COMPARATIVE STUDY ON LIQUEFACTION BEHAVIORS OF MICROCRYSTALLINE CELLULOSE AS TREATED BY DIFFERENT HYDROTHERMAL METHODS

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Title Comparative Study on Liquefaction Behaviors of Microcrystalline Cellulose as treated by Different Hydrothermal Methods
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Abstract

This study investigated liquefaction behaviors of microcrystalline cellulose (MCC) as treated by four different hydrothermal methods, i.e. hot-compressed water under N_2 or CO_2, and hot-compressed 0.1wt% H_2O_2 solution under N_2 or CO_2. The experiments were carried out in the treatment temperature range of 150-290°C at 0 min by using 10-ml batch-type reactor. Various hydrolyzed saccharides and decomposed compounds were analyzed and quantified. As treated by four different hydrothermal methods, it was elucidated that cello-saccharides were highly recovered at the same treatment temperature of 250°C. Under such conditions, cello-saccharide yields were 61.1, 68.8, 57.1, and 42.8wt%, respectively. The appropriated condition was hot-compressed water treatment under CO_2, where carbonic acid could be formed in water inset at elevated temperature and high pressure, resulting in the highest recoverable yield of cello-saccharides. The presence of carbonic acid by using CO_2 instead of N_2 in hot-compressed water treatment, moreover, helped promote hydrolysis of cello-oligosaccharides to monomer and ended up with more glucose proportion by its catalytic effect. On the other hand, liquefaction degree of MCC and decomposition of hydrolyzed saccharides were found to be intensified by hot-compressed 0.1wt% H_2O_2 solution under N_2 or CO_2, where oxidation reaction became predominant. Higher yields of monosaccharides and decomposed compounds such as furan compounds and organic acids were realized by the oxidative conditions. As a consequence, lower yields of cello-saccharides were obtained. Due to an inferior effect to the liquefaction and saccharification of MCC by using CO_2 instead of N_2 for the hot-compressed of 0.1wt% H_2O_2 solution treatment, formation of peroxy-carbonic acid, a strongly oxidizing agent, was still unclear. It might be probably decomposed or instable under the studied conditions. Through these lines of this comparative study, it would help provide a clear perception on different liquefaction behaviors of MCC under various hydrothermal treatment conditions. Their appropriate applications, in addition, would be revealed by a variety of the liquefied products obtained.

Keywords: microcrystalline cellulose, hydrothermal methods, oxidation, hydrogen peroxide, liquefaction.

เรื่อง การศึกษาเชิงเปรียบเทียบพฤติกรรมการกลายเป็นผลิตภัณฑ์ของเหลวของจุลผลึกเซลลูโลสด้วยวิธีการไฮโดรเทอร์มัลที่ต่างกัน
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บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาพฤติกรรมการกลายเป็นผลิตภัณฑ์ของเหลวของจุลผลึกเซลลูโลสด้วยวิธีการไฮโดรเทอร์มัลที่แตกต่างกัน 4 แบบ ได้แก่ น้ำร้อนอัดความดันภายใต้บรรยากาศไนโตรเจนหรือคาร์บอนไดออกไซด์ สารละลายไฮโดรเจนเพอร์ออกไซด์ความเข้มข้นร้อยละ 0.1 โดยน้ำหนัก อัดความดันภายใต้บรรยากาศไนโตรเจนหรือคาร์บอนไดออกไซด์ ทำการทดลองที่ช่วงอุณหภูมิ 150-290 องศาเซลเซียส และเวลา 0 นาที โดยใช้เครื่องปฏิกรณ์แบบกะปริมาตร 10 มิลิลิตร โดยวิเคราะห์ชนิดและปริมาณของน้ำตาลที่ได้จากการไฮโดรไลซิส และสารประกอบที่เกิดจากการสลายตัว จากการเปรียบเทียบผลได้ของเซลโลแซ็กคาไรด์จากจุลผลึกเซลลูโลสที่ถูกทำปฏิกิริยาไฮโดรเทอร์มัลที่แตกต่างกัน 4 แบบ พบว่ามีค่าสูงสุดที่อุณหภูมิเดียวกันคือ 250 องศาเซลเซียส ภายใต้ภาวะดังกล่าวมีร้อยละผลได้โดยมวลของไซโลแซ็กคาไรด์เท่ากับ 61.1, 68.8, 57.1, และ 42.8 ตามลำดับ วิธีการไฮโดรเทอร์มัลที่สามารถผลิตเซลโลแซ็กคาไรด์ได้สูงสุด คือ น้ำร้อนอัดความดันภายใต้บรรยาย คาร์บอนไดออกไซต์ ซึ่งทำให้เกิดกรดคาร์บอนิกละลายอยู่ในน้ำที่อุณหภูมิและความดันสูงได้ นอกจากนี้กรดคาร์บอนิกที่เกิดขึ้นในระบบน้ำร้อนอัดความดันยังสามารถช่วยเร่งปฏิกริยาไฮโดรไลซิสของเซลโลแซ็กคาไรด์เกิดเป็นกลูโคส และทำให้มีสัดส่วนของน้ำตาลโมเลกุลเดี่ยวเพิ่มขึ้น สำหรับการทดลองที่ใช้สารละลายไฮโดรเจนเพอร์ออกไซด์ความเข้มข้นร้อยละ 0.1 โดยมวล อัดความดันภายใต้บรรยากาศไนโตรเจนหรือคาร์บอนไดออกไซด์ซึ่งเกิดปฏิกิริยาออกซิเดชั่นเป็นหลัก พบว่าภาวะดังกล่าวทำให้จุลผลึกเซลลูโลสถูกทำปฏิกิริยาเปลี่ยนเป็นน้ำตาลโมเลกุลเดี่ยวเพิ่มขึ้น อีกทั้งยังพบสารประกอบที่เกิดจากการสลายตัว ได้แก่ สารประกอบฟูแรน และ กรดอินทรีย์มากขึ้นด้วย ผลที่ตามมาได้แก่ผลได้ของเซลโลแซ็กคาไรด์มีค่าลดลง เมื่อใช้คาร์บอนไดออกไซด์เป็นบรรยากาศแทนไนโตรเจนในการอัดสารละลายไฮโดรเจนเพอร์ออกไซด์ทำให้พบว่าการกลายเป็นผลิตภัณฑ์ของเหลวของจุลผลึกเซลลูโลสลดลงและเกิดผลได้น้ำตาลที่มีค่าน้อยกว่า จึงยังไม่สามารถสรุปได้ว่าเกิดกรดเพอร์ออกซิคาร์บอนิกซึ่งเป็นสารออกซิไดส์รุนแรงขึ้นในระบบหรือไม่ทั้งนี้อาจปีนไปได้ว่ากรดเพอร์ออกซิคาร์บอนิกสลายตัวหรือไม่เสถียรสภาพใต้สภาวะการทดลอง จากการเปรียบเทียบผลลัพธ์จากวิธีการไฮโดรเทอร์มัลทั้ง 4 แบบ สามารถชี้ให้เห็นพฤติกรรมการกลายเป็นผลิตภัณฑ์ของเหลวของจุลผลึกเซลลูโลสที่แตกต่างกันได้อย่างชัดเจน นอกจากนี้ยังช่วยเผยให้เห็นการประยุกต์ใช้วิธีการไฮโดรเทอร์มัลที่เหมาะสมต่อผลิตภัณฑ์ของเหลวที่เกิดขึ้นอย่างหลากหลายอีกด้วย

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CHAPTER I

INTRODUCTION

1.1 Background

Nowadays, the world populations grow rapidly. This growth effects directly to the demand of using energy. BP statistical reviews (2017) reported that the energy consumption increased on average 23,371.69 terawatt-hours compared to the one in last decade, while the energy resources decreased continuously. The price of fossil energy, in addition, vastly fluctuates. Not only the economic problem but also the environmental issues such as carbon dioxide emissions and global warming are of concerned. Therefore, the topics relating to alternative energy such as solar energy, geothermal energy, wind energy and bio-energy have gained much attention for years. Among these alternatives, biomass is globally abundant and its conversion to fuels and valuable chemicals plays an important role in mitigating the energy problems in agriculture-based countries, especially Thailand.

Lignocelluloses are biomass obtained from plant cell wall. Their compositions consist of three main components, i.e. cellulose, hemicelluloses and lignin. Chemical compositions of lignocelluloses, however, vary among plant species. In general, contents of cellulose, hemicelluloses and lignin are approximately 35-45%, 20-35% and 20-35%, respectively, on dried-weight basis (Rabemanolontsoa and Saka, 2013). Cellulose is composed of linearly long chains of glucan made up with a number of glucose, which are linked together in a form of D-anhydroglucopyranose with (1→ 4)-β-D-glycosidic linkage. Its crystalline structure makes cellulose of great resistance to degradation, insoluble in water, and stable configuration. Hemicelluloses are built up mainly from pentoses and hexoses. There are two major types of hemicelluloses, i.e. xylan and glucomannan. They are amorphous and easier to decompose than cellulose. Lignin is 3-dimensional phenolic polymer, composed of three basic compounds, trans-p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. It exists in lignocellulosic amorphous portion together with hemicelluloses.

At present, there are many technologies to convert lignocelluloses to bio-fuels and bio-chemicals. Liquefaction by mean of wet oxidation, hydrolysis reaction or enzymatic hydrolysis is an interesting technique to convert hemicelluloses and cellulose to reducing sugars. Wet oxidation is the oxidative method which employs oxygen or air as an oxidant in the presence of water. Such treatment under alkaline conditions can help improve reducing sugar yields. Its high cost due to the use of chemicals and effect to environments is a drawback of this wet oxidation technique. Hydrolysis reaction undergoes at elevated temperature with or without catalyst by adding water to cleave chemical bonds in carbohydrate polymeric structure. Major hydrolyzed products are poly-, oligo and monosaccharides. Enzymatic hydrolysis, on the other hand, involves biological reaction. Specific enzymes such as cellulase and xylanase are employed to produce monosaccharides from cellulose and hemicelluloses (Alvira, 2010). Need for a pretreatment step and high price of enzymes still limit enzymatic hydrolysis to liquefy lignocelluloses in industrial scale.

