted to lactic acid, levulinic acid, glucose, and HMF (0.7, 4.0, 6.6%, and 16.4%, respectively). It has been reported that glucose was converted to fructose and that fructose was dehydrated into HMF in water with or without Brønsted acid

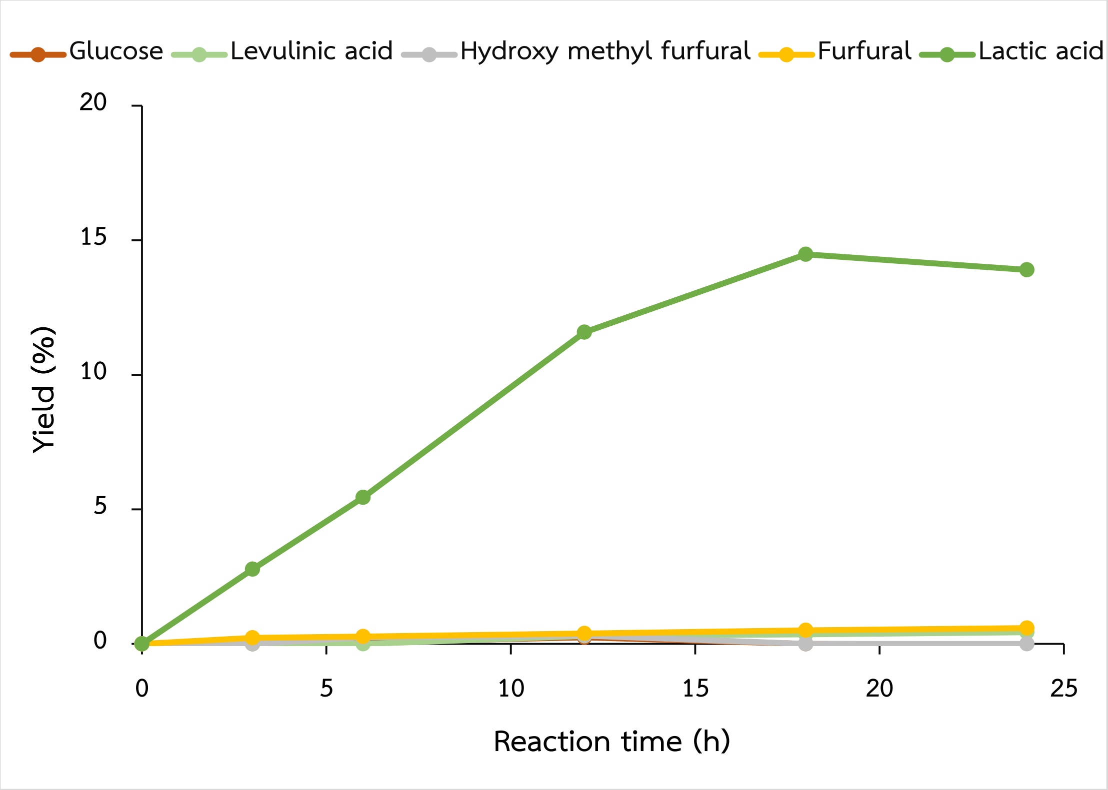
[95]. Finally, levulinic acid obtained from dehydration reaction of HMF [78] (Scheme 2). Previous studies have indicated that lactic acid occurred by fructose was converted to glyceraldehyde and dihydroxyacetone via retro-aldol condensation reaction instead of fructose dehydration into HMF [96, 97] (Scheme 2). The result of catalyst screening showed that the yield of levulinic acid increased from 4.0% to 12.1% by using Al_2O_3 as a catalyst. Al_2O_3 could convert cellulose into levulinic acid because Al_2O_3 might be acid sites as Bronsted acid. Moreover, the metal oxides (ZrO_2, CeO_2, HfO_2, and V_2O_5) could convert cellulose to the high yield of lactic acid because the presence of these metal oxides promoted a retro-aldol condensation reaction of fructose into glyceraldehyde and dihydroxyacetone. The maximum yield of lactic acid obtained from using ZrO_2 as a catalyst with 21.2%. Previous studied also indicated that ZrO_2 has stable catalyst in high temperature water [26, 27]. The active sites of this step will be discussed in part of characterizations. Thus, the result of catalyst scanning showed that Al_2O_3 was effective catalyst for cellulose conversion into levulinic acid but ZrO_2 was the most effective catalyst for cellulose conversion into lactic acid in condition (473 K, 6 h).

4.2.2 Reaction conditions

The reaction conditions such as reaction temperature, reaction time, and amount of catalyst were explored to obtain high yield of lactic acid from cellulose. The conversion of cellulose with ZrO_2 (ZRO-7) catalyst was carried out in the range of temperature 453-483 K and reaction time 3 to 24 h.

4.2.2.1 The effect of reaction time and reaction temperature

4.2.2.1.1 Reaction time at 453 K

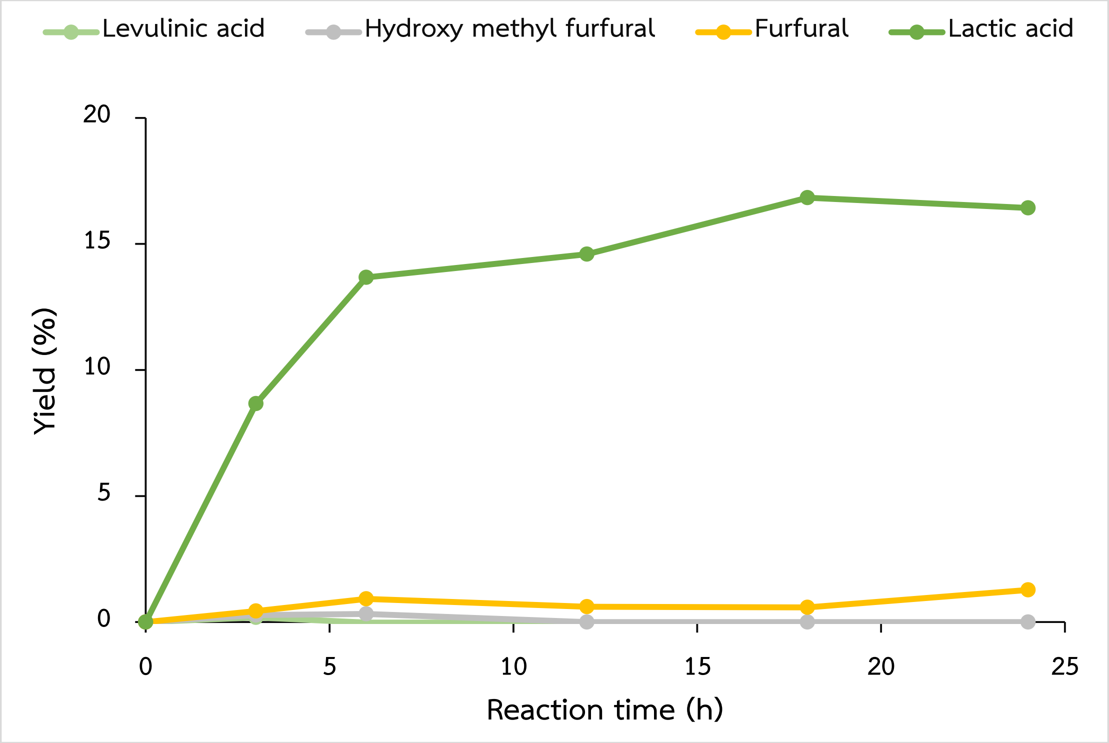


(**Condition**; Temperature 453 K, deionized water 50 mL, amount of ZrO_2 1 g, and 0.5 g of ball-milled cellulose.)

Figure 4.5 The effect of reaction time at 453 K on cellulose conversion into lactic acid using ZrO_2

The result of Figure 4.5 showed that the yield of lactic acid increased from 2.8 to 14.5% with increasing of reaction time from 3 to 18 h. The yield of lactic acid decreased with 13.9% when the reaction time increased to 24 h because of the decomposition of lactic acid product. Temperature 453 K, and reaction time 18 h gave the highest yield of lactic acid with 14.5%.

4.2.2.1.2 Reaction time at 463 K

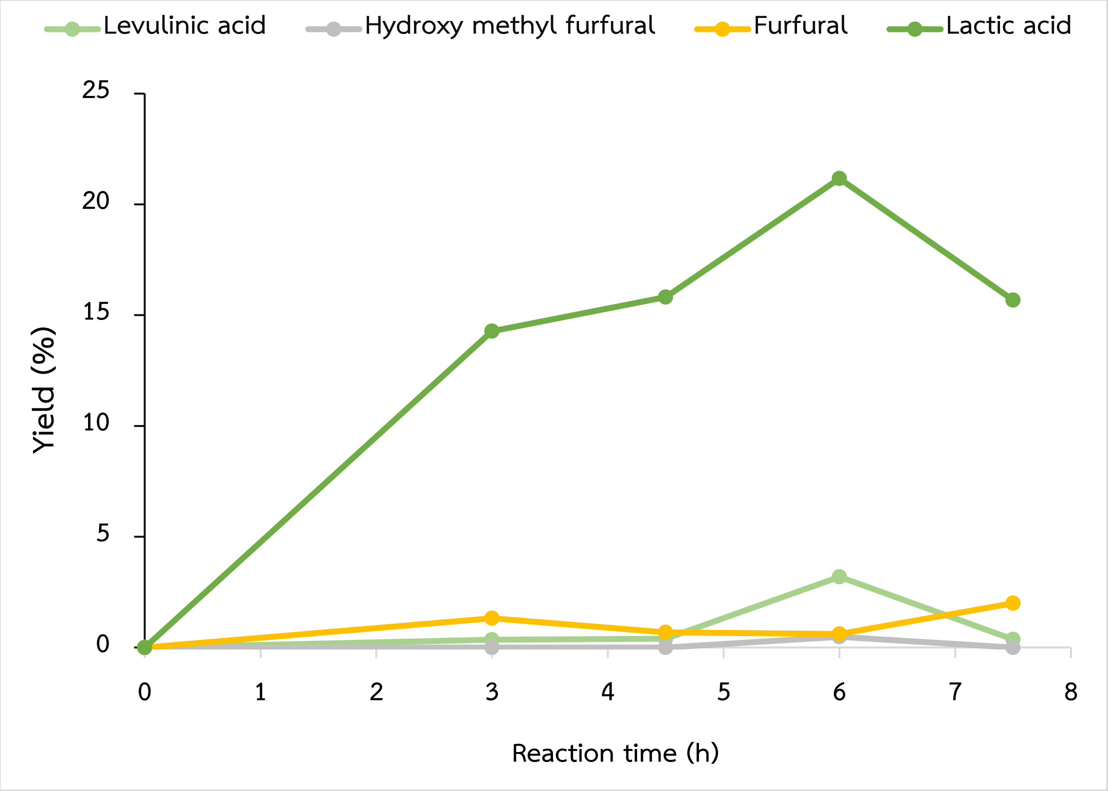


(**Condition**; Temperature 463 K, deionized water 50 mL, amount of ZrO_2 1 g, and 0.5 g of ball-milled cellulose.)

Figure 4.6 The effect of reaction time at 463 K on cellulose conversion into lactic acid using ZrO_2

The yield of lactic acid increased from 8.7 to 16.4% with increasing of reaction time from 3 to 18 h. When the reaction time was increased to 24 h, the yield of lactic acid slightly decreased. Thus, the reaction time 18 h was suitable for reaction temperature 463 K with the maximum yield of lactic acid 16.4%.

4.2.2.1.3 Reaction time at 473 K

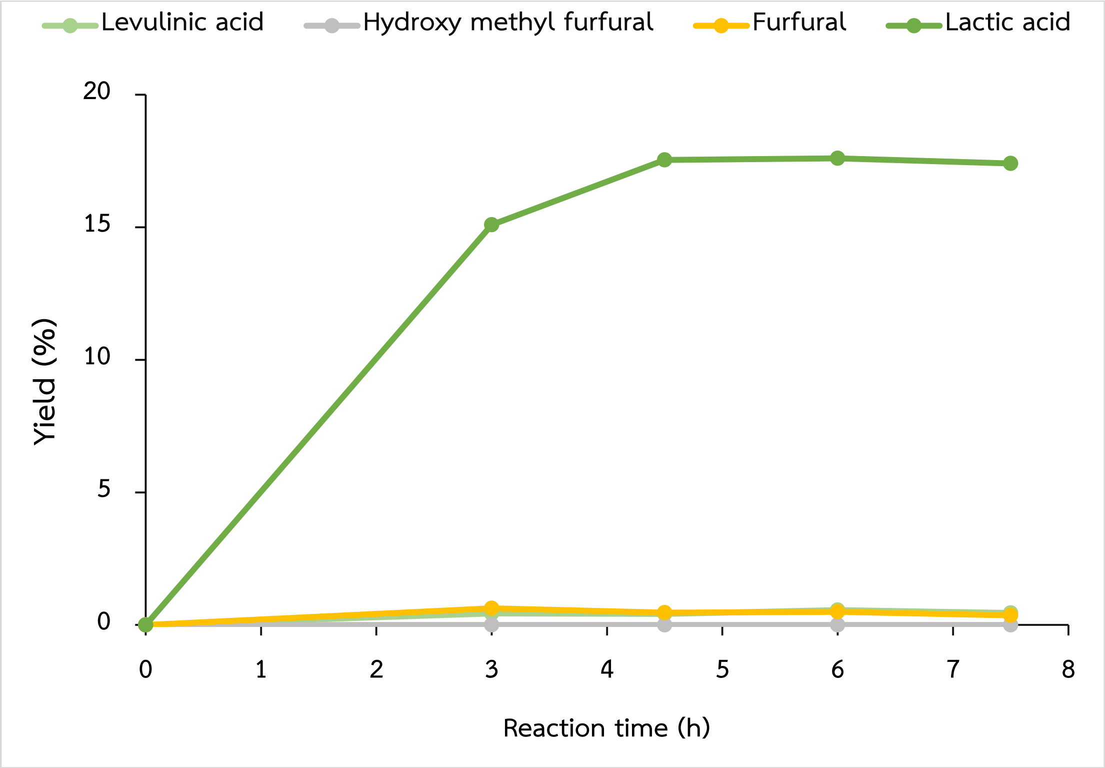


(**Condition**; Temperature 473 K, deionized water 50 mL, amount of ZrO_2 1 g, and 0.5 g of ball-milled cellulose.)

Figure 4.7 The effect of reaction time at 473 K on cellulose conversion into lactic acid using ZrO_2

Figure 4.7 showed the yield of lactic acid at reaction temperature 473 K. The result showed that the yield of lactic acid increased from 14.3 to 21.2% with increasing of reaction time from 3 to 7.5 h. When the reaction time was increased to 7.5 h, the yield of lactic acid decreased because the prolonged reaction time led to decomposition of lactic acid.

4.2.2.1.4 Reaction time at 483 K

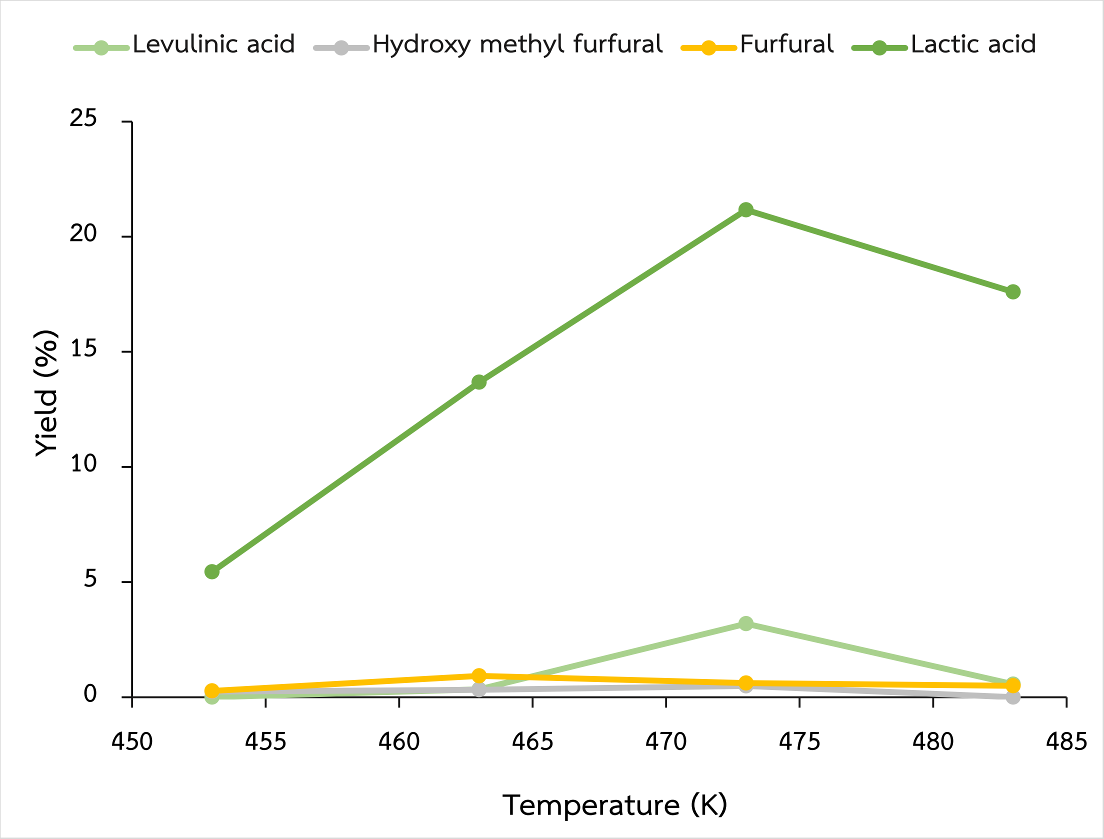


(**Condition**; Temperature 483 K, deionized water 50 mL, amount of ZrO_2 1 g, and 0.5 g of ball-milled cellulose.)

Figure 4.8 The effect of reaction time at 483 K on cellulose conversion into lactic acid using ZrO_2

The result of reaction temperature 483 K showed in Figure 4.8. The yield of lactic acid increased from 15.1 to 17.5% with increasing of reaction time from 3 to 4.5 h. After that the yield of lactic acid slightly differed when increasing of reaction time 6 to 7.5 h (17.6, and 17.4, respectively). Thus, the reaction time 6 h was the optimum of reaction time at reaction temperature 483 K.

4.2.2.1.5 Reaction temperature at 6 h



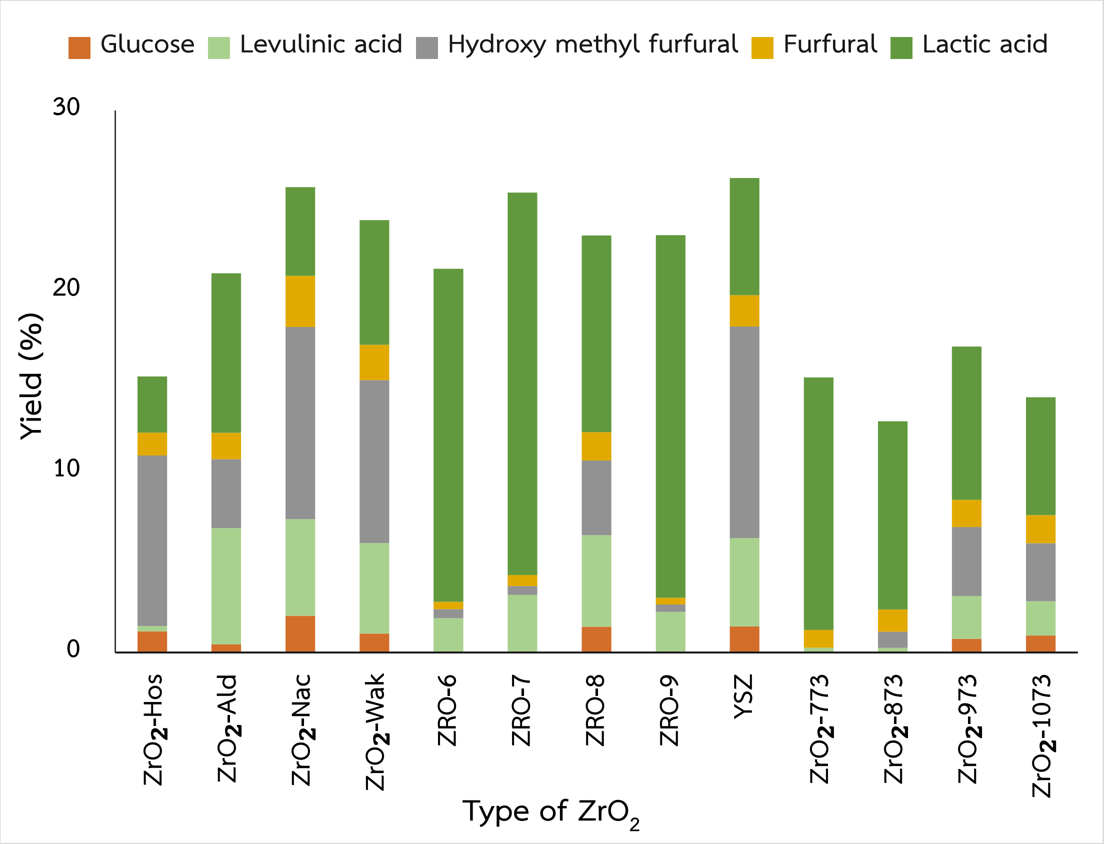
(**Condition**; Reaction time 6 h, deionized water 50 mL, amount of ZrO_2 1 g, and 0.5 g of ball-milled cellulose.)

Figure 4.9 The effect of reaction temperature at 6 h on cellulose conversion into lactic acid using ZrO_2

Figure 4.9 showed that the yield of lactic acid also increased with increasing of reaction temperature up to at 473 K. However, the lactic acid yield decreased at 483 K from 473 K, which was caused by the decomposition of product lactic acid at high reaction temperature.

The result of the effect of reaction temperature exhibited that temperature 473 K gave the maximum yields of lactic acid. The result of reaction temperature and reaction time showed that reaction temperature 473 K at 6 h was the optimum condition for cellulose conversion into lactic acid because we obtained a maximum yield of lactic acid with 21.2%. The decomposition of lactic acid was checked by using lactic acid as a reactant and ZrO_2 as a catalyst in the optimum condition (473 K, 6 h). The recovery of lactic acid was 90.8%, the indication being that some of lactic acid decomposed or polymerized into other materials. This result could explain the decrease of lactic acid when increasing of reaction time in each reaction temperature.

4.2.3 The different types of zirconium oxide



(**Condition**; Temperature 473 K, deionized water 50 mL, amount of catalyst 1 g, and 0.5 g of ball-milled cellulose.)

Figure 4.10 The different types of zirconium oxide

Figure 4.10 showed the yields of lactic acid from various types of ZrO_2 catalysts. The yield of lactic acid ranged from 3.1% to 21.2%. These results indicate that production of lactic acid requires specific active sites on the ZrO_2 catalysts and that the concentration of active sites varied widely between ZrO_2 catalysts. ZrO_2 (ZRO-7) gave a highest yield of lactic acid with 21.2%. In the case of a prepared ZrO_2 catalyst, the ZrO_2 was calcined at the different temperature in range 773 to 1073 K. The calcined samples are denoted as ZrO_2-773, ZrO_2-873, ZrO_2-973, and ZrO_2-1073. The result showed that the lactic acid yield decreased from 14.0% to 6.5% with increasing calcination temperature. These zirconium oxides have the difference of specific area, active sites, and the concentration of active sites. Thus, the properties of ZrO_2 have the effect to lactic acid yield.

4.2.4 Characterization

To understand the reason of the differences between the yield of lactic acid and types of zirconium oxide. We characterized the catalysts using XRD, N_2-adsorption, NH_3-TPD, and CO_2-TPD (Table 4.1).

4.2.4.1 XRD

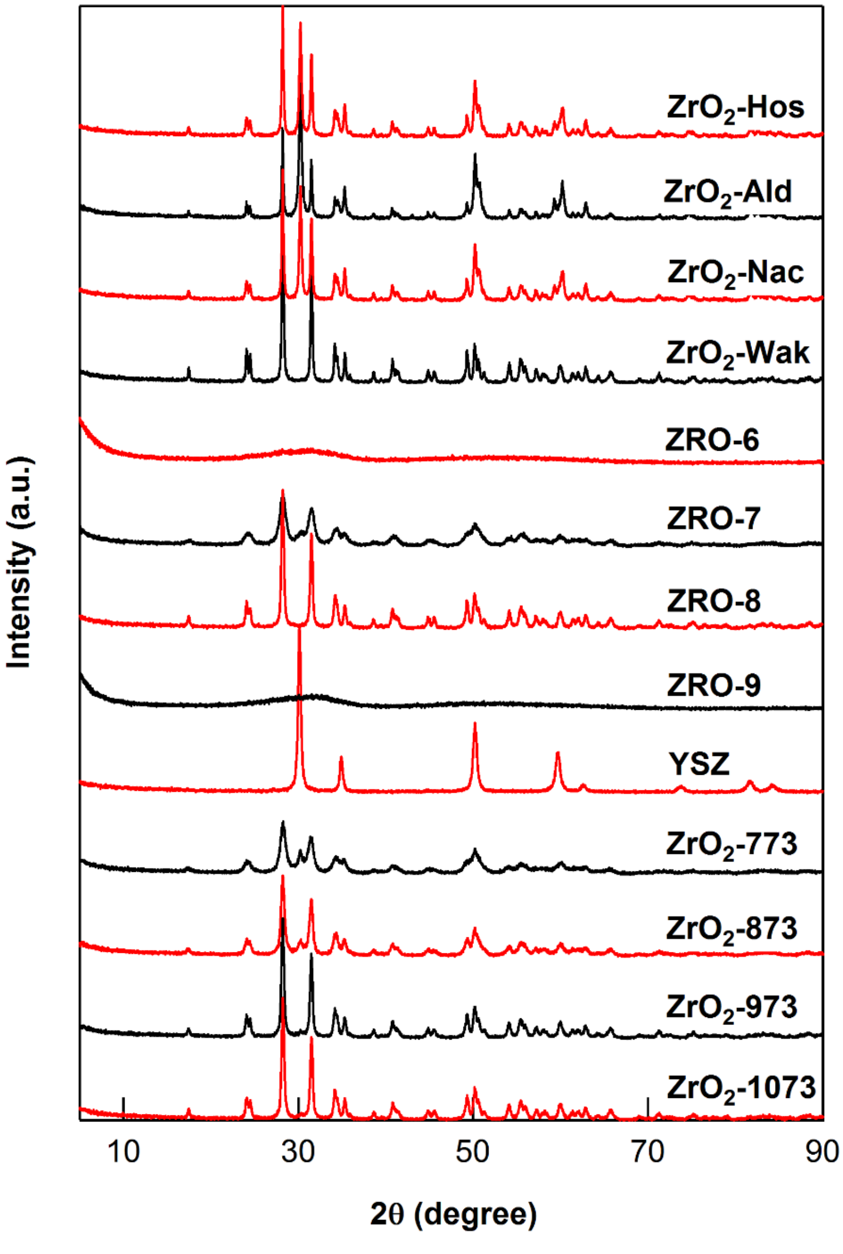


Figure 4.11 XRD Patterns [98]

The XRD patterns (Figure 4.11) [98] showed the crystal phase of ZrO_2 catalysts as follows: monoclinic, monoclinic/tetragonal mixtures, cubic crystal structures, and amorphous ZrO_2. The crystal phase and the crystal sizes of each ZrO_2 was showed in Table 3. The crystal sizes of the crystalline ZrO_2 ranged from 11.7 to 47.7 nm.