In the previous study by our research group member, hydrolysis of sugarcane bagasse by different hydrothermal methods such as hot-compressed water under pressurization of N_2 or CO_2 and hot-compressed 1wt% H_2O_2 solution under pressurization of CO_2 was performed. The results revealed that various reducing sugars could be obtained from two major cell wall components, hemicelluloses and cellulose. In addition, it was remarkably found that oxidation of the two components could occur in the treatment with hot-compressed 1wt% H_2O_2 solution under pressurization of CO_2. By this oxidative condition, higher yields of monosaccharides were achieved at a lower temperature, compared to the yields obtained in hot-compressed water treatments, where hydrolysis merely occurred (Juttamalakul, 2016). Hydrolysis mechanisms of hemicelluloses and cellulose were already well established for hydrothermal conversion of lignocelluloses (Lu et al., 2009; Phaiboonsilpa et al., 2011; 2013). However, the oxidation-dominated reaction pathways during liquefaction of lignocelluloses were not clarified yet due to the coexistence of various saccharides and other compounds in hydrolysates from liquefaction of three cell wall components. In this present study, therefore, microcrystalline cellulose (MCC) was used as a reagent to study its liquefaction behaviors as treated by different hydrothermal methods. An interference of hemicelluloses and lignin could then be avoided. The decomposition pathways of MCC would be expected to be clarified. The results from this study can provide more insights into the understanding in chemical conversion of lignocelluloses and their utilizations for bio-fuels and bio-chemicals.

1.2 Objective

To study liquefaction behaviors of MCC to cello-saccharides as treated by different hydrothermal methods

1.3 Scopes of the research

1.3.1 To study liquefaction behaviors of MCC by using 10-ml batch reactor as treated by four different hydrothermal methods as follows:

- Hot-compressed water under pressurization of N_2
- Hot-compressed water under pressurization of CO_2
- Hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2
- Hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2

1.3.2 To explore effect of temperature (150-290°C) and time 0 min on liquefaction of MCC as treated by those hydrothermal methods
1.3.3 To qualitatively and quantitatively analyze various products in hydrolysates from MCC as treated by those hydrothermal methods
1.3.4 To investigate the decomposition pathway of MCC as treated by the different hydrothermal methods

1.4 Benefits from this study

1.4.1 Appropriate treatment conditions, i.e. treatment temperature, for each hydrothermal method in terms of the highest yield of cello-saccharides obtained from MCC
1.4.2 A novel hydrothermal technique to chemically convert MCC to cello-saccharides by hot-compressed H_2O_2 solution under pressurization of N_2 and CO_2
1.4.3 Application of the obtained appropriate hydrothermal treatment conditions to chemically convert cellulosic portion in lignocelluloses for the production of reducing sugars and other compounds such as organic acids.

CHAPTER II

THEORY AND LITERATURE REVIEWS

In this chapter, chemical compositions of lignocellulose were briefly described, including their three main types of polymer which are cellulose, hemicellulose and lignin. In addition, structure and characteristic of microcrystalline cellulose (MCC) and hydrolysis conversion techniques of cellulose are glucose monomer. Furthermore, methods used carbon dioxide and hydrogen peroxide is in water at high pressure. Considering oxidation pathway of cellulose was in hydrolysis technique. Some literature review related to thermal liquefaction method were according reviewed suitable to research methodology for this work

2.1 Lignocelluloses

Lignocellulose is organic material of plant cell wall that consists of three main type of polymer which is cellulose, hemicellulose and lignin. Lignocelluloses are classified based on their sources, including agricultural residues, industrial residues, forestry residues and energy crop. The percent of three major polymers that previously refers in each plant are different portions. Table 2.1 showed that amounts of the several of composition in lignocellulose. As mentioned mostly lignocellulose consists of cellulose 40%, hemicellulose 30%, lignin 20% and others compound including protein, extractive, starch and ash.

Table 2.1 Percentage composition of main component lignocelluloses (Rabemanolontsa and Saka, 2013)

Lignocellulose	Component (wt%)			
	Cellulose	Hemicellulose	Lignin	Other*
Cupressaceae (Softwoods) Japanese Cedar	38.67	23.16	33.78	4.36
Fagacceae (Hardwoods) Japanese beech	43.94	28.43	24.02	3.60
Poaceae (Grass)				
- Rice husk	37.00	17.78	24.77	20.45
- Wheat straw	37.55	34.41	20.24	7.8
- Sugar bagasse	40.92	33.01	22.33	3.74
Aracaceae (Palmae) - Oil palm trunk	31.09	28.86	28.66	11.39

Other* are protein, extractive, starch and ash

2.1.1 Cellulose

Cellulose is mostly composition of lignocellulose found around plant cell wall mixed with hemicellulose. The amount of percentage cellulose in lignocellulose are different composition in each part of plant such as wood 40-50%wt and cotton fiber 98%wt. Cellulose is long linearly chains polymer, homogeneous biopolymer, formed by glucose monomer. The type of glucose is β-ᴅ-Glycopyranose connect with β-(1→4)-ᴅ -Glycosidic bond. Cellulose has intermolecular which is H-bond with adjacent cellulose molecule. This cause effect to theirs characterizes and structure which are water-insoluble and flexible but fix configuration. Two types of cellulose are crystalline cellulose and semi-crystalline cellulose. The part of the cellulose crystal which is more difficult to digest reaction or enzyme than semi-crystalline cellulose. Molecular structure of cellulose showed in Figure 2.1.1

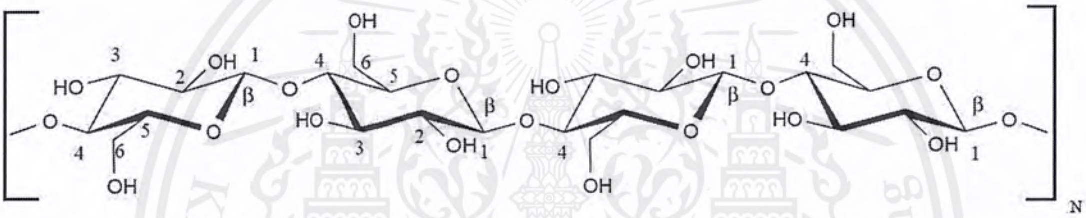


Figure 2.1 Chemical structure of cellulose (Laine, 2005)

2.1.2 Hemicelluloses

Hemicelluloses is heterogeneous-polymer contained various sugars such as xylose, arabinose, mannose, glucose and galactose. Hemicelluloses make up most of plant cell wall. The mainly unit of long chains polymer is xylose 85-93wt% connect each other with β-(1→4)-glycosidic linked or α-(1→2)-bonded 4-O-methylglucuronic acids. The side chains are mannose, glucose or galactose unit. This formation of polymer making hemicellulose is amorphous structure. The hemicelluloses structure showed in Figure. 2.1.2

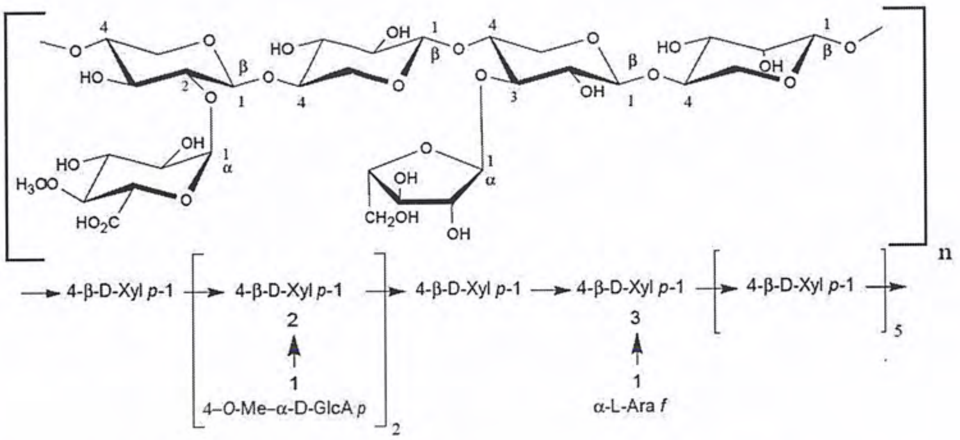


Figure 2.2 Chemical major structure of hemicellulose (Laine, 2005)

2.1.3 Lignin

Lignin is an aromatic compound mostly found at the edge of plant cell walls, In nature, lignin is a component that prevents cellulose from degraded by microbial enzymes. The lignin structure consists of a randomly linked ring molecule. This make lignin formed 3D structure with ether bond, ester bond (non-condensed type bond) and carbon-carbon bonds (condensed type bond). Due to the complexity and polarity of the molecule lignin makes resistant to chemical degradation and enzymes. The lignin structure showed in Figure. 2.1.3

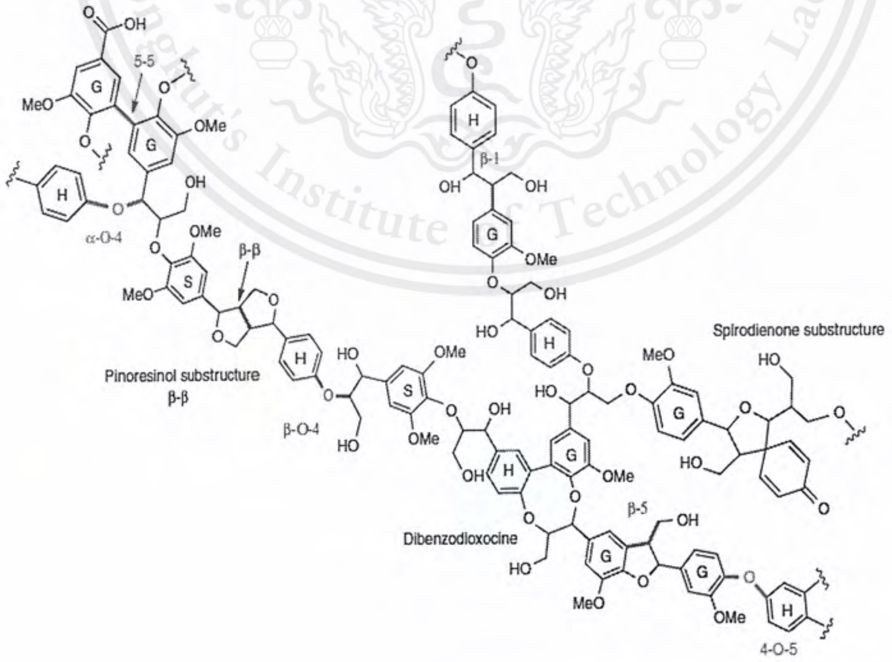


Figure 2.3 Chemical structure of lignin (Joffer, 2013)

2.2 Hydrothermal pretreatments of lignocelluloses

The purposes of pretreatment are remove lignin and hemicellulose from the lignocellulose structure for decrease crystalline, increase the porosity of the material, increase surface area of cellulose which enzymes can work effectively and completely hydrolysis (Zheng et al., 2009).