4.2.4.2 NH_3 Temperature programmed desorption

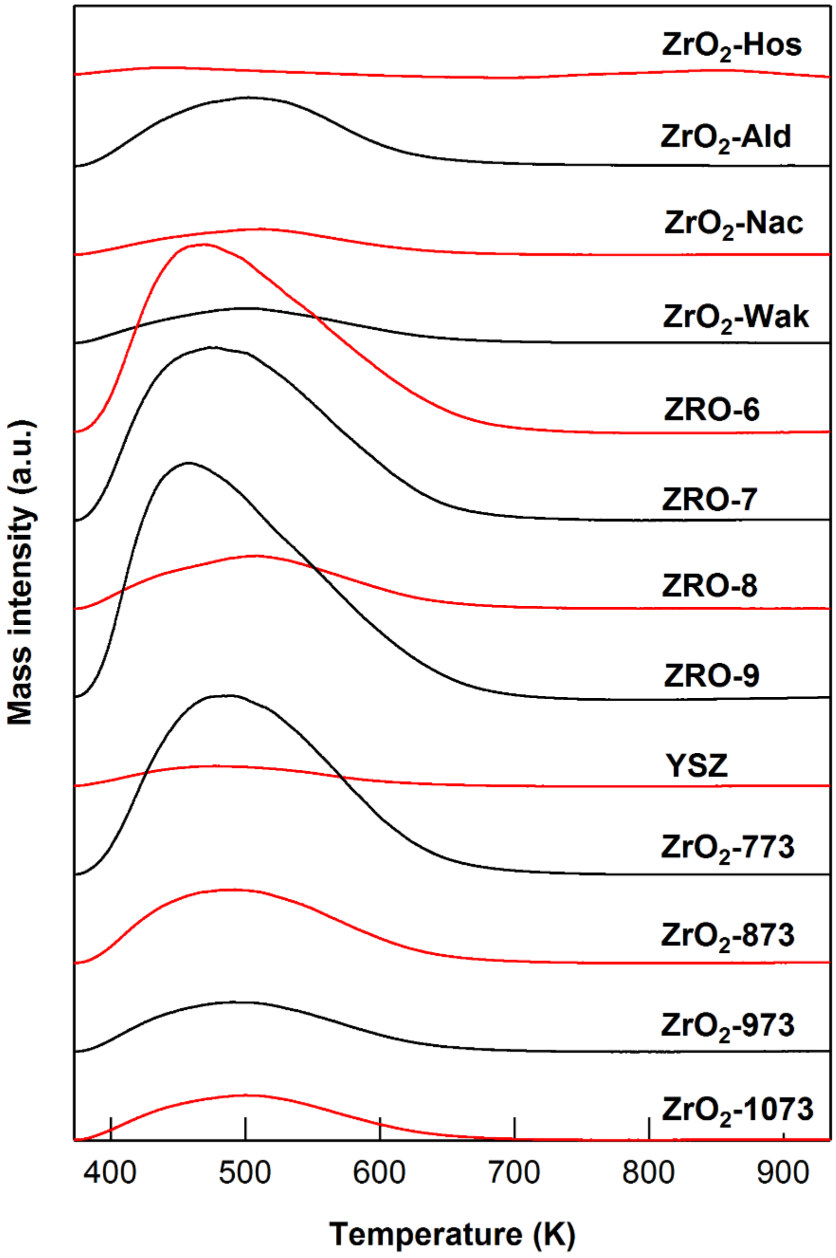


Figure 4.12 Profiles of temperature-programmed desorption of NH_3 [98]

Figure 4.12 showed only one peak of NH_3 desorption about 470 K, and no NH_3 desorption peak was occurred at a temperature above 673 K. This peak was indicated that ZrO_2 was weakly acidic on the acid sites. Moreover, the acid sites of ZrO_2 was classify as Lewis acids because the desorption peak of NH_3 on a Brønsted acid has been reported to be more than 673 K [99]. The result of concentration of acid sites was showed in Table 4.1.

4.2.4.3 CO_2 Temperature programmed desorption

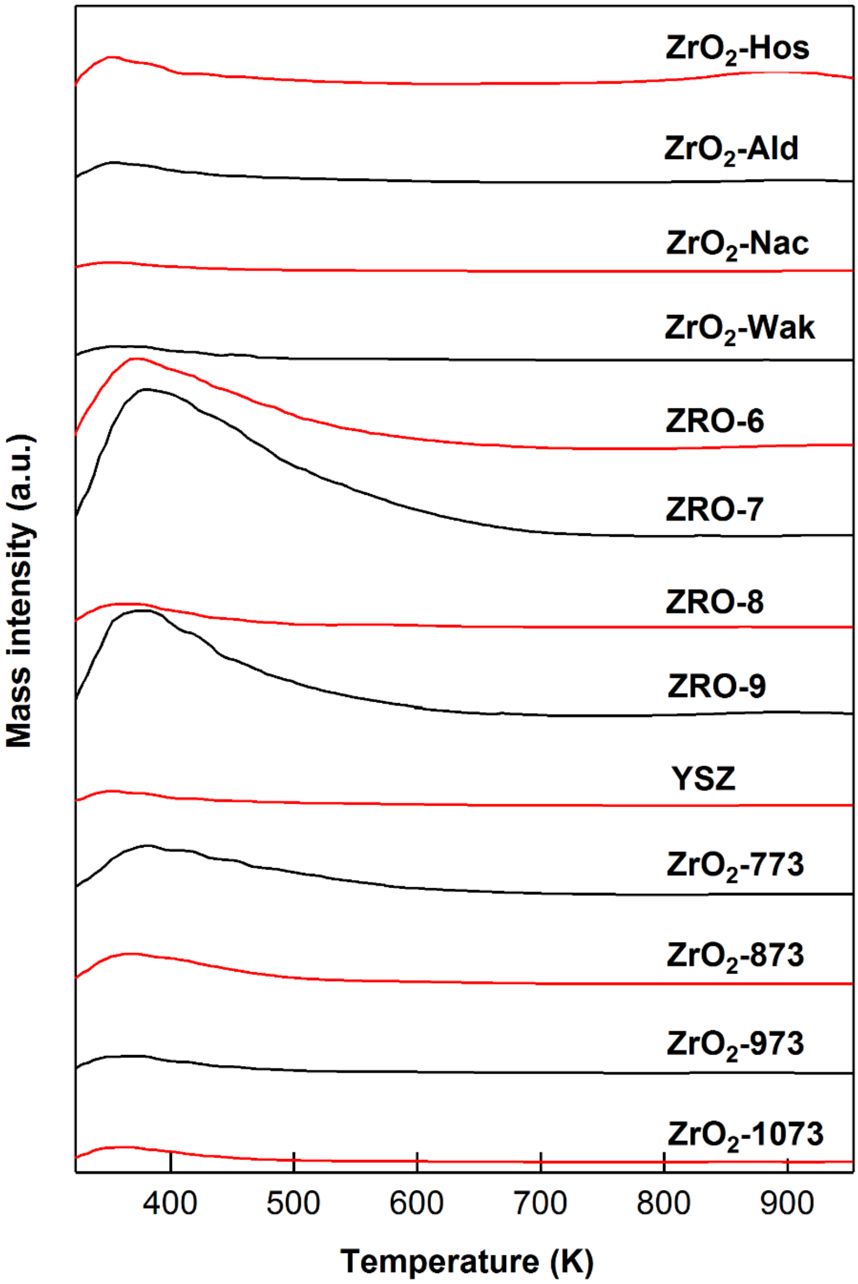


Figure 4.13 Profiles of temperature-programmed desorption of CO_2 [98]

The desorption temperatures of CO_2 from the ZrO_2 catalysts were 340–450 K (Figure 4.13). This peak was indicated the weakly basic on base sites of ZrO_2 [100].

4.2.4.4 Atomic emission spectrometer

The leaching of metal species was the problem for solid catalyst. Therefore, we studied the leaching of ZrO_2 by atomic emission spectrometer technique. The result showed that only 10^{-4}% of the Zr, which almost no leached out of Zr, was leached out during the reaction. Thus, ZrO_2 catalyst was stable in high-temperature water.

Table 4.1 demonstrated the result of Nitrogen adsorption and lactic acid yield. The result of Nitrogen adsorption shown that the specific surface areas ranged widely from 7.7 to 325 m^2 g^{-1}. Thus, these result in Table 4.1 indicated the crystal phases, crystal sizes, and specific surface areas of the ZrO_2 catalysts were poorly correlated with the yields of lactic acid from cellulose in condition 473 K, 6h.

Table 4.1 Structural characterization of zirconium oxides [98]

Catalyst	Crystal phase [a]	Crystalline size (nm) [a]	Specific surface area (m^2 g^{-1})	Acid site amount (mmol g^{-1})	Base site amount (mmol g^{-1})	Lactic acid yield (%) [b]
ZrO_2-Hos	Monoclinic, Tetragonal	44.8	19.4	0.004	0.092	3.1
ZrO_2-Ald	Tetragonal, Monoclinic	34.1	34.4	0.046	0.036	8.8
ZrO_2-Nac	Monoclinic	47.7	7.7	0.017	0.011	4.9
ZrO_2-Wak	Monoclinic	41.9	11.7	0.024	0.028	6.9
ZRO-6	Amorphous	–[c]	279.3[c]	0.122	0.348	18.4
ZRO-7	Monoclinic	12.1[c]	100.5[c]	0.118	0.485	21.2
ZRO-8	Monoclinic	23.4	22.1[c]	0.035	0.053	10.9
ZRO-9	Amorphous	–[c]	325.0[c]	0.144	0.396	20.0
YSZ	Cubic	23.4	7.8	0.012	0.028	6.5
ZrO_2-773	Monoclinic, Tetragonal	11.7	57.1	0.114	0.193	14.0
ZrO_2-873	Monoclinic	18.8	30.8	0.049	0.082	10.4
ZrO_2-973	Monoclinic	26.7	18.6	0.033	0.039	8.5
ZrO_2-1073	Monoclinic	25.8	17.4	0.029	0.032	6.5

[a] Crystal phase and crystalline size were determined by XRD pattern.

[b] Reaction condition: ball-milled cellulose 0.5 g, ZrO_2 1 g, deionized water 50 g, reaction temperature 473 K, reaction time 6 h.

[c] Data cited from reference

4.2.5 Correlation between the lactic acid yields with acid sites and base sites

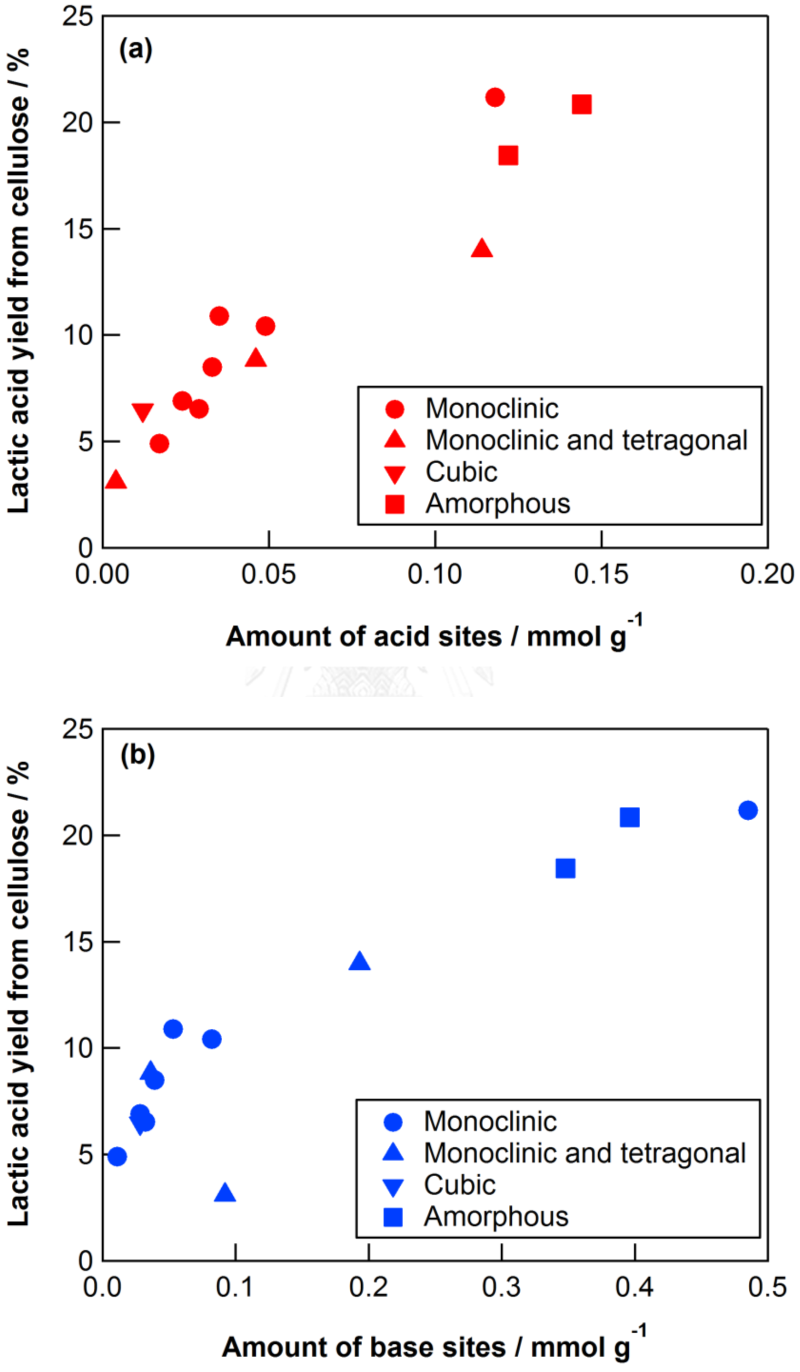
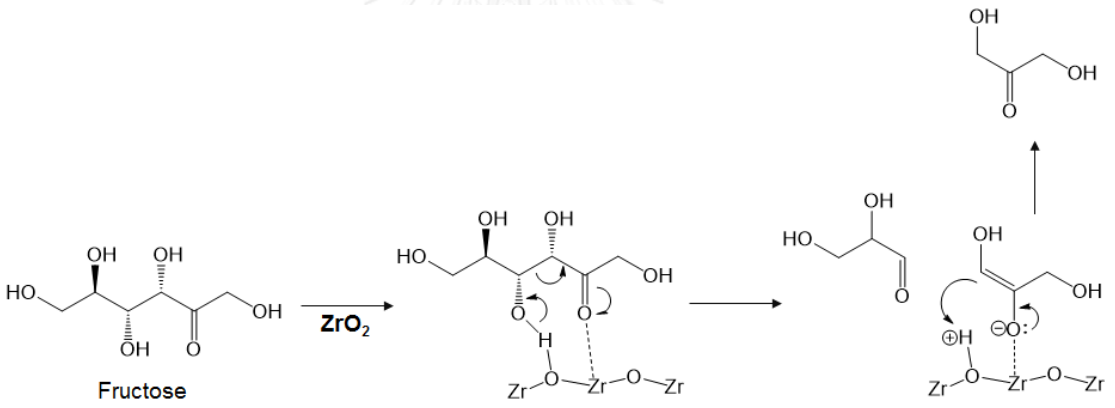


Figure 4.14 Lactic acid yield from cellulose using ZrO_2 catalysts with amount of (a) acid and (b) base sites [98].

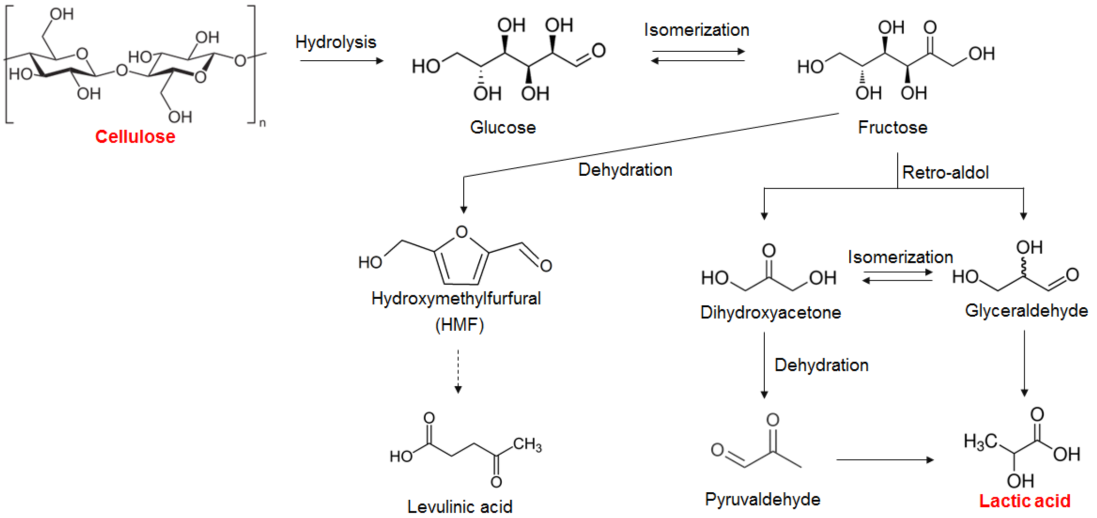
Figure 4.14 showed the correlation between the lactic acid yields and the concentration of acid and base sites on the ZrO_2 catalysts. A plot of the lactic acid yields with the concentration of acid and base sites on the ZrO_2 catalysts revealed that the lactic acid yield did not depend on the ZrO_2 crystal phase, and crystalline size but it depended on acid sites and base sites of ZrO_2. The results showed almost a linear relationship between the lactic acid yield and the concentration of acid and base sites on the ZrO_2 samples. Yang et al. reported that a combination of Lewis acid and base sites catalyzes xylose conversion into glyceraldehyde and glycolaldehyde via a retro-aldol reaction [101]. We proposed that the reaction mechanism of fructose conversion into glyceraldehyde and dihydroxyacetone by a retro-aldol reaction and the role of acid and base sites on ZrO_2. First, the carbonyl group of the fructose interacts with the Zr site of the Lewis acid, and in the same time the OH group at the position of the C-4 carbon adsorbs onto the O site of the week base (Scheme 1).



Scheme 1 Proposed mechanism for fructose conversion into glyceraldehyde and dihydroxyacetone by a retro-aldol reaction on acid and base sites on ZrO_2 [98].

4.2.6 Reaction pathway

Cellulose was hydrolysis to glucose after that glucose was converted to fructose. The presence of Lewis acid enhanced cleavage of the C–C bond between the C-3 and C-4 of fructose lead to the formation of glyceraldehyde and dihydroxyacetone. Thus, the key step of the production of lactic acid is fructose conversion into glyceraldehyde and dihydroxyacetone by a retro-aldol condensation reaction (Scheme 2) [101-103]. Dihydroxyacetone and glyceraldehyde was directly converted to lactic acid and converted to pyruvaldehyde. Finally, pyruvaldehyde was converted lactic acid.



Scheme 2 Proposed mechanism for cellulose conversion into chemicals [98].

To understand pathway of cellulose into lactic acid and how ZrO_2 catalyzes the conversion of intermediates into lactic acid after the retro-aldol reaction, we used dihydroxyacetone, glyceraldehyde, and pyruvaldehyde as reactants under the same conditions using ZrO_2 (Table 4.2).

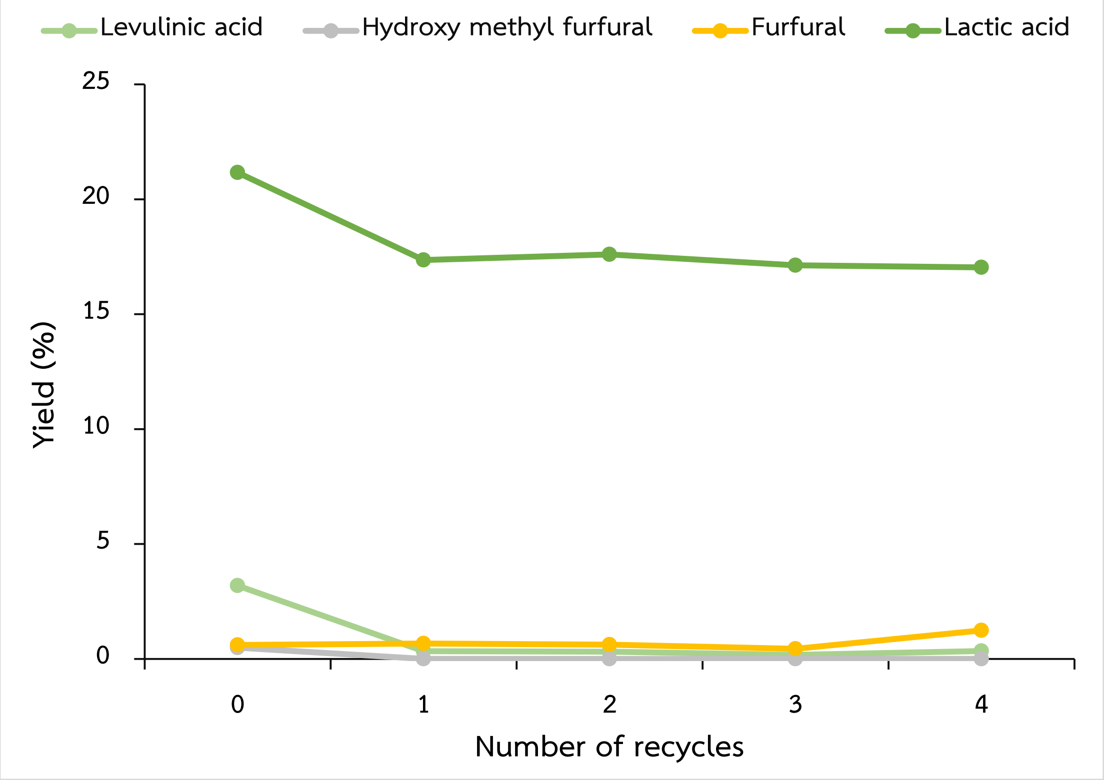
Table 4.2 Conversion of dihydroxyacetone, glyceraldehyde, and pyruvaldehyde with and without zirconium oxide [a] [98]

Reactant	Catalyst	Yield (%)			
		Lactic acid	HMF	Levulinic acid	Furfural
Dihydroxyacetone	–	17.5	0.0	0.0	0.0
Dihydroxyacetone	ZrO_2	28.7	0.0	0.0	0.0
Glyceraldehyde	–	22.5	0.0	0.0	0.0
Glyceraldehyde	ZrO_2	24.0	0.0	0.0	0.0
Pyruvaldehyde	–	1.0	0.0	0.0	0.0
Pyruvaldehyde	ZrO_2	22.8	0.0	0.0	0.0

[a] **Condition**: reactant 0.25 g, ZrO_2 (ZRO-7) 1 g, deionized water 50 g, reaction temperature 473 K, reaction time 6 h.

Glyceraldehyde and dihydroxyacetone were converted from fructose by the intermediates in the retro-aldol reaction of fructose. The both intermediates were studied to convert into lactic acid with or without of ZrO_2. The result showed that glyceraldehyde and dihydroxyacetone could convert to lactic acid in high-temperature (473 K) water without a ZrO_2 catalyst. In case dihydroxyacetone was a reactant. The yield showed higher with ZrO_2 (28.7%) than without ZrO_2 (17.5%). Without ZrO_2, dihydroxyacetone was isomerized into glyceraldehyde, and the glyceraldehyde was converted into lactic acid. This sequence of reactions occurred because pyruvaldehyde, the other possible intermediate produced from dihydroxyacetone, requires ZrO_2 as a catalyst to produce lactic acid. The conversion of pyruvaldehyde into lactic acid was reported to require Lewis acid sites workable in water such as TiO_2 [104-106]. In the case of dihydroxyacetone conversion catalyzed by ZrO_2, the ZrO_2 catalyst enhanced dihydroxyacetone isomerization into glyceraldehyde or dihydroxyacetone conversion into pyruvaldehyde, and then both glyceraldehyde and pyruvaldehyde were converted into lactic acid with ZrO_2 as the catalyst.

4.2.7 Reusability of catalyst



(**Condition**; Temperature 473 K, deionized water 50 mL, amount of ZrO_2 1 g, and 0.5 g of ball-milled cellulose.)