2.2.1 Steam explosion pretreatment

The concept of this method is enhancing lignocellulose saturated with steam and under pressure. After that immediately decrease pressure makes water rapidly evaporated out of lignocellulose molecule. This method results to fiber teared each other and hemicellulose hydrolyzed to monomer. The benefits of this method are hydrolysis effective and reduce occurring of enzyme inhibited. (Ragg and Fields, 1987)

2.2.2 Carbon dioxide explosion pretreatment

The carbon dioxide explosion method is similar to steam explosion but different using carbon dioxide instance steam. This way leads to form carbonic acid by reaction of carbon dioxide with water. The carbonic acid presented to be catalyst of hydrolysis reaction resulted to lignin removal more effective. Mostly, using carbon dioxide explosion method have to use organic solvent such as ethanol for helping lignin removal. This procedure gives lower yield than steam explosion, but enzyme inhibited haven't appear in this explosion. (Ragg and Fields, 1987)

2.2.3 Hot-compressed water pretreatment

The hot water temperature is around 160-240°C with under high pressure which is more than 5 MPa. At high pressure lignocellulose is saturated for hydrolysis treatment. Mosier et al. (2005) reported that the addition of acid to hydrolysis of hemicellulose with hot compressed water for adjust pH in the range of 4-7, it can produce 88-90% of the xylose by weight and reduce condensing of the reducing sugar to form polymer. In addition, hot compressed water hydrolysis produces enzyme inhibitors that inhibit the growth of small-scale microorganisms such as furfural, hydroxyl methyl furfural, and carboxylic acids.

2.2.4 Hot-compressed water under pressurization of CO_2 pretreatment

Compressing carbon dioxide at a pressure higher than 5 MPa result carbonic acid to dissolve in water and increase hydrolysis rate of polysaccharide to monosaccharide in the range of 150-230 ° C. The research reported that the yield of xylose is significantly increased comparing with compressed hot water (Van Walsum et al., 2004; Miyazawa and Funazukuri, 2005). The carbon dioxide compressed water hydrolysis is alternative choose for safe, hazardous and friendly environment because carbonic acid can decompose into carbon dioxide and water by itself after reaction.

2.2.5 Hot-compressed H_2O_2 solution under pressurization of CO_2 pretreatment

This pretreatment is similar to using carbon dioxide but differently using a hydrogen peroxide solution instead of water. The dissolved carbon dioxide in the liquid phase reacts with hydrogen peroxide to form peroxy-carbonic acid. It can be used as the acid catalyst which is stronger than carbonic acid. This method was not founded to using in hydrolysis of lignocellulose. However, it has been used to make epoxidation natural rubber (Hydroxyl Telechelic liquid Natural Rubber: HTNR) at 40-60°C and 12 MPa (Amnuaysin et al., 2015). However, the peroxy-carboxylic acids that occurring are not stable. It decomposes into carbon dioxide and hydrogen peroxide at atmospheric and atmospheric pressure (Nolen et al., 2002).

2.2.6 Supercritical or subcritical water pretreatment

The super or subcritical water (critical point temperature 374.2 °C and pressure 22.1 MPa) is a mixture of liquid phase and gas phase. The dielectric constant is decreases effect to the polar properties of chemical and ionic product properties. It makes molecule be nonpolar molecule (hydrophobic molecule) and resulting to water can become a source of hydrogen ion and hydroxide ion. The super or subcritical water which as catalyst used to degrade lignocellulosic hydrolyze, resulting to rate of hydrolysis for sugar production is increase. While side effects including dehydration and fragmentation can occur under this condition resulting to yield of sugar decreases dramatically (Lu et al., 2009).

2.2.7 Acid pretreatment

Acid pretreatment process aims to remove lignin from lignocellulosic molecule for increase surface area of cellulose. The types of acid that can be used to treat in hydrolysis process are various types such as sulfuric acid, hydrochloric acid, nitric acid and phosphoric acid (Palmqvist et al, 2002). The using of dilute acid solution treats lignocellulose almost using for hemicellulose conversion. Following step is using enzymatic hydrolysis convert cellulose to glucose (Silverstein et al, 2007).

2.2.8 Alkali pretreatment

The mechanism of alkaline pretreatment for converting lignocellulose is the expansion of the molecule and internal bonding of xylenes in hemicellulose molecule. It effects to increase porosity properties of the material because intermolecular bond is destroyed. Using of diluted alkalis to treat lignocellulose results in internal swelling molecule. This cause increases the surface area of hydrolysis and porosity in the molecule but decrease crystallization of cellulose. In addition, alkali is capable of breaking the chemical bond between lignin molecules and chemical bonding between lignin with hemicellulose molecules. The alkaline used in lignin separation include sodium hydroxide and ammonium hydroxide (Kim et al, 2008).

2.3 Reducing sugars

Reducing sugar is a sugar with aldehydes or ketones group which are reducing ability properties. Sugars that classified to be reducing sugar is all of a single molecule called monosaccharide such as xylose, arabinose, glucose, galactose, mannose, some of disaccharide and polysaccharide that in open chain formation such as cellulose, lactose, and isotope. The sugar products which have many formations are derived by hydrolysis reaction. It is classified reducing sugar. So, the amount of sugar from lignocellulose in the hydrolysate can be reported in total reducing sugars. (Campbell and Farrell, 2012; Nelson, 1994; Miler, 1959)

2.4 Hydrolysis of lignocellulose

Hydrolysis is the reaction using water to cleavage bonding for degrading large molecules into smaller molecule. The initial water condition of reaction is higher 170 °C and pressure equal 5 Mpa. The rate of reaction is increase by adding some catalyst such as acid or enzyme. The aim lignocellulose hydrolysis is degrading long chain lignocellulose into smaller molecule and break down cellulose and hemicellulose bonding. Hydrolysate is including of many reducing sugar types. The types and ratio of the reducing sugar depends on the type of plant and hydrolysis process (Bosch et al., 2010). Next steps, the reducing sugar is fermented into ethanol. Hydrolysis of hemicellulose produce monosaccharide that five carbon atoms such as xylose and arabinose. Furthermore, hemicellulose hydrolysis produces reducing sugar that a single molecule composed of 6 carbon atoms such as glucose, galactose and mannose. It produces not only reducing sugar but also produces other product in hemicellulose polymer such as organic acid. Hydrolysis cellulose produces glucose and other sugar that compose in cellulose polymers such as cellobiose, cellotriose and cellulose.

2.4.1 Alkali hydrolysis

Alkali hydrolysis has 2 possible types: (1) End-wise degradation (peeling), which occurs under temperature <170°C. In this condition, the glycosidic β (1→4)-linkages between glucose molecule under sodium hydroxide solution is stable. On the other hand, cellulose has significant reduction of molecular weight. The research suggests that the losses were cause by the dissolution of short-chain chemical at reducing end of cellulose molecule (known peeling). (2) Alkali scission, which occur higher temperature (>170°C). It hydrolyzes at β (1→4)-glyosidic linkage resulting weight loss of cellulose. The weight loss does not depend on only the linkage but also peeling at the reducing end of cellulose molecule. The resulting of weight loss is higher than the alkaline hydrolysis at low temperature (Charles, 2003).

2.4.2 Acid hydrolysis

The types inorganic acids used in lignocellulose hydrolysis are sulfuric acid, hydrochloric acid, nitric acid and phosphoric acid. In addition, the types organic acids in lignocellulose hydrolysis are acetic acid and formic acid the concentration and type of acid depend on the temperature used in the hydrolysis. Mostly use sulfuric acid because it is cheap and also give the results of high yield of reducing sugar. The research reported that hydrolysis with sulfuric acid at 1% by weight, it produces yield of glucose 50% by weight at 240 ° C for 10 seconds, which is higher than the sulfuric concentration 0.2% by weight at the same temperature and time. As shown in Figure 2.4 (Fagan et al, 1971), when adding acid that higher concentration, it gives higher yield of glucose at the same temperature. In addition, acid hydrolysis produces various byproducts such as furfural and hydroxyl methyl furfural. It produces due to the removal mechanism of water from the sugar molecules and gives enzyme inhibitor in the fermentation process (Kumar et al, 2015).

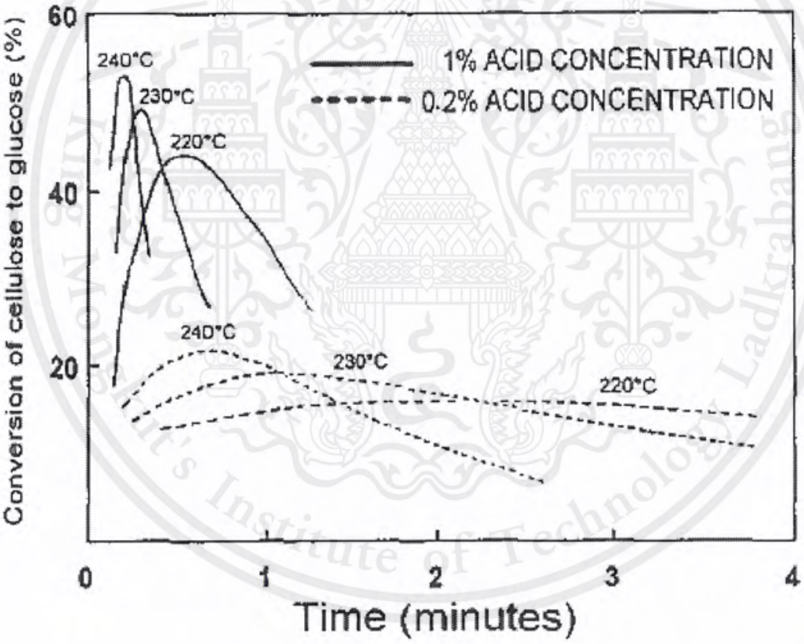


Figure 2.4 Yield of glucose as treated by sulfuric concentration 1wt% and 0.2wt% at various temperature and time (Fagan et al., 1971)

2.4.3 Enzymatic hydrolysis

Enzymatic hydrolysis produces large amount of reducing sugar and non-byproduct forming such as furfural and hydroxyl methyl furfural. The byproduct has ability to inhibit enzymes to producing ethanol which is side product. The kind of lignocellulose enzymatic hydrolysis is cellulose which has specific digesting for cellulose. In enzymatic hydrolysis process use various of enzyme such as endo-cellulose which destroy H-bonding in glucan molecule making cluster glucan into straight chain and exocellulase enzyme make glucan become cellobiose after that β-glycosidase enzymes digest cellobiose to glucose (Yu and et la., 2008).

2.5 Carbonic acid formation

The carbon dioxide gas can dissolve in water and react with water to form carbonic acid. Because the henry's law constant of carbon dioxide makes it dissolved. The mechanism showed following equation 2.1 and 2.2. The carbonic acid can dissociate 2 times. First, the carbonic acid dissociates to bicarbonate ion and hydronium ion. Second, bicarbonate dissociate to carbonate ion and hydronium ion. The mechanism of carbonic acid dissociation shows in equation 2.3 and 2.4

$$CO_2(g) \rightleftharpoons CO_2(aq) \tag{2.1}$$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \tag{2.2}$$

$$H_2CO_3(aq) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \tag{2.3}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-} \tag{2.4}$$

The first and second basic dissociation of carbonic acid values (K_{a1} and K_{a2}) are 4.5×10^{-7} and 4.7×10^{-11} at temperature 25 °C (CRC Handbook of Chemistry and Physics, 2004)

2.5.1 Solubility and Dissociation correlation

The geochemistry literature reported that the solubility of CO_2 in water barely dissolves near 160-170°C. In general, the literature reported that the solubility of carbon dioxide relates Henry's constant to temperature. Figure 2.5 showed that have several studies. A curve plots with three data give the equation to find Henry's constant. The equation was found to be

$$H(T) = -0.017037 \times T^2 + 6.1553 \times T + 78.227 \tag{2.5}$$

where T is temperature in °C and H in MPa defines the partial pressure of gaseous CO_2 in equilibrium with mole fraction of solve CO_2

In this research, the limited of batch reactor is 5 MPa at room temperature but temperature that using 170-290°C resulting to the value of Henry's constant equal around 430.45-632.26 MPa in order to increasing mole fraction of CO_2 in liquid phase.

$$P_{CO2} = X_{CO2}H \tag{2.6}$$

$$P_{CO2} + P_{H2O} = P_{total}(Y_{CO2} + Y_{H2O}) = P_{total} \tag{2.7}$$

The Henry's constant, which shows the solubility of carbon dioxide in water at various temperatures as shown in Figure 2.5, the constant Henry's experiment (data points) is related to temperature as a parabolic function. It can convert to find partial pressure of CO_2 in system which follow equation 2.6 and 2.7.

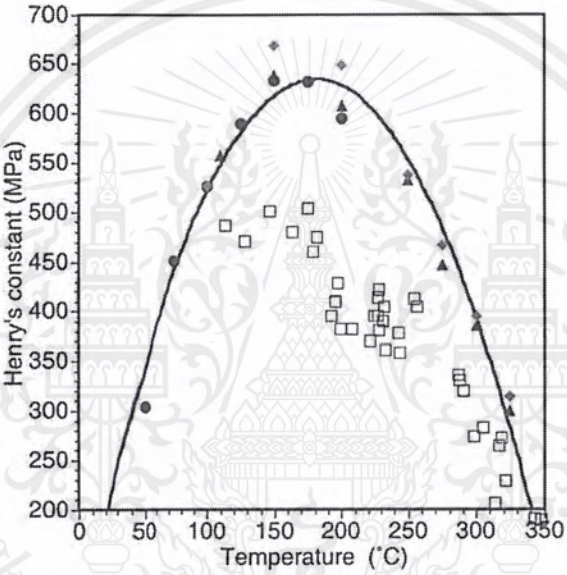


Figure 2.5 Henry's constant for solubility of CO2 in water as a function of temperature (Walsum et al, 2001)

2.5.2 The dissociation for carbonic acid

The pH can predict by pK_{a1} of H_2CO_3. So, the literature reported that the pK_{a1} highly depend on temperature and to find pK_{a1} value by plotting several studies. Figure 2.6 show the pK_{a1} correlation curve can generate formula of pK_{a1} correlation. The equation is to be:

$$pK_{a1} = (2382.3/T) - 8.153 + 0.02194 \times T \tag{2.8}$$

where T is expressed in K (Kelvin)

After that the pH is estimated by dissociation equation for CO_2 in water

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_{2(aq)}]} \tag{2.9}$$

The H^+ ions present to be the dissociation of carbonic acid because the dissociation constant of water is low. Thus, the predict pH parameter is assumed that the concentration of [H+] of carbonic acid dissociation and bicarbonate.

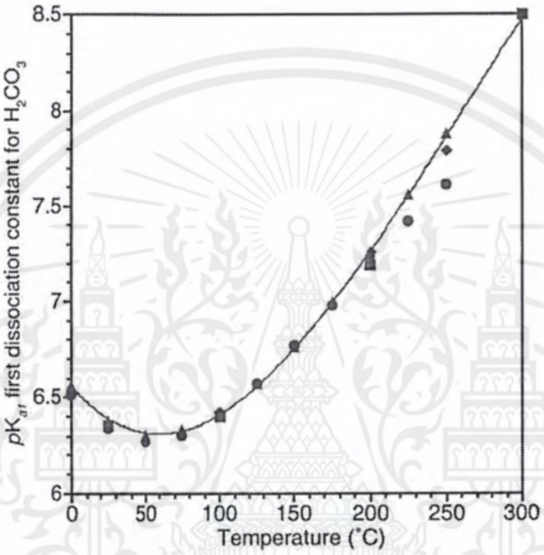


Figure 2.6 pKa1 values for first dissociation constant of H_2CO_3 in water as a function of temperature (Walsum et al, 2001)

The literature has the experiment to predict the pH and plot in different of partial pressure of CO_2 as show in figure 2.7. From that graph, it gives the equation that predicted pH formula as show in the equation 2.10. The equation is:

$$pH = 8.00 \times 10^{-6} \times T^2 + 0.00209 \times T - 0.216 \times \ln(P_{CO_2}) + 3.92 \tag{2.10}$$

where T expressed as temperature in °C, P_{CO_2} in atm

In this research, the temperature lignocellulose hydrolysis is 170-290°C and it estimated the pH parameter equal to be around 3.66-4.35.

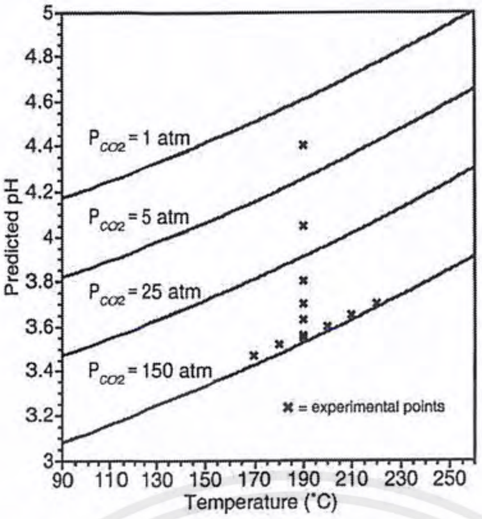


Figure 2.7 Experiment graph that using different pressure to predict pH parameter (Walsum and et la., 2001)

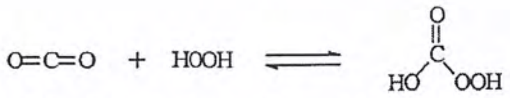
2.6 Peroxy-acid formation

Peroxy-acid is the acid, including the –OOH group, which has two types. First types is inorganic peroxy-acid and second is organic peroxy-acid. They have ability strong oxidative agent. The inorganic peroxy-acid, such as peroxymonosulfuric acid, is used to blend paper in pulp process and eliminate cyanides in mining industrial. (jakob and et la., 2012) The organic peroxy-acid can be occurring by reaction of hydrogen peroxide with organic acid, such as peroxy-carboxylic acid that occurring from carboxylic acid react with hydrogen peroxide. They mechanism shows in equation 2.9. The stabilize increasing of carboxylic acid depend on a number of carbon atom in molecule (Brandsch and Piringer, 2000) but the dissociation value of peroxy-carboxylic acid is lower that the initial reactant 1000 times. Cause of electron in molecules occur resonance in stabilization of anion. (Klenk and et la., 2012)

$$RCO_2H \quad + \quad H_2O_2 \quad \rightleftharpoons \quad RCO_3H \quad + \quad H_2O \qquad (2.11)$$

Carbon Dioxide Hydrogen Peroxide Peroxycarbonic Acid Water

In this research, the pressure that using in experiment is 5 MPa result to proxy carboxylic acid formation following in equation 2.11. The peroxy-carbonic is higher oxidative agent than hydrogen peroxide (Brandsch and Piringer, 2000) but in general the peroxy-carbonic acid is not stable as pure chemical. In this research, it is prepared by compressed immediately carbon dioxide gas into hydrogen peroxide solution. (Nolen and et la., 2002)



CarbonDioxide HydrogenPeroxide Peroxycarbonic acid (2.12)

Thidarat et la., 2015 reported that modifying natural rubber by cutting hydroxyl group use hydrogen peroxide concentration 30% by weight solution and compressed carbon dioxide gas as 12 Mpa, temperature 60°C. It found that the peroxy-carbonic acid, occurring, can be oxidized a natural rubber which has hydroxyl group. The molecular weight of natural rubber is decrease from 1.9×10^4 gram per mol to 4.2×10^3 gram per mol. This result show preparing peroxy-carbonic acid via the previous method has effective resulting. So, this research assigned the preparing procedure to the study.

2.7 Decomposition pathway of cellulose under hydrothermal pretreatment

Lu et al., (2009) reported the cellulose degradation pathways by two step wise hydrolysis method. The research is reported using hot-compressed water in Japanese beech hydrolysis. The cellulose can decompose to cello-saccharides and glucose respectively. Glucose monomer was isomerized to fructose and mannose. The three isomerization are dehydrated to Furfural, 5-HMF and deep hydrolyze levoglucosan. They can ferment to erythrose, glycolaldehyde and methylglyocal. The other products are organic acid as show in figure 2.8.