Figure 4.15 Cellulose conversion using a recycled ZrO_2 catalyst

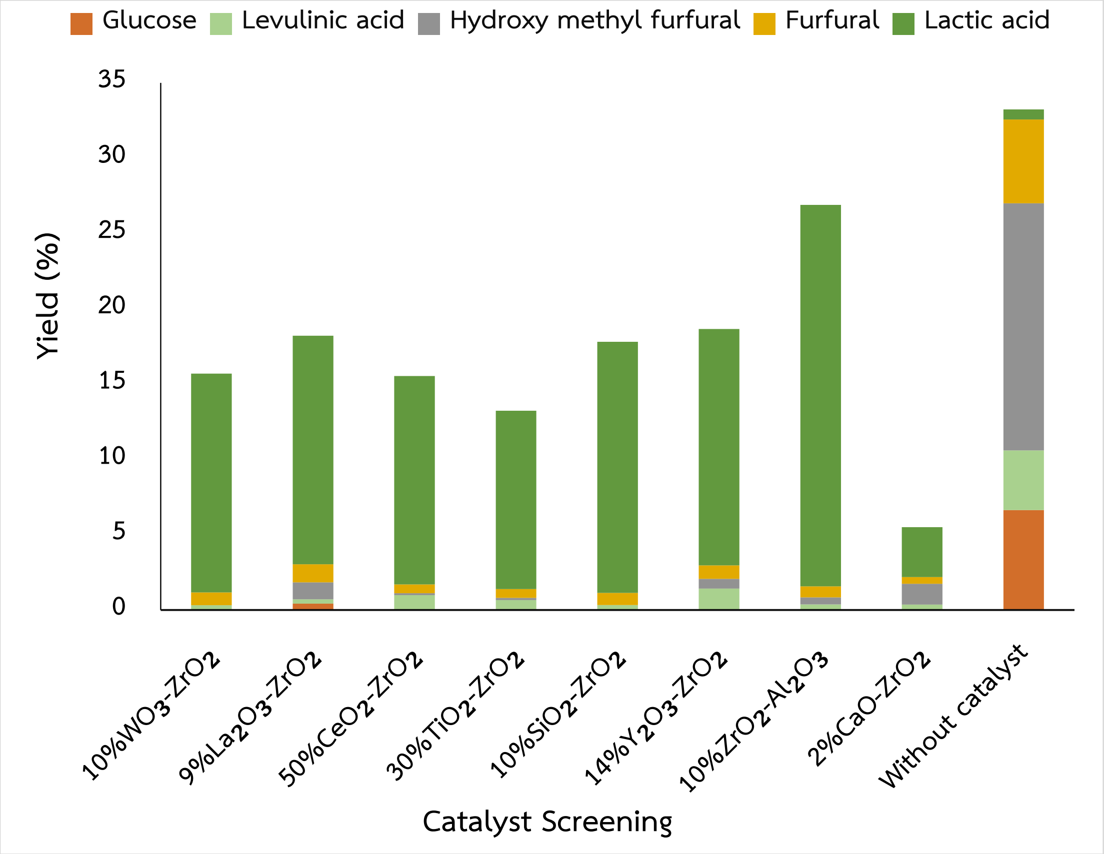
We investigated the reusability of ZrO_2 catalyst. After each reaction, the catalyst was separated from the liquid product by filtration, and then it was calcined at 673 K for 15 h in air to remove any carbon deposited on the surface of the catalyst. The lactic acid yield decreased slightly after the first reaction from 21.2% to 17.4%. After the second reaction the yield of lactic acid was stable. After five uses, the ZRO-7 catalyst was characterized in order to understand the decreasing of yield of lactic acid. The result showed that the concentration of acid sites did not change (0.128 mmol g^{-}

^{1}) from 0.118 mmol g^{-1} of the fresh ZRO-7 catalyst. However, the concentration of base sites decreased from 0.485 mmol g^{-1} to 0.350 mmol g^{-1} after the ZrO_2 was used five times. Thus, the result being a slight decrease of catalytic activity.

4.3 Cellulose conversion into lactic acid by using mixed metal oxides as a catalyst.

In second part, we studied the effect of various transition metal oxides for the catalytic conversion of cellulose to lactic acid by using (i.e., 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) [98]. The result showed that ZrO_2 gave the highest activity for lactic acid production from cellulose (yield 21.2%) at 473 K. To understand the effect of mixed metal oxide between ZrO_2 with other metal oxides were investigated. In this study, 10%WO_3-ZrO_2, 9%La_2O_3-ZrO_2, 50%CeO_2-ZrO_2, 30%TiO_2-ZrO_2, 10%SiO_2-ZrO_2, 14%Y_2O_3-ZrO_2, 10%ZrO_2-Al_2O_3, and 2%CaO-ZrO_2 were used in experiment.

4.3.1 Catalyst Screening



(**Condition**; Temperature 473 K, deionized water 50 mL, amount of catalyst 1 g, and 0.5 g of ball-milled cellulose.)

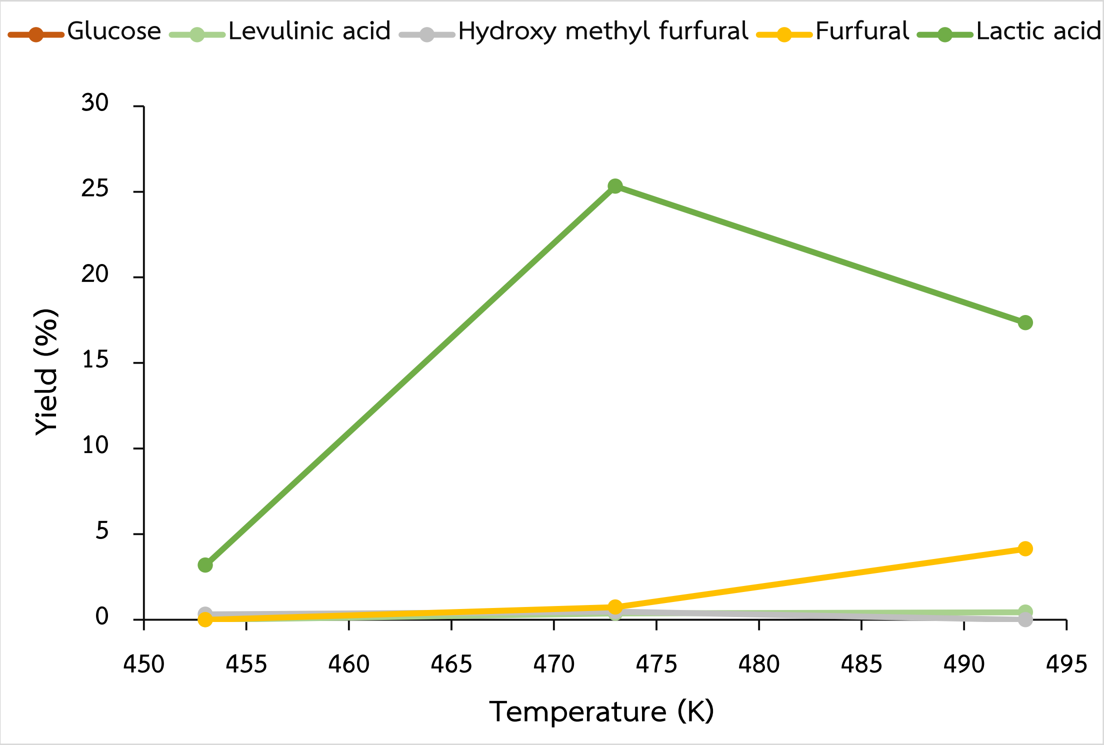
Figure 4.16 Catalyst screening

Figure 4.16 shown that result of catalyst screening. The conversion of cellulose was carried out at 473 K and 6 h using various mixed-metal oxides: 10%WO_3-ZrO_2, 9%La_2O_3-ZrO_2, 50%CeO_2-ZrO_2, 30%TiO_2-ZrO_2, 10%SiO_2-ZrO_2, 14%Y_2O_3-ZrO_2, 10%ZrO_2-Al_2O_3, and 2%CaO-ZrO_2. The result shown that a maximum yield of lactic acid obtained from using 10%ZrO_2-Al_2O_3 as a catalyst. In case of without solid catalysts, only 0.7% yield of lactic acid could be obtained. Thus, mixed metal oxide catalyst has performance for cellulose conversion into lactic acid.

4.3.2 Reaction conditions

The reaction conditions such as reaction time and reaction temperature were studied to obtain high yield of lactic acid from cellulose.

4.3.2.1 Effect of temperature

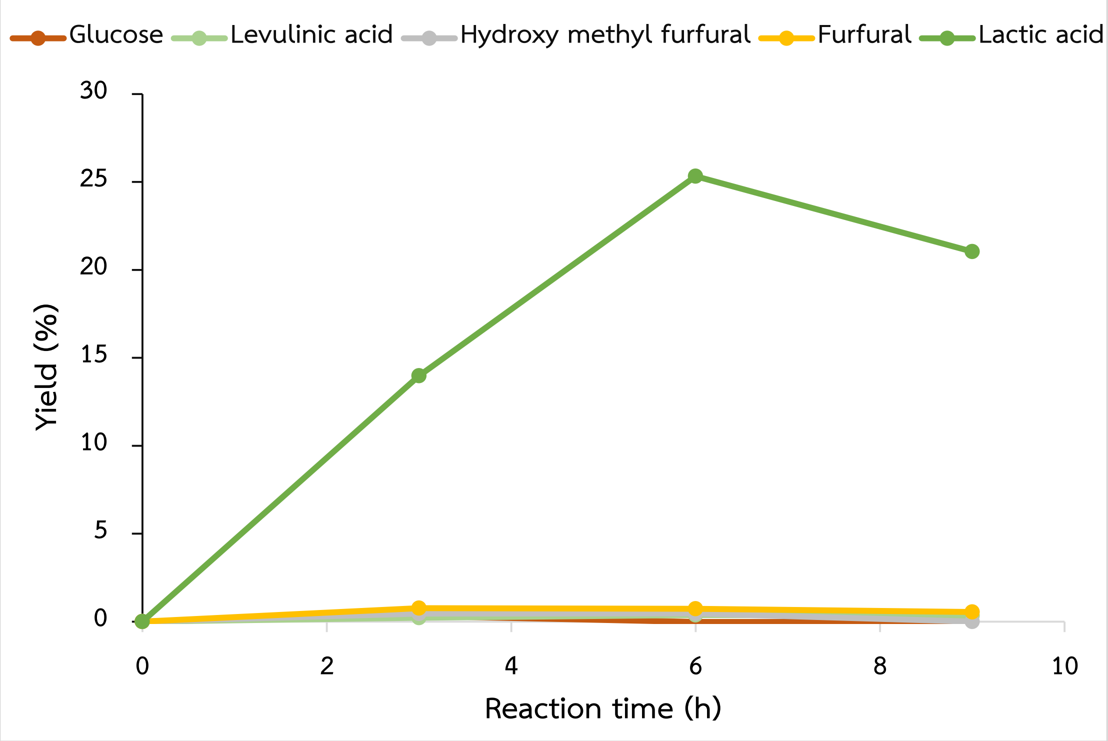


(**Condition**; Reaction time 6 h, deionized water 50 mL, amount of 10%ZrO_2-Al_2O_3 1 g, and 0.5 g of ball-milled cellulose.)

Figure 4.17 The effect of temperature

The conversion of cellulose using 10%ZrO_2-Al_2O_3 was carried out in the range of reaction time 453 to 493. The yield of lactic acid increased from 3.2 to 25.3% with increasing of reaction temperature from 453 to 473. When the reaction temperature was increased to 493 K, the yield of lactic acid decreased because the decomposition of lactic acid product.

4.3.2.2 Effect of reaction time



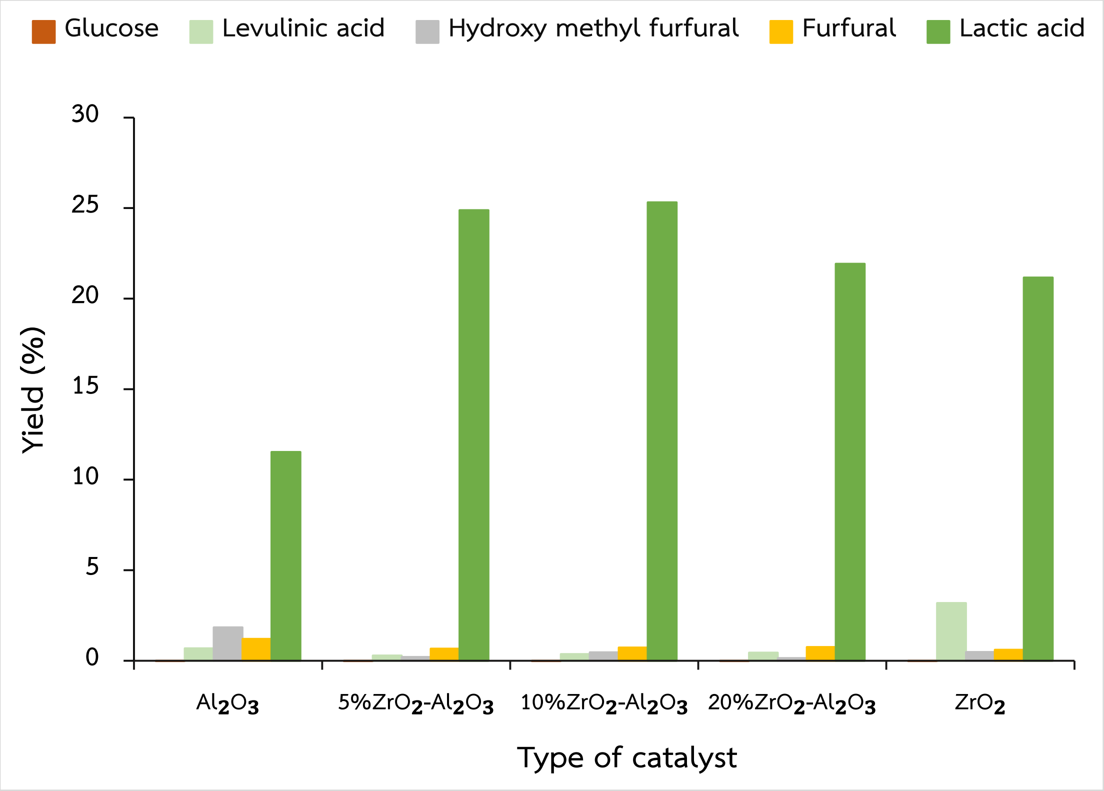
(**Condition**; Temperature 473 K, deionized water 50 mL, amount of 10%ZrO_2-Al_2O_3 1 g, and 0.5 g of ball-milled cellulose.)

Figure 4.18 The effect of reaction time 473 K

The result showed that the yield of lactic acid increased from 14.0 to 25.3% when the reaction time increased from 3 to 6 h. After reaction time 6 h, the yield of lactic acid decreased because the prolong reaction time would cause decomposition of lactic acid. Thus, reaction time 6 h was suitable for cellulose conversion into lactic acid using 10%ZrO_2-Al_2O_3 as a catalyst.

To understand the effect of difference ratio between Al_2O_3 and ZrO_2. The 5%ZrO_2-Al_2O_3, 10%ZrO_2-Al_2O_3, and 20%ZrO_2-Al_2O_3 were investigated. The result was shown in Figure 4.19.

4.3.3 The effect of difference ratio of Al_2O_3 and ZrO_2



(**Condition**; Temperature 473 K, deionized water 50 mL, amount of catalyst 1 g, and 0.5 g of ball-milled cellulose.)

Figure 4.19 The effect of difference ratio of Al_2O_3 and ZrO_2

Figure 4.19 showed the result of the difference ratio between Al_2O_3 and ZrO_2. A maximum yield of lactic acid was obtained from using 10%ZrO_2-Al_2O_3 catalyst with 25.3%. The result showed that the yield of lactic acid increased when increasing ratio of zirconium oxide on Al_2O_3 from 5% to 10%. When ZrO_2 was increased to 20%, the yield of lactic acid decreased from 25.3 to 21.9%. Thus, increasing of amount of zirconium oxide has the effect to properties of catalyst. The lactic acid yield using ZrO_2–Al_2O_3 catalysts were higher than those using individual metal oxide, ZrO_2 and Al_2O_3, indicating that dispersion of active species ZrO_2 on supports was effective to increase the catalytic activity. The properties of catalysts were analyzed by XRD, NH_3-TPD, and CO_2-TPD (as shown in Table 4.3). Table 4.3 showed that the acid site of zirconium oxide increased when the amount of zirconium oxide was increased. To understand the type of acid site and amount of acid site on catalyst. The ZrO_2-Al_2O_3 was characterized by NH_3-TPD. The result shown that the desorption temperatures of NH_3 from the ZrO_2-Al_2O_3 catalysts were about 470 K, which were almost same as that from ZrO_2 (Figure 4.21). This was indicated that the acid sites on the ZrO_2-Al2O_3 catalysts were Lewis acids [78]. The presence of Lewis acid and base site on catalyst promoted retro-aldol condensation reaction from fructose to glyceraldehyde and dihydroxyacetone (Scheme 1.) [96]. The desorption temperatures of CO_2 of ZrO_2–Al_2O_3 and ZrO_2 catalysts appeared peak around 340–450 K (Figure 4.22). It was indicated as weakly basic for the base sites on the ZrO_2 catalysts [100]. The amount of desorbed CO_2 from ZrO_2–Al_2O_3 catalysts was smaller than that from ZrO_2. Table 4.3 showed that the amount of acid sites of ZrO_2–Al_2O_3 was larger than that of ZrO_2; the amount of base sites of ZrO_2–Al_2O_3 was smaller than that of ZrO_2. However, the yield of lactic acid decreased after the ratio of zirconium oxide was increased from 10% to 20%.

4.3.4 Characterizations

4.3.4.1 XRD

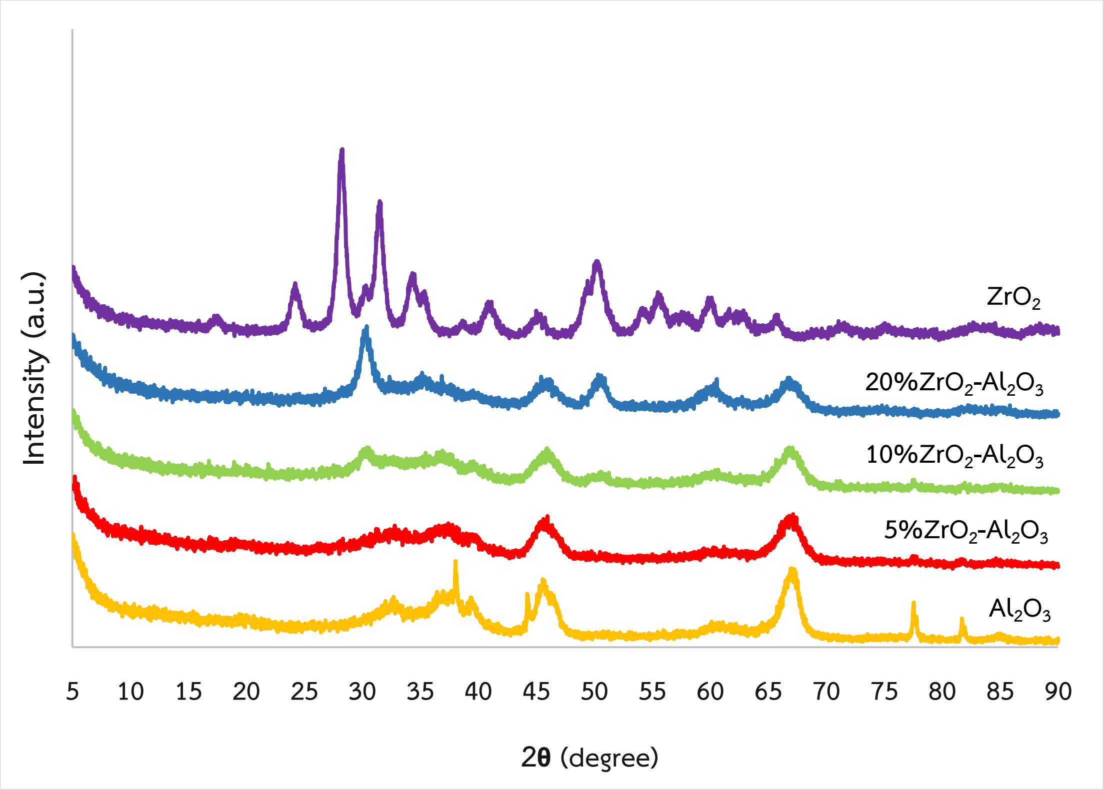


Figure 4.20 XRD patterns

The XRD patterns of the different ratio of ZrO_2-Al_2O_3, Al_2O_3, and ZrO_2 were shown in Figure. 4.18. XRD pattern of Al_2O_3 shown two peak (2θ = 45.6 and 67.0), which was attributed to the γ-Al_2O_3 [107]. XRD pattern of 5%ZrO_2-Al_2O_3 showed only two peak in same position of XRD pattern of Al_2O_3. The increasing of the ZrO_2 contents, the mixed-oxide samples of 10%ZrO_2-Al_2O_3 and 20%ZrO_2-Al_2O_3 showed other peaks. The XRD pattern of 10%ZrO_2-Al_2O_3 shown a weak intensity peak at 2θ = 30.4, which was the characteristics of the tetragonal ZrO_2. However, the XRD pattern of 20%ZrO_2-Al_2O_3 shown two sharp peaks at 2θ = 30.4 and 50.4, which was the characteristics of the tetragonal ZrO_2 [108]. However, XRD patterns of pure ZrO_2 shown monoclinic phase. Thus, the lactic acid yield did not depend on the ZrO_2 crystal phase.

Table 4.3 Properties of Al_2O_3, ZrO_2–Al_2O_3, and ZrO_2

The type of ZrO_2-Al_2O_3	Surface area (m^2/g)[a]	Crystal phase of ZrO_2[b]	Crystal phase of Al_2O_3	Acid sites (mmol/g)	Base sites (mmol/g)	Yield of lactic acid (%)[c]
5%ZrO_2–Al_2O_3	135	-	γ-Al_2O_3	0.109	0.093	25.0
10%ZrO_2–Al_2O_3	126	Tetragonal	γ-Al_2O_3	0.131	0.057	25.3
20%ZrO_2–Al_2O_3	130	Tetragonal	γ-Al_2O_3	0.180	0.098	21.9
ZrO_2	100.5[d]	Monoclinic	-	0.118	0.485	21.2

[a] Data were shown by the company.

[b] Crystal phase were determined by XRD pattern.

[c] Reaction condition: ball-milled cellulose 0.5 g, ZrO2 1 g, water 50 g, reaction temperature 473 K, reaction time 6 h.

[d] Data cited from reference

In second part, we discussed that the combination of acid and base sites on the ZrO_2 was hypothesized to enhance the fructose conversion into glyceraldehyde and dihydroxyacetone [98]. However, Table 4.3 showed that lactic acid yield from cellulose using ZrO_2–Al_2O_3 did not depend on the amount of both acid and base sites because the yield of lactic acid was not decrease when the amount of base sites decreased. The ZrO_2–Al_2O_3 catalysts provide higher yield of lactic acid than ZrO_2 Thus, the base sites was not important for lactic acid production in the case of ZrO_2–Al_2O_3 catalysts. Lewis acid sites on ZrO_2–Al_2O_3 catalysts played an important role [109]. Table 4.3 also showed that lactic acid was not proportional to amount of acid sites. Dispersion of ZrO_2 on support might be key factors for lactic acid yield.

$10\%ZrO_2–Al_2O_3$ was reused to study performance of catalyst for cellulose conversion into lactic acid. After the first experiments, the recovered solid containing the used $10\%ZrO_2–Al_2O_3$ catalyst and the unreacted cellulose was treated at 673 K for 15 h under air atmosphere to remove the carbon material on surface of catalyst. Lactic acid yield using the reused $10\%ZrO_2–Al_2O_3$ catalyst at 673 K for 6 h was 31.7%, which was a little higher than lactic acid yield of the first reaction. This result showed that $10\%ZrO_2–Al_2O_3$ catalyst could be recyclable.

4.3.4.2 NH_3 Temperature programmed desorption

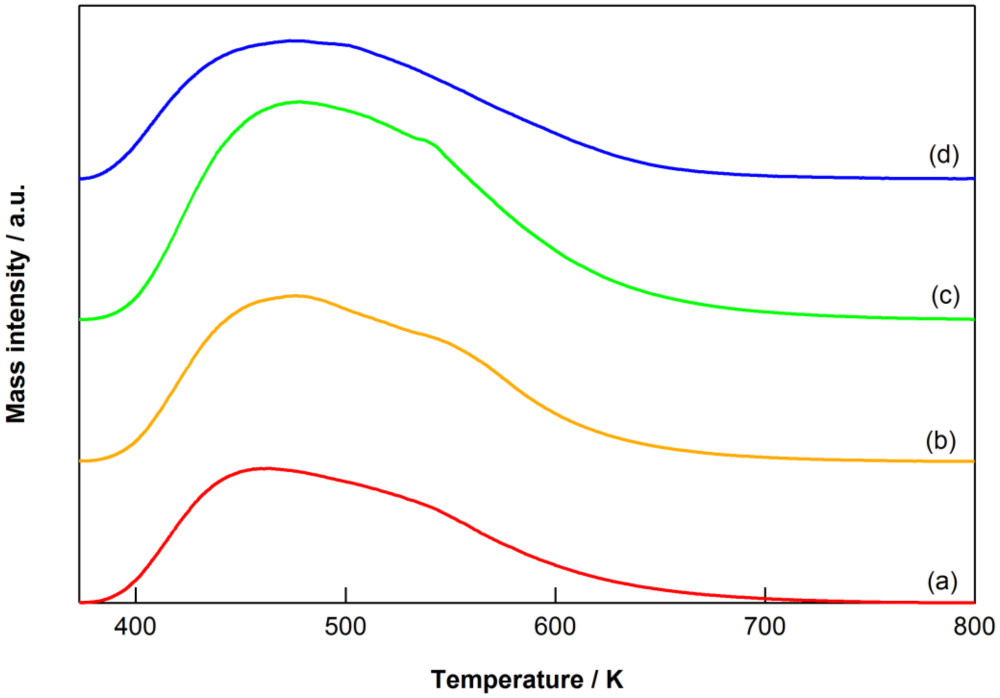


Figure 4.21 NH_3–TPD profiles of the (a) $5\%ZrO_2–Al_2O_3$, (b) $10\%ZrO_2–Al_2O_3$, (c) $20\%ZrO_2–Al_2O_3$, and (d) ZrO_2.