Aldehydes are easy to oxidize with present of oxidative agent, for example hydrogen peroxide and etc., the figure 2.9 show simple of oxidation with Ag^+ oxidative agent. First, the sugar is induced to open cyclic form by Ag^+ in system Next the sugar give electron to Ag^+ to form silver metal and sugar is converted to organic acid. (Shapley, 2012)

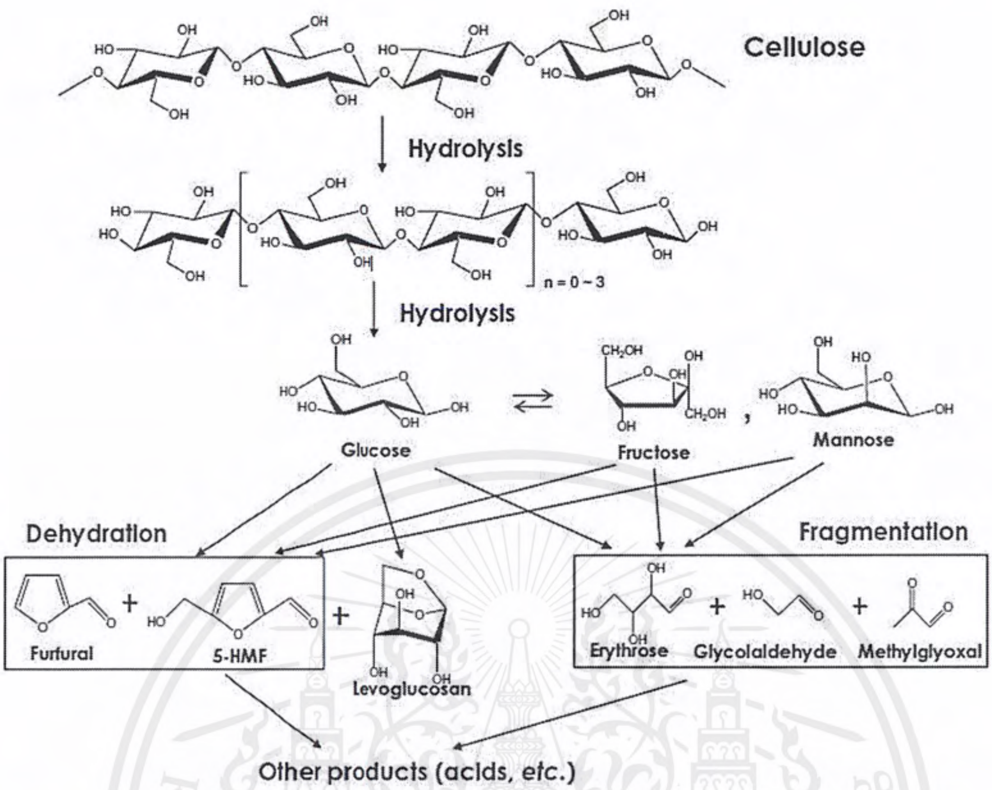


Figure 2.8 Decomposition pathway of cellulose as treated by hot-compressed water (Lu et al., 2009)

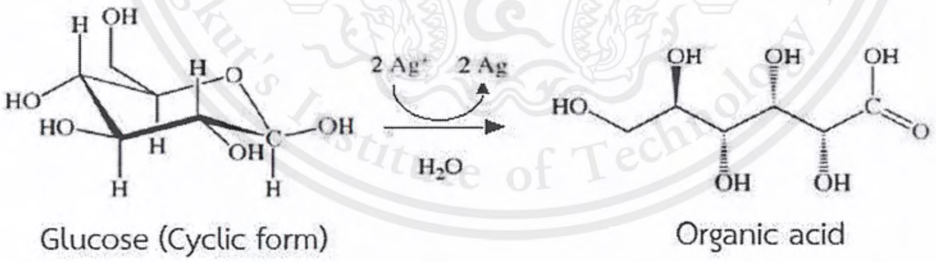


Figure 2.9 Simple mechanism of glucose conversion as treated by oxidation treatments (Shapley, 2012)

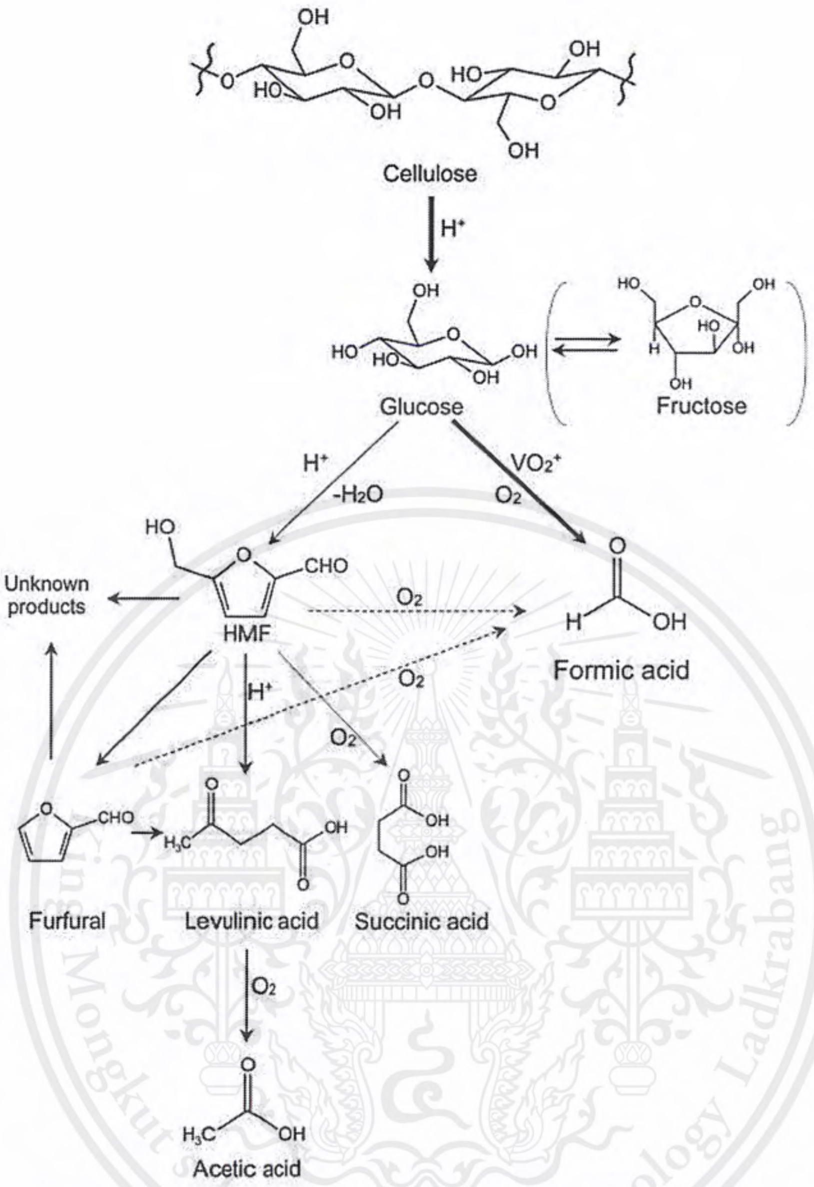


Figure 2.10 Cellulose oxidation pathway as treated by presence of catalytic oxidation in hydrolysis treatment (Niu et al, 2014)

Niu et al., (2014) reported that they study about the possibility of cellulose hydrolysis product, because in hydrolysis reaction has side product which is cellulose oxidation reaction. Their experiment uses MCC as reactant and $NaVO_3$-H_2SO_4 as catalyst. The reaction occurs in batch reactor which temperature condition is 140-180°C and pressure is 3 MPa with time 10 min. The result of this research showed in figure 2.10. From the result hydrolysis product are HMF and furfural, the product of oxidation with O_2 present are formic acid, succinic acid, levulinic acid and acetic acid. So the paper concludes the relationship between hydrolysis with oxidationis competitive relationships.

Lu et al., (2016) reported that using $H_5PV_2Mo_{10}O_{40}$ + H_2SO_4 solution to study oxidation reaction lignocellulosic biomass by batch-25 cm_3 reactor. The result reveals that $H_5PV_2Mo_{10}O_{40}$ as present oxidative agent convert cellulose to oxidative products. The products are glycolaldehyde, glyoxal, glyceraldehyde and formic acid. In previous research (Niu et al., 2014) conclude relationship between hydrolysis and oxidation is competitive reaction as the same way in this research presented hydrolysis products are levulicnic acid and acetic acid as show in figure 2.11

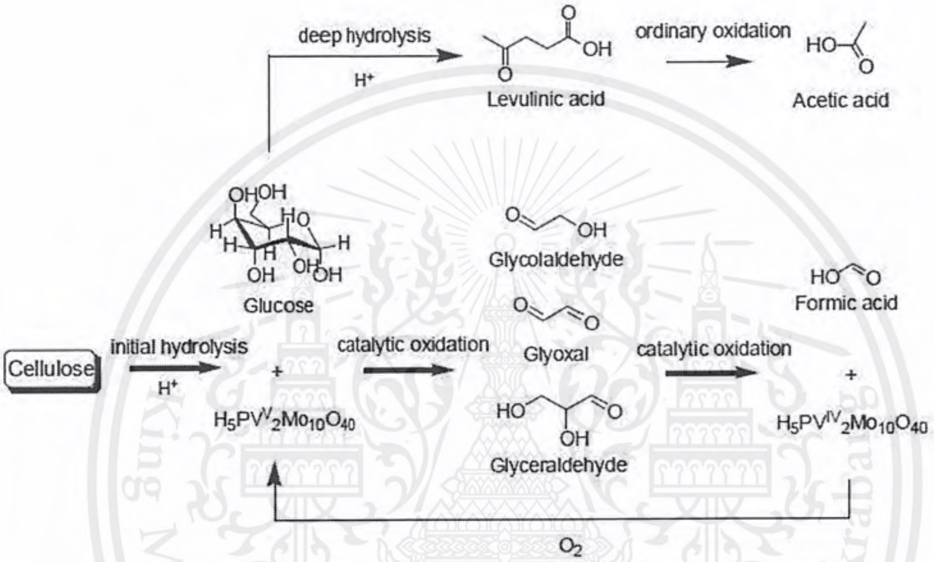


Figure 2.11 Oxidation pathway of cellulose conversion as treated by hydrolysis treatment with presences catalytic catalyst $H_5PV_2Mo_{10}O_{40}$ + H_2SO_4 aqueous solutions with O_2 (Lu et al., 2016).