4.3.4.3 CO_2 Temperature programmed desorption

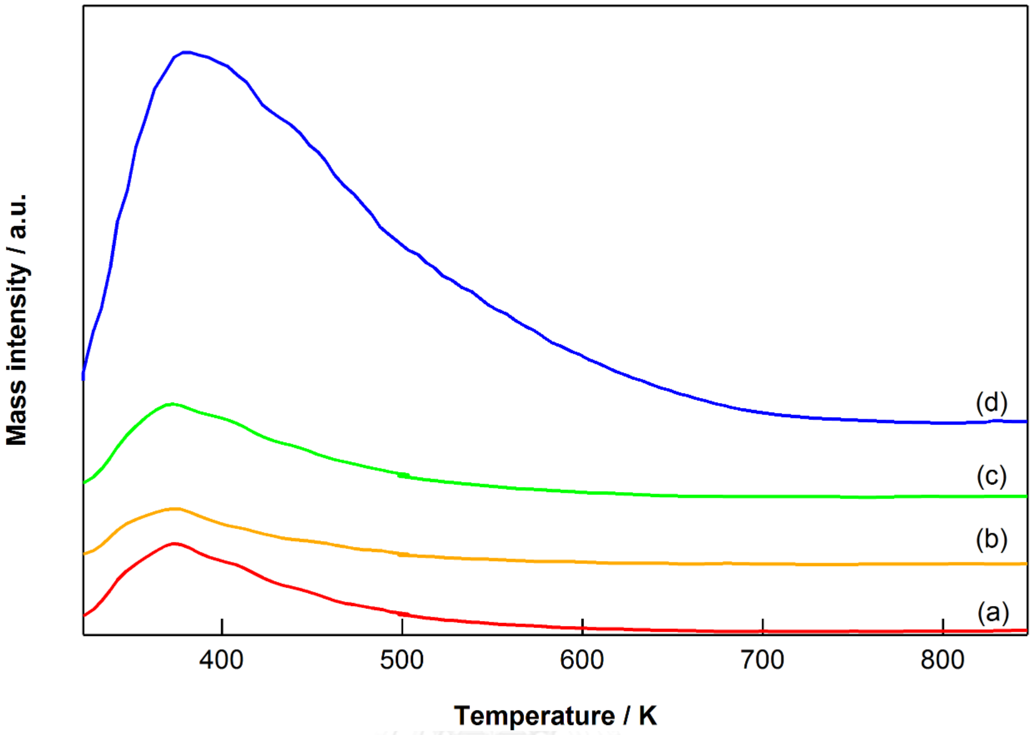


Figure 4.22 CO_2–TPD profiles of the (a) 5%ZrO_2–Al_2O_3, (b) 10%ZrO_2–Al_2O_3, (c) 20%ZrO_2–Al_2O_3, and (d) ZrO_2.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Cellulose conversion into levulinic acid by hot compressed water and carbon dioxide method

In this section, we have applied hot compressed water and carbon dioxide method for cellulose conversion into levulinic acid. We found that this method could directly convert cellulose into levulinic acid in condition (Temperature 473 K, 15 MPa of carbon dioxide pressure, and reaction time 6 h). However, the yield of levulinic acid from water and carbon dioxide method was not significantly different when it was compared with the yield of levulinic acid from the use of only hot compressed water. Thus, the result of this method showed that the use of hot compressed water and carbon dioxide was not enough for cellulose conversion into levulinic acid because carbonic acid was classified as a weak acid.

5.2 Cellulose conversion into lactic acid by using metal oxides as a catalyst

We have successfully converted cellulose into lactic acid using simple metal oxide as a catalyst. ZrO_2 had much higher catalytic performance for cellulose conversion into lactic acid than other metal oxides. The result of comparison of the different brands of ZrO_2 showed that ZRO-7 could convert cellulose into the highest yield of lactic acid. Moreover, we obtained 21.2% yield of lactic acid from ZRO-7. The optimum condition of cellulose conversion into lactic acid was carried out at temperature 473 K, reaction time 6 h, amount of catalyst 1 g, 50 mL of water, and 0.5 g of ball-milled cellulose. The correlation of yield of lactic acid with properties of ZrO_2 was described by the result of characterization. All zirconium oxides were analyzed by XRD, N_2-adsorption, NH_3-TPD, and CO_2-TPD. The results of characterization of ZrO_2 showed that the yield of lactic acid did not depend on crystal phase, crystalline size or specific areas of ZrO_2 but depended on the amount of acid sites and base sites of ZrO_2. Acid sites of ZrO_2 was classified as a Lewis acid. The role of Lewis acid and base sites were cleavage C-C bond of fructose to dihydroxyacetone and glyceraldehyde by retro-aldol condensation reaction. This sequence was a key step for cellulose conversion into lactic acid. Pathways of cellulose conversion into lactic acid was also studied. The intermediates such as dihydroxyacetone, glyceroldehyde, and pyruvaldehyde were used as a reactant. Dihydroxyacetone and glyceraldehyde could directly convert to lactic acid in reaction without ZrO_2 catalyst. ZrO_2 accelerated pyruvaldehyde to lactic acid. The result of reusability of ZrO_2 showed that the yield of lactic acid decreased after first reaction because the base site of ZrO_2 decreased after that the yield of lactic acid was stable.

5.3 Cellulose conversion into lactic acid by using mixed metal oxides as a catalyst

Mixed metal oxides were used to study the effect to cellulose conversion into lactic acid. The result showed that the use of 10%ZrO_2–Al_2O_3 could convert cellulose into 25.3% yield of lactic acid in condition (Temperature 473 K, reaction time 6 h, amount of catalyst 1 g, 50 mL of water, and 0.5 g of ball-milled cellulose). Tetragonal ZrO_2 and γ-Al_2O_3 was observed in 10%ZrO_2–Al_2O_3 from XRD. The ZrO_2–Al_2O_3 catalysts had more Lewis acid sites and much less base sites than ZrO_2 from NH_3-TPD and CO_2-TPD. We found the correlation of the yield of lactic acid with properties was that Lewis acid sites on ZrO_2–Al_2O_3 catalysts played an important role for the cellulose conversion into lactic acid. The base sites were not important for lactic acid production in the case of ZrO_2–Al_2O_3 catalysts.

5.4 Suggestion and Recommendation

Some aspects of cellulose conversion into levuinic acid and lactic acid need further investigation as the following:

5.4.1 Cellulose conversion into levulinic acid by hot compressed water and carbon dioxide method

Although the use of hot compressed water could directly convert cellulose into levulinic acid but the problem of using hot compressed water and carbon dioxide was low yield of levulinic acid. Therefore, exploration of catalyst with high yield of levulinic acid is required for further study. Bronsted acid of solid catalyst is interesting for combination with hot compressed water and carbon dioxide.

5.4.2 Cellulose conversion into lactic acid by using metal oxides as a catalyst

The catalytic process for cellulose conversion into lactic acid is very important because the process can directly convert non-edible cellulose into lactic acid. The result of experiment showed that the yield of lactic acid depended on the amount of acid sites and base sites of catalyst. Therefore, the future work should find the new preparation method for synthesis of the high amount of acid sites and base sites of ZrO_2.

5.4.3 Cellulose conversion into lactic acid by using mixed metal oxides as a catalyst

The use of mixed metal oxide could convert the high yield of lactic acid. In the future work, ZrO_2-Al_2O_3 will characterized to understand active site and reaction mechanism. This mixed metal oxide was the mix of ZrO_2-Al_2O_3. Thus, mixed metal-metal oxide such as ZrAlO should be studied for cellulose conversion.

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APPENDIX

APPENDIX A
CELLULOSE CONVERSION

Table 1A.1 The data of experiment

Temperature (K)	Weight of reactant (g)	Weight of catalyst (g)	Weight solid residue (g)
453	0.5030	1.0018	1.2118
463	0.5016	1.0017	1.0712
473	0.5036	1.0034	1.0633
483	0.5004	1.0032	1.0146

The cellulose conversion was calculated by using equation (1)

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

<u>Calculation of reaction, temperature 453 K</u>

Weight solid residue = 1.2118 g

Weight of solid catalyst = 1.0018 g

Weight of reactant = 0.5030 g

Conversion (%) = (1- $\frac{(1.2118)-(1.0018)}{(0.5030)}$) x 100

Therefore,

Cellulose conversion = 58.25%

APPENDIX B
CALCULATAION OF PRODUCT YIELD

Table 1B.1 The data of experiment

Temperature (K)	Weight of solvent (g)	Flask Weight (g)	Recovered Flask weight (g)	Liquid for recovery (g)	Total TOC sample (g)
453	50.15	75.8453	124.0984	48.2531	22.7916
463	50.20	62.8431	111.3733	48.5302	22.8425
473	50.11	62.7618	111.0110	48.2492	23.2385
483	50.10	77.0819	125.2767	48.1948	23.0054

Table 1B.1 (Continue) The data of experiment

Temperature (K)	Mole of carbon atom in reactant	Sample in GC-FID vial (g)	Internal standard in GC-FID vial (g)	TOC sample (g)
453	0.0174	1.4717	0.0107	1.9880
463	0.0174	1.4892	0.0100	1.9952
473	0.0174	1.4684	0.0143	1.9769
483	0.0174	1.4936	0.0090	1.9769

Table 1B.1 (Continue) The data of experiment

Temperature (K)	TC (mg/L)	IC (mg/L)	TOC (mg/L)	TOC (mol/L)	Glucose
453	157.9	1.768	1756.4895	0.1462	2732
463	256.0	1.860	2877.1452	0.2395	0
473	245.8	1.722	2831.1262	0.2357	0
483	205.9	1.811	2321.4053	0.1933	0

Table 1B.1 (Continue) The data of experiment

Temperature (K)	1-BtOH	Levulinic acid	Hydroxy methyl furfural	Formic acid	Furfural	Lactic acid
453	1511621	300	2869	0	2483	21579
463	1408997	3549	3788	0	8403	54231
473	1935759	31991	5479	0	5340	80300
483	1194563	5609	0	0	4296	66226

The product yield was calculated by using equation (1)

$$\text{Product yield (\%)} = \left(\frac{\textbf{mole of carbon atom in product}}{\textbf{mole of carbon atom in cellulose}}\right) \times 100 \qquad (1)$$

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

In this case, we calculated the yield of glucose at reaction temperature 453 K

1.1 Calibration curve of standard sample

Example Calibration curve of glucose

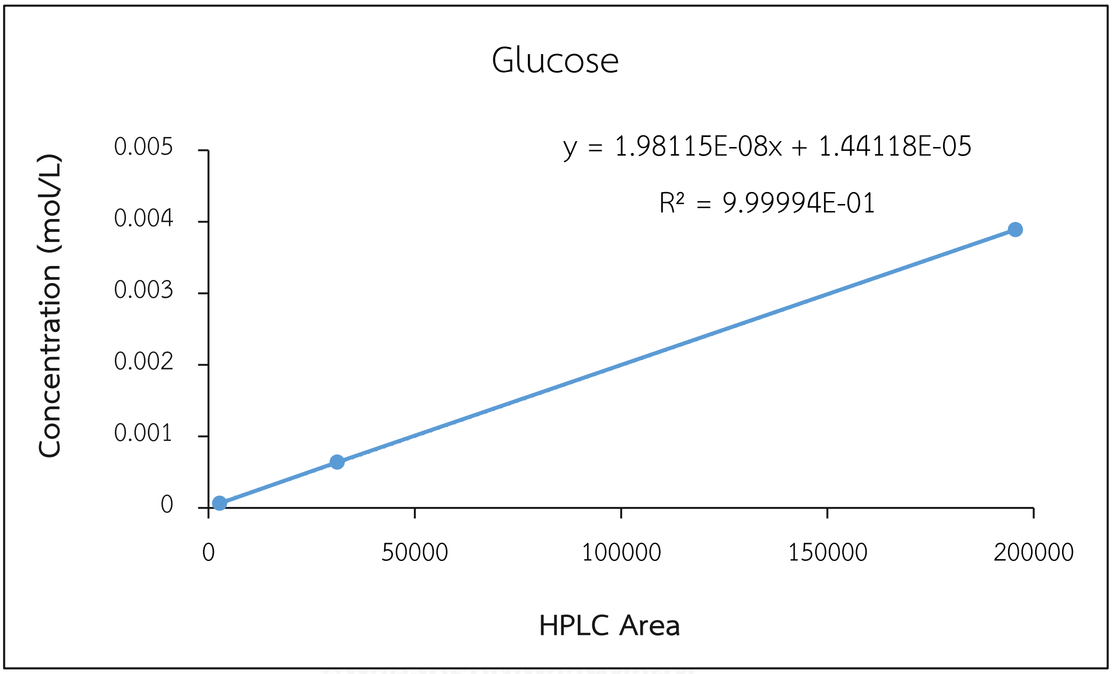

Figure 1B.1 Calibration curve of glucose

1.2 Concentration of glucose was calculated by equation (2)

$$y = 1.98115\text{E-}08x + 1.44118\text{E-}05 \quad (2)$$

y = Concentration of glucose (mol/L)

x = Peak area of glucose

The data from experiment

Peak area of glucose at temperature 453 K = 2732

y = 1.98115E-08 x (2732) + 1.44118E-05

Therefore,

Concentration of glucose = 0.0000446 mol/L

1.3) Calculation of mole of carbon atom in product

Mole of carbon atom in product = $\frac{\textbf{(Concentration of glucose) x (Weight of liquid recovery)}}{\textbf{1000}}$ x amount of carbon atom in product