Zhou et al. (2015) reported that it was study about Oxidation-hydrolysis strategy was developed for depolymerization of cellulose. Part of hydroxymethyl groups on glucose units were oxidized to carboxyl groups in the peroxidation treatment, and the generated acid sites act as the catalytic active centersf or the following depolymerization of cellulose. After α-cellulose was pretreated by air at 210 oC for 48 h, 23.3% yield of glucose was given in water at 150 oC for 8 h without additional catalyst. The ratio of cellulose/water has no obvious influence on the yield of glucose. 17.9% yield of glucose for α-cellulose can still be obtained even at the weight ratio of 0.4, where up to 75 g L-1 of glucose solution is given. For MCC, 25.2% yield of glucose was obtained for hydrolysis at 170oC for 8 h. It was revealed that the generated carboxyl acid groups in oxidation step are the catalytic sites for the hydrolysis of cellulose

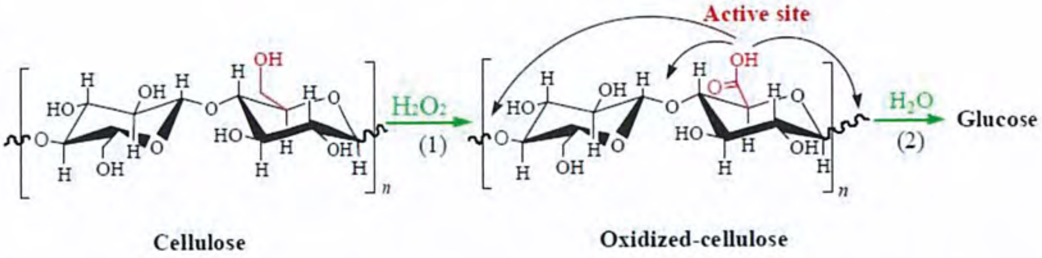


Figure 2.12 The oxidation pathway of cellulose depolymerization. (Zhou et al., 2015)

2.8 Literature reviews

In the last decade, the researcher study about lignocellulose hydrolysis not only without catalyst for example super and subcritical water, hot compressed water, steam explosion but also with catalyst such as acid hydrolysis, alkaline hydrolysis. In previous research has study about sugarcane hydrolysis with compressed carbon dioxide and hydrogen peroxide solution but in actually plant cell wall has lignin that inhibited factor to hydrolysis of cellulose. It is hard to understand the behavior of cellulose under hydrolysis reaction. In this research aims to study the behavior of cellulose in the hydrolysis reaction with carbon dioxide compressed hydrogen peroxide solution. The significant literature reviews are:

Sluiter et al., (2010) study the composition of lignocellulose by using hydrolysis with sulfuric acid as catalyst to separate lignin. This method uses sulfuric acid with concentration 72% by weight at ambient temperature and pressure. After that dilute the acid solution by adding water into system and heating temperature to 100-125°C, it effects to all oligosaccharide converted to monosaccharide which can analysis the amount of hemicellulose and cellulose in lignocellulose. The lignocellulose residue was separated by vacuum filter for analyze weight of lignin. This method is widely accepted and used to study the chemical compositions of lignocellulosic materials and it is less error than other methods.

Phaboonsilpa et al., (2011; 2013) study hydrolysis of lignocellulose using hot compressed water two step wise. The sample on this research are Japanese beech, Japanese cedar, nipa frond, rice straw and rice husk. It covers the all vascular plants species. In the experiment use flow through reactor at 10 MPa with time equal 60 minute and flowrate of hot compressed water 10 millimeter per minute. It found that the optimize temperature of two step between hemicellulose and cellulose have different value which temperature of hemicellulose is 230°C and cellulose is 270-280°C. The yield showed that all hemicellulose was hydrolyzed into reducing sugar, but cellulose was hydrolyzed 70% by weight.

Rahman et al., (2007) study increasing efficiency of acid hydrolysis empty palm or palm bunch for produce xylose. The various factors are temperature time and concentration of sulfuric acid. They use temperature around 100-130°C, time about 30-90 minute and concentration 2-6% by weight. The research found that the optimize conditions are temperature 119°C, time 60 minute and concentration 2% by weight. It gives yield of xylose 91.27% by weight.

Zhang and Wu, (2013) study pretreatment of sugarcane by using supercritical carbon dioxide is increase efficiency of enzymatic hydrolysis. This method using conditions are temperature 140-180°C, pressure 1-5 MPa and time 60-100 minute. The research showed that pretreat with supercritical carbon dioxide at 160 °C and 5 MPa in 100 minutes. It increases efficiency in lignocellulose enzymatic hydrolysis, resulting to yield of xylo-saccharide 15.78% by weight which including xylose 3.16% by weight, xylo-oligosaccharide 12.62% by weight and glucose recovery 91.87% by weight. In this research show the optimize condition of pretreatment lignocellulosic biomass with supercritical carbon dioxide produce reducing sugar.

Walsum et al., (2001) study hydrolysis reaction of xylan from beech wood via using carbonic acid. In the experiment, they use batch reactor which size is 15 ml and the conditions of this method are compressed carbon dioxide gas at 0-5.5MPa into 1 gram per liter, temperature 170-230°C and time 2-30 minute. The result showed that the carbonic acid can increase rate of hydrolysis of xylan into xylose in range of studied temperature. When comparing with using dilute sulfuric acid, it found that carbonic acid is less efficiency in hydrolysis than dilute sulfuric acid at 190°C and time 14.5 minute. Although the reactor with using dilute sulfuric acid has higher pressure 14 MPa than using carbonic acid.

Walsum et al., (2004) study about increasing efficiency of corn stover with using carbonic acid in batch reactor 15 milliliter. The size of corn stover is 0.5-1 millimeter. The conditions are temperature 180-220°C, compressed carbon dioxide gas 5.5 MPa, and time of reaction 2-32 minute. The result showed that using carbonic acid can increase rate of hydrolysis and the yield of xylose is higher 2 times when comparing with using hot compressed water.

From the literature reviews that related with this research effected to the conditions in MCC hydrolysis this study. The conditions that adjusted are hot-compressed water under pressurization of N_2, hot-compressed water under pressurization of CO_2, hot-compressed 0.1%wt H_2O_2 solution under pressurization of N_2 and hot-compressed 0.1%wt H2O2 solution under pressurization of CO_2.The temperature range is 170-290°C and pressure 5 MPa the compressing carbon dioxide into water and hydrogen peroxide needs to occur carbonic acid and peroxy carbonic acid formed. Because they can increase higher efficiency of hydrolysis reaction than using hot compressed water.

CHAPTER III

RESEARCH METHODOLOGY

This research study about microcrystalline cellulose (MCC) liquefaction with using hot compressed water, carbon dioxide compressed water and carbon dioxide compressed hydrogen peroxide to converts cellulose into glucose.

3.1 Hot-compressed water under pressurization of N_2 or CO_2

3.1.1 Conditions

The conditions of this research are temperature 170-290°C and treatment time 0 minute in batch reactor. Before start batch reaction compressed nitrogen gas 5 MPa at ambient temperature because the limit of experimental equipment such as valve that controlled pressure. So, the highest pressure, that experimental equipment achieved, is 5 MPa

3.1.2 Material and Chemical

1. Microcrystalline cellulose Cas. Number. 9004-34-6
2. N_2 gas purity 99.99 %
3. Deionized water
4. CO_2 gas purity 99.99%

3.1.3 Equipment

1. Batch reactor volume 10 milliliter
2. Heater
3. Vacuum filter
4. Filter paper porous 8 micrometer (Whatman No.4)
5. Pipet 10 ml

3.1.4 Procedure

1. Weight MCC 0.05 gram and pour into reactor
2. Pipet deionized water 6 milliliter into reactor
3. Tighten the bottle cap of reactor well
4. Compressed nitrogen or carbon dioxide gas into reactor at 5 MPa and check leak of reactor.
5. Install the reactor into heater and heating to designed temperature.
6. Start the reaction by switch on the system

7. When finished reaction at approach design temperature, turn off the Heater and cool the temperature down by quenching in iced-water bath for 15-30 min
8. Release pressurized nitrogen in the reactor by gently open the reactor valve
9. Open a reactor and filter the mixture by vacuum filtration
10. Collect the hydrolysate at 4°C for experiment and analysis
11. Wash the reactor with deionized water many times to recover all of the residue deposited in the reactor
12. Oven-dry the solid residue at 105°C for 4 hours and then store in desiccator for further chemical composition analysis

3.2 Hot-compressed 0.1%wt H_2O_2 solution under pressurization of N_2 or CO_2

3.2.1 Conditions

The conditions of this research are temperature 170-290°C and treatment time 0 minute in batch reactor. Before start batch reaction compressed nitrogen gas 5 MPa at ambient temperature. The concentration of hydrogen peroxide that using is 0.1% by weight

3.2.2 Material and Chemical

1. Microcrystalline cellulose Cas. Number. 9004-34-6
2. N_2 gas purity 99.99 %
3. Hydrogen peroxide 0.1% by weight
4. CO_2 gas purity 99.99%

3.2.3 Equipment

1. Batch reactor volume 10 milliliter
2. Heater
3. Vacuum filter
4. Filter paper porous 8 micrometer (Whatman No.4)
5. Pipet 10 ml

3.2.4 Procedure

1.Similar procedure to 3.1.4 but different using 0.1%wt hydrogen peroxide mix with 6 ml water.

3.3 Analytical procedures

3.3.1 Analytical and quantification of liquefaction products

Reducing sugars in hydrolysates from MCC hydrolysis determination method comprise of monosaccharides from cellulose which are glucose. The amounts of such monosaccharides were analyzed by using high performance liquid chromatography (HPLC) under the following conditions:

HPLC Column:	Aminex HPX-87H
Eluent:	0.005 M of sulfuric acid
Eluent Flow Rate:	0.5 ml/min
Column Temperature:	, 65°C
Detector:	Refractive index (RI)

Each reducing sugar standard solutions, which are glucose, xylose, and arabinose, were firstly analyzed by HPLC for individual identifications based on their retention times. Calibration curves of the standard solutions were constructed by plotting between the concentrations and peak areas obtained from the HPLC chromatograms. At least two known concentrations of the reducing sugar standard solutions were incorporated. The curves were used for quantification of the reducing sugars in hydrolysates from their peak areas in chromatograms measured by HPLC. Sugar yields were reported in percentage on the oven-dried extractives-free sugarcane bagasse basis.

For calculated total sugar, percent yield and recovery sugar in MCC which get concentration (mg/ml) from HPLC graph following equations 2.13, 2.14 and 2.15 respectively.

$$\text{Total sugar} = \frac{\text{HPLC graph concentration x volume batch}}{\text{1000 x sample initial weight}} \qquad (2.13)$$

$$\text{Yield} = \frac{\text{Total sugar}}{\text{Sample initial weight}} \text{x} 100 \qquad (2.14)$$

Analyzed furfural and hydroxyl methyl furfural in hydrolysis using high performance liquid chromatography (HPLC) under the following conditions:

HPLC Column: KS-801 (Shodex)
Eluent: Deionized water
Eluent Flow Rate: 1 ml/min
Column Temperature: 80°C
Detector: Refractive index (RI)

The process uses to know the amounts of furfural and hydroxyl methyl furfural similar to analytical the reducing sugar by using graph plotting analysis.

3.3.2 Removal of hydrogen peroxide from hydrolysates

1. Pipet hydrolysates 2 ml pour into 10 ml bottle
2. Tighten the bottle cap well
3. Set up the heater and star boil water by switch on the heater
4. Heating temperature to 80°C and install the hydrolysates into heater
5. Boil it for 60 min with constant temperature
6. Adjust the volume to 10 ml and pipet 4 ml to analyze quantitation of oligosaccharides

3.3.3 Quantitation of oligosaccharides

1. Sonicate the hydrolysates and pipet 1 ml pour into bottle
2. Pipet sulfuric acid 98wt% for 0.01725 ml and pour into the hydrolysates bottle. Besides, if use sulfuric acid 72wt%, pipetting 0.02634 ml.
3. Warp the whole a glass bottle of hydrolysates with plastic bag and tighten the bottle cap well
4. Put it in an autoclave, heat up to 121°C, and keep at this temperature for 30 min
5. Turn off the heater and release pressure inside the autoclave. Allow the autoclave temperature to decrease for a few minutes. Then bring the glass bottle out, and cool down to room temperature
6. Analyzed the amounts of various liquefied products by dilute concentration 10 times with Type I water

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the results of liquefaction behavior of microcrystalline cellulose (MCC) under different hydrothermal methods were discussed including (4.1) effect of temperature on liquefaction of MCC, (4.2) production of recoverable monosaccharides and cello-saccharides, (4.3) production of decomposed compounds, and (4.4) mass balance and cellulose decomposition pathway.

4.1 Effect of temperature on liquefaction of microcrystalline cellulose

The MCC was treated by using hydrothermal methods including hot-compressed water under pressurization of N_2, hot-compressed water under pressurization of CO_2, hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2, and hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2. As illustrated in Fig. 4.1, the obtained results demonstrated that the residue weights of MCC decreased when liquefaction degree of MCC was intensified. These results were elucidated that difference of liquefied MCC was treated by the treatment with hydrogen peroxide, where oxidation reaction was a dominant reaction, and the treatment with water. where hydrolysis was a dominant,. The decreasing of residue weights of MCC, which treated by hydrogen peroxide, was more higher effect than in the hot-compressed water treatment. It demonstrated that liquefaction of MCC was more dissolved in oxidation reaction than hydrolysis. As seen in Fig 4.2, In a particular case of hot-compressed water treatment under pressurization of CO_2, residue weight at temperature of 190°C was found to be effect of carbon dioxide solubility in water and the solubility of MCC in this condition was more similar as hot-compressed 0.1wt% H_2O_2 solution than hot-compressed water. This result was probably due to the effect of acid addition by pressurization CO_2 in water, which the presence of carbonic acid. The research that clarified occurring carbonic acid in water was reported compressing carbon dioxide at higher than 5MPa in water could produce carbonic acid and the highest carbon dioxide dissolve in water was explored at 190°C on initial pressure was 5MPa. (Van Walsum et al., 2004; Miyazawa and Funazukuri, 2005).

As seen in Fig 4.2, Besides, MCC had significantly individual character, which structure of amorphous cellulose that consist of cellulose I_α, cellulose I_β and para-crystalline. The study that reported primally cellulose I_α was hydrolyzed to para-crystalline cellulose in primary acid hydrolysis temperature, which temperature is ~160-190°C. It was followed by conversion to cellulose I_β, while simultaneously a small fraction of para-crystalline cellulose slowly transforms into crystalline cellulose (Foston et al., 2010). Another study on structure of cellulose reported that a large increase in the relative proportion of cellulose I_β accompanied by a decrease in the relative proportions of both cellulose I_α and para-crystalline region from dilute acid pretreated pine. This suggests that the types of lignocellulosic materials and exact pretreatment conditions influence cellulose crystalline allomorphs and para-crystalline contents during dilute acid pretreatment (Sannigrahi et al., 2008). It clearly demonstrated noted particular changing at 190°C is decomposed of cellulose I_α or/and para-crystalline cellulose. These studies discussed in above, it was assumption that the author had been done the research to demonstrate the realization of strange decreased liquefaction in MCC as treated by hot-compressed water under CO_2.

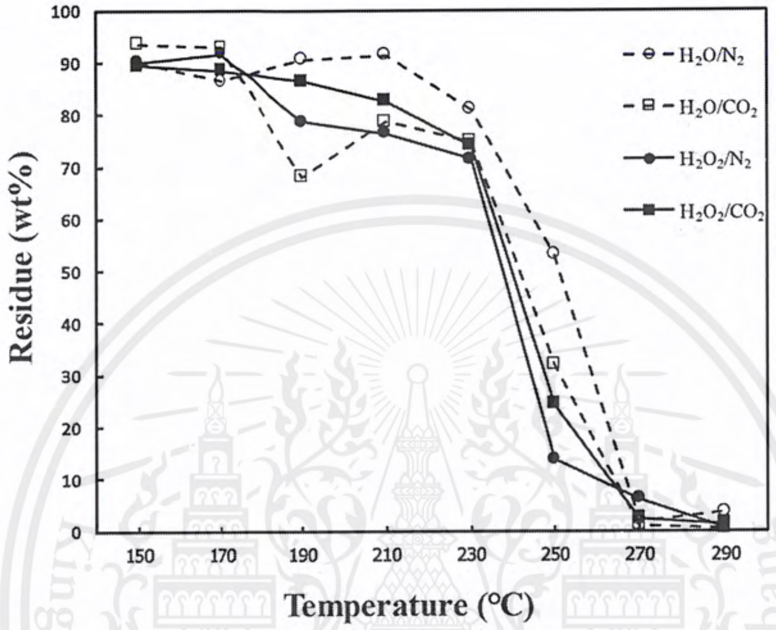


Figure 4.1 Change in residues of MCC as treated by different hydrothermal methods

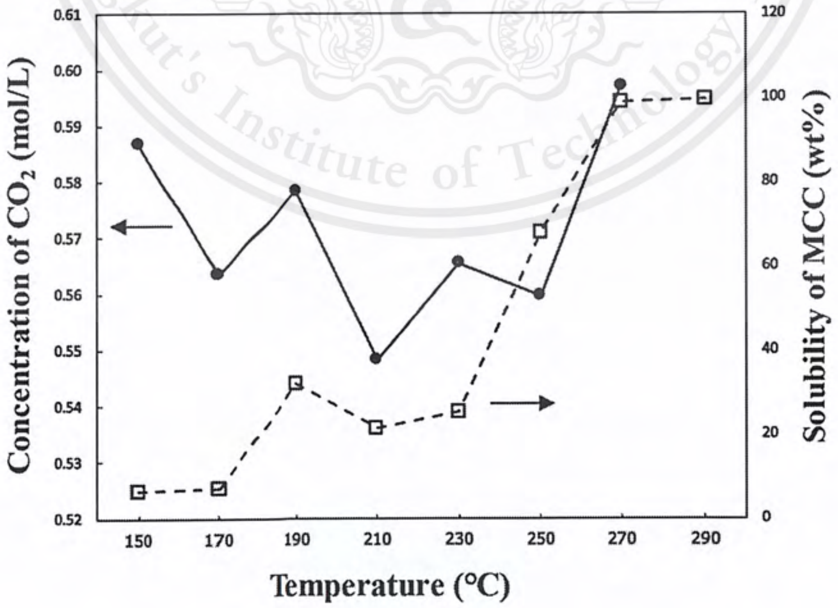


Figure 4.2 Liquefaction of MCC and solubility of CO_2 in water under pressurization of CO_2 at different temperatures

4.2 Hydrolyzed products from microcrystalline cellulose as treated by different hydrothermal methods

4.2.1 Recoverable monosaccharides

Based on the obtained results, illustrated in figure 4.3, elucidated that the yields of highly recoverable monosaccharides were 13.5, 20.6, 28.8, and 21.4wt% at the same condition of 250°C as treated by hot-compressed water under pressurization of N_2, hot-compressed water under pressurization of CO_2, hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2, and hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2. The appropriated condition of the highest recoverable monosaccharides was hot-compressed 0.1wt% H_2O_2 solution under N_2. These results were elucidated that liquefaction of MCC was more hydrolyzed by oxidation reaction than both hydrolysis reaction. The study that accord with this result was (Zhou et al., 2015). They were using MCC for oxidation reaction with present H_2O_2 at 170°C for 8hr, 25.5wt% yield of glucose was obtained Comparing with hydrolysis reaction 10wt% yield glucose. The glucose yield, which the presence of oxidation, was higher that treatment by hydrolysis for 15wt%. This study reported that, due to, hydroxymethyl groups on glucose units were oxidized to carboxyl groups in the treatment, and acid sites act as the catalytic active centers for depolymerization of cellulose to glucose in hydrolysis reaction. It was resulted to higher recovery yield of monosaccharides than hydrolysis without presence of oxidizing agent. In a particular case, the treatment which is hot-compressed 0.1wt% H_2O_2 solution under CO_2 was inferior and unexpected effect of CO_2 pressurization where formation of peroxy-carbonic acid was occurred. The peroxy-carbonic acid, which is strongly oxidizing agent, could be affect higher yields of recoverable monosaccharides than hot-compressed 0.1wt% H_2O_2 solution under N_2. The obtained results elucidated that the yield of recoverable monosaccharides, which the presence of peroxy-carbonic acid couldn't provide higher than treatment with hot-compressed 0.1wt% H_2O_2 solution under N_2. Therefore, the effect of peroxy-carbonic acid could not be confirmed yet for liquefaction of MCC

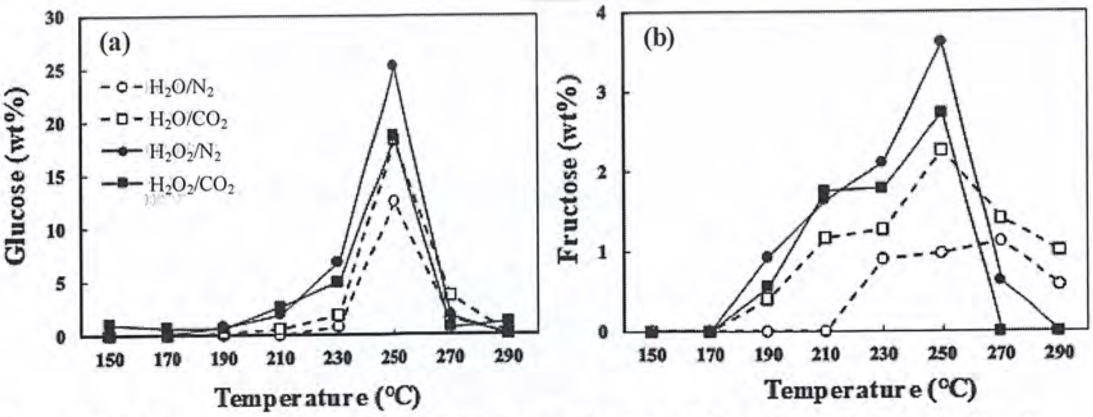


Figure 4.3 Production of glucose and fructose from MCC as treated hydrothermal methods