The data from experiment

Weight of liquid recovery = 48.2531

Mole of carbon atom in product = $\frac{\textbf{(0.0018679) x (48.2531)}}{\textbf{1000}}$ x 6

Therefore,

Mole of carbon atom in product = 0.00001290

1.4) Product yield was calculated in equation (1)

Mole of carbon atom in cellulose = 0.0174

Product yield (%) = $\left(\frac{\mathbf{0.00001290}}{\mathbf{0.0174}}\right) \times 100$

Therefore,

Product yield of glucose = 0.07 %

2) Calculation of product yield of Gas chromatography (GC)

In this case, we calculated the yield of levulinic acid at reaction (temperature 453 K)

2.1) Calibration curve of standard sample

Example Calibration curve of levulinic acid

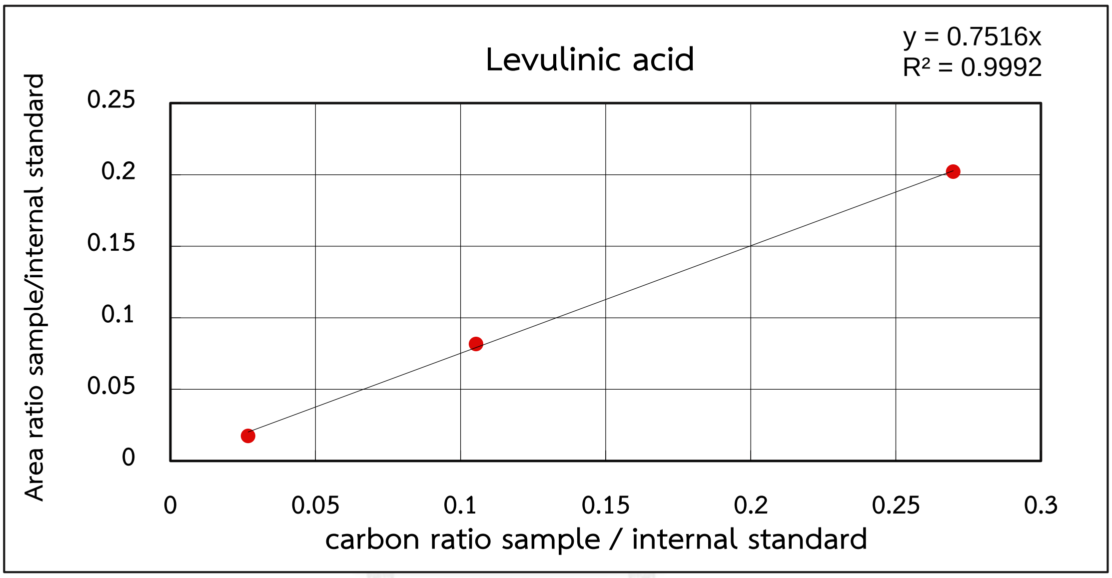

Figure 1B.2 Calibration curve of glucose

2.2) Mole of carbon atom in product was calculated by equation (3)

Mole of carbon atom in product =

$$\left(\left(\frac{\textbf{Peak area of levulinic acid}}{\textbf{Peak area of 1−buthanol}}\right) \times \left(\frac{\textbf{Weight of internal standard in vial}}{\textbf{Molecular weight of 1−butanol}}\right) \times \left(\frac{\textbf{4}}{\textbf{5 x 0.7516}}\right) \times \left(\frac{\textbf{Liquid recovery}}{\textbf{Sample in vial}}\right)\right) \times$$
amount of carbon atom in product

(3)

<u>The data from experiment</u>

Peak area of levulinic acid = 300

Peak area of 1-buthanol = 1511621

Weight of internal standard in vial = 0.0107 g

Molecular weight of 1- buthanol = 74.1228 g/mol

Liquid recovery = 48.2531 g

Sample in vial = 1.4717 g

Mole of carbon atom in product =

$$\left(\left(\frac{\mathbf{300}}{\mathbf{1511621}}\right) \times \left(\frac{\mathbf{0.0107}}{\mathbf{74.1228}}\right) \times \left(\frac{\mathbf{4}}{\mathbf{5\ x\ 0.7516}}\right) \times \left(\frac{\mathbf{48.2531}}{\mathbf{1.4717}}\right)\right) \times 5$$

Therefore,

Mole of carbon atom in product = 0.00000500

2.3) Product yield was calculated in equation (1)

$$\text{Product yield (\%)} = \left(\frac{\mathbf{0.00000500}}{\mathbf{0.0175}}\right) \times 100$$

Therefore,

Product yield of glucose = 0.30 %

APPENDIX C
THE DATA OF PRODUCT YIELD

4.1.1 The effect of ball milled pre-treatment

	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
Non-ball milled	4.2	-	0.1	5.6	1.2	0.0
24 h	8.4	-	1.4	15.2	3.3	0.6
48 h	6.6	-	4.0	16.4	5.6	0.7

4.1.2 The effect of addition of carbon dioxide

	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
Without CO_2	6.6	-	4.0	16.4	5.6	0.7
CO_2	5.8	-	2.8	17.8	2.0	1.3

4.2.1 Catalyst Screening

Catalyst	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
ZrO_2	0.0	-	3.2	0.5	0.6	21.2
Al_2O_3	0.0	-	12.1	0.9	0.3	8.7
Anatase-TiO_2	0.0	-	7.4	3.8	2.0	2.8
Rutile-TiO_2	0.0	-	5.5	13.3	2.0	1.5
Fe_3O_4	1.7	-	0.3	17.6	1.6	2.8
V_2O_5	0.0	-	4.1	0.1	2.0	6.1
CeO_2	0.1	-	0.7	1.6	0.5	12.9
Tm_2O_3	0.0	-	0.4	0.7	0.3	2.6
HfO_2	0.0	-	2.4	5.2	1.3	12.5
Ga_2O_3	5.7	-	3.4	1.7	2.3	2.5
Nb_2O_5	5.4	-	1.9	12.3	2.2	0.6
Ta_2O_5	5.3	-	1.4	14.7	3.5	0.6
La_2O_3	0.0	-	0.0	0.0	0.2	1.1
Y_2O_3	0.0	-	0.0	0.0	0.0	0.3
MgO	0.0	-	0.0	0.3	0.2	0.0
Without catalyst	6.6	-	4.0	16.4	5.6	0.7

4.2.2.1.1 Reaction time at 453 K

Time (hour)	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
3	0.0	2.6	0.0	0.0	0.2	2.8
6	0.1	-	0.0	0.2	0.3	5.4
12	0.2	-	0.3	0.3	0.4	11.6
18	0.0	-	0.4	0.0	0.5	14.5
24	0.0	-	0.4	0.0	0.6	13.9

4.2.2.1.2 Reaction time at 463 K

Time (hour)	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
3	0.2	-	0.2	0.3	0.4	8.7
6	0.0	-	0.3	0.3	0.9	13.7
12	0.0	-	0.4	0.0	0.6	14.6
18	0.0	-	0.6	0.0	0.6	16.8
24	0.0	-	0.5	0.0	1.3	16.4

4.2.2.1.3 Reaction time at 473 K

Time (hour)	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
3	0.0	-	0.4	0.0	1.3	14.3
4.5	0.0	-	0.4	0.0	0.7	15.8
6	0.0	-	3.2	0.5	0.6	21.2
7.5	0.0	-	0.4	0.0	2.0	15.7

4.2.2.1.4 Reaction time at 483 K

Time (hour)	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
3	0.0	-	0.4	0.0	0.6	15.1
4.5	0.0	-	0.4	0.0	0.5	17.5
6	0.0	-	0.6	0.0	0.5	17.6
7.5	0.0	-	0.5	0.0	0.4	17.4

4.2.2.1.5 Reaction temperature at 6 h

Temperature (K)	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
453	0.1	-	0.0	0.2	0.3	5.4
463	0.0	-	0.3	0.3	0.9	13.7
473	0.0	-	3.2	0.5	0.6	21.2
483	0.0	-	0.6	0.0	0.5	17.6

4.2.3 The different types of zirconium oxide

Type of ZrO_2	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
ZrO_2-Hos	1.2	-	0.3	9.4	1.3	3.1
ZrO_2-Ald	0.4	-	6.4	3.8	1.5	8.8
ZrO_2-Nac	2.0	-	5.4	10.6	2.8	4.9

4.2.3 (Continue) The different types of zirconium oxide

Type of ZrO_2	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
ZrO_2-Wak	1.0	-	5.0	9.0	2.0	6.9
ZRO-6	0.0	-	1.9	0.5	0.4	18.4
ZRO-7	0.0	-	3.2	0.5	0.6	21.2
ZRO-8	1.4	-	5.1	4.1	1.6	10.9
ZRO-9	0.0	-	2.2	0.4	0.4	20.1
YSZ	1.4	-	4.9	11.7	1.7	6.5
ZrO_2-773	0.0	-	0.3	0.0	1.0	14.0
ZrO_2-873	0.0	-	0.3	0.9	1.2	10.4
ZrO_2-973	0.8	-	2.4	3.8	1.5	8.5
ZrO_2-1073	0.9	-	1.9	3.2	1.6	6.5

4.2.7 Reusability of catalyst

Number of recycles	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
Fresh	0.0	-	3.2	0.5	0.6	21.2
1	0.0	-	0.3	0.0	0.7	17.4
2	0.0	-	0.3	0.0	0.6	17.6
3	0.0	-	0.2	0.0	0.4	17.1
4	0.0	-	0.3	0.0	1.2	17.0

4.3.1 Catalyst Screening

Catalyst	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
10%WO_3-ZrO_2	0.0	-	0.3	0.0	0.8	14.5
9%La_2O_3-ZrO_2	0.4	-	0.3	1.1	1.2	15.2
50%CeO_2-ZrO_2	0.0	-	1.0	0.1	0.6	13.8
30%TiO_2-ZrO_2	0.0	-	0.7	0.2	0.6	11.8
10%SiO_2-ZrO_2	0.0	-	0.3	0.0	0.8	16.7

4.3.1 (Continue) Catalyst Screening

Catalyst	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
14%Y_2O_3-ZrO_2	0.0	-	1.4	0.6	0.9	15.7
10%ZrO_2-Al_2O_3	0.0	-	0.4	0.5	0.7	25.3
2%CaO-ZrO_2	0.0	-	0.4	1.4	0.4	3.3
Without catalyst	6.6	-	4.0	16.4	5.6	0.7

4.3.2.1 Effect of temperature

Temperature (K)	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
453	1.2	-	0.0	0.3	0.0	3.2
473	0.0	-	0.4	0.5	0.7	25.3
493	0.0	-	0.4	0.0	4.1	17.3

4.3.2.2 Effect of reaction time

Time (hour)	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
3	0.3	-	0.2	0.5	0.8	14.0
6	0.0	-	0.4	0.5	0.7	25.3
9	0.0	-	0.3	0.0	0.5	21.0

4.3.3 The effect of difference ratio of Al_2O_3 and ZrO_2

Catalyst	Yield of product (%)					
	Glucose	Fructose	Levulinic acid	5-HMF	Furfural	Lactic acid
Al_2O_3	0.0	-	0.7	1.9	1.2	11.5
5%ZrO_2-Al_2O_3	0.0	-	0.3	0.2	0.7	24.9
10%ZrO_2-Al_2O_3	0.0	-	0.4	0.5	0.7	25.3
20%ZrO_2-Al_2O_3	0.0	-	0.5	0.2	0.8	21.9
ZrO_2	0.0	-	3.2	0.5	0.6	21.2

VITA

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Publication

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Presentation Experience

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Oral presentation: Best Presentation Award in Topic "Conversion of cellulose into lactic acid using transition metal oxides", the 46th Petroleum-Petrochemical Symposium of JPI, JPIJS International Session, 17-18/11/2016, Kyoto, Japan.