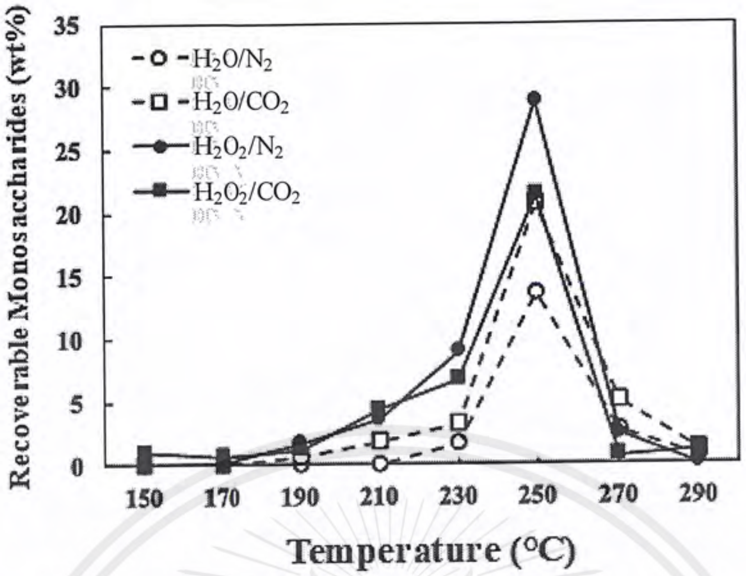


Figure 4.4 Production of recoverable monosaccharides from MCC as treated by different hydrothermal methods

4.2.2 Cello-saccharides

Figure 4.4, moreover, depicts to composition of mono and oligosaccharides in the hydrolysates of MCC as treated by hot-compressed water under pressurization of N_2 and CO_2 and hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2 and CO_2. For all hydrothermal methods, the appropriated temperature which providing the highest yield of recoverable saccharides was found at 250°C. The recoverable saccharides yield from under such conditions were 61.1, 68.8, 57.1, and 42.8wt%, respectively. Moreover, the appropriated condition was hot-compressed water under CO_2, where carbonic acid could be formed in water inset at elevated temperature and high pressure, resulting in the highest recoverable yield of cello-saccharides. the presence of carbonic acid by pressing CO2 instead of N2 in hot-compressed water treatment, moreover, helped promoted hydrolysis of cello-oligosaccharides to monomer. This result was affected the carbonic acid act like acid catalyst in hydrolysis reaction, which hydrolysis treatment became acid hydrolysis treatment.

At high temperature 250°C, the production of recoverable monosaccharides was more pronounced due to oxidation effects in hydrolysis. They were convert cello-oligosaccharides to monosaccharides, which as seen in Fig.4.4 treated with hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2 provided the highest yield of recoverable monosaccharides was 28.8wt%. Moreover under 0.1wt%H_2O_2 oxidation conditions, although these treatments were performed at lower temperature, but the hydrolysates of such conditions were found recoverable monosaccharides as illustrated in Fig.4.4 at temperature range 150-190°C on solid-filled portion bars. The similar observation in more production of recoverable monosaccharides in low temperature were also realized in the study (Zhou et al., 2015) on the effect of oxidization reaction. It reported that hydroxymethyl groups on glucose units were oxidized to carboxyl groups in the treatment, and acid sites act as the catalytic active centers for depolymerization of cellulose to glucose in hydrolysis reaction. This study was carried out reaction in low temperature as the same as our study, so it could be this effect to provide recoverable monosaccharides at low temperature.

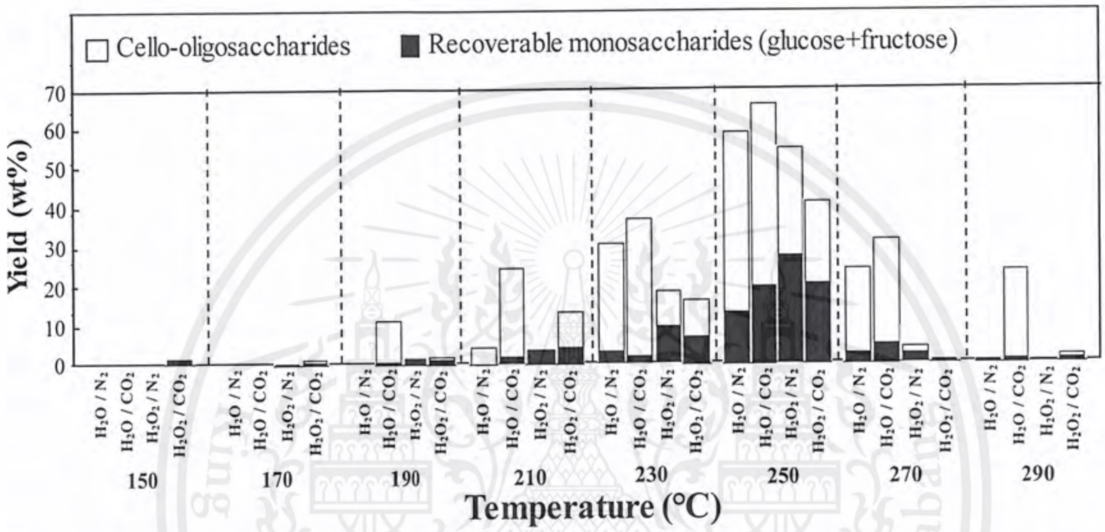


Figure 4.5 Compositions of glucose and cello-oligosaccharides in hydrolysates from MCC as treated by different hydrothermal methods

4.3 Decomposed compounds from microcrystalline cellulose as treated by different hydrothermal methods

4.3.1. Dehydrated compounds as treated by different hydrothermal methods

After hydrolysis of cellulose, the hydrolyzed products aren't consisting of only glucose. The significant by-products are furfural and 5-hydroxymethylfurfural, which glucose were dehydrated. if treatment by hydrothermal method is prolonged in batch reactor, the hexose such as glucose was dehydrated to 5-hydroxymethylfurfural (Kruse et al. 2007). Another study reported that the major product of decomposed glucose was 5-hydroxymethylfurfural, which is a precursor continuously dehydrated reaction of glucose to furfural, as treated by hydrothermal methods under 275°C (Krishna et al., 1986). This study was clearly demonstrated that furfural, which is normally dehydrated compound of pentose, was appear on liquefaction of MCC as treated by hydrothermal method. Based on obtained results, the yields of decomposed compounds increased when the liquefaction degree was intensified. These results could indicate that dehydrated compounds were temperature dependence. It accords with discussed above studies. As seen in Fig.4.5, the highest yields of decomposed compound were observed at temperature ranged 230-290°C for hot-compressed water under pressurization of N_2 and CO_2 and hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2 and CO_2. They represented performed in hydrolysis, hydrolysis with adding acid, oxidation condition and oxidation with strongly oxidizing agent, respectively. These results provide optimized conditions at the same temperature. The results were elucidated that the oxidation more producing glucose than hydrolysis reaction resulting to provides higher yields of decomposed compound higher than hydrolysis due to higher the number of monosaccharides were dehydrated than hydrolysis. The major product of decomposed glucose was most likely to be 5-hydroxymethlyfurfural than furfural about 4 times. Since 5-hydroxymethlyfurfural was precursor of furfural decomposed pathway as reviews in above study. When compared between two different oxidation condition, it illustrated that oxidation without strongly oxidizing agent performed in higher yield of decomposed compound than oxidation with strongly oxidizing agent. In hydrolysis case, it compared between hydrolysis without adding acid and hydrolysis with adding acid. These results demonstrated that hydrolysis with adding acid performed in higher yield of decomposed compound than hydrolysis without adding acid.

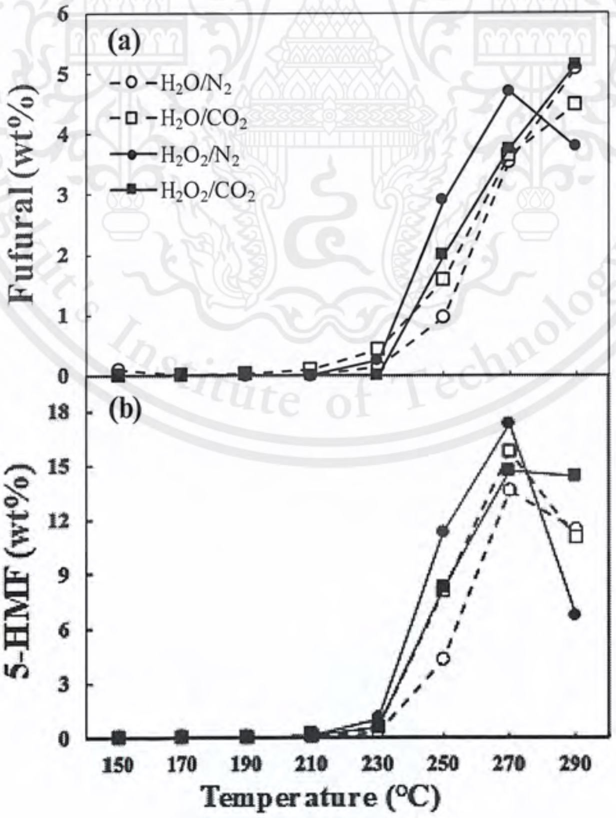


Figure 4.6 Production of dehydrated compounds from MCC as treated by different hydrothermal methods

4.3.2 Organic acids as treated by different hydrothermal methods

As seen in Fig 4.6, the organic acids increased when the liquefaction degree was intensified. However, the acetic acid decreased after 250°C. This result was assumed that acetic acid was more oxidized to formic acid if the conditions was intensified and prolonged. Besides, the formic acid yield as treated by hot-compressed 0.1wt% H_2O_2 under pressurization of N_2 and CO_2, where oxidation become predominant, were higher than the hot-compressed water under pressurization of N_2 and CO_2, where hydrolysis was dominant, at high temperature range of 250-290°C. It clarifies that the oxidation conditions could be likely produced organic acids than hydrolysis conditions at high temperature. In case acetic acid, the high yield of acetic acid was observed at both oxidation conditions on high temperature range. However, the yield of acetic acid was slightly drop after 250°C for both oxidation conditions. This result was could be assumed that acetic acid could more oxidized to formic acid when temperature was higher than 250°C. The formic acid could be indexing to determine oxidation in hydrothermal methods. On the other hand, some study claimed that monosaccharides and dehydrated compounds could be converted by oxidation reaction to organic acids and unknown products (Niu et al., 2014). It could explain decreasing of mono and oligosaccharides, dehydrated products and acetic acid at high temperature range 250-290°C. When compared between two different oxidation condition, it illustrated that oxidation without strongly oxidizing agent performed in higher yield of organic acids than oxidation with strongly oxidizing agent. The treatment which is hot-compressed 0.1wt% H_2O_2 solution under CO_2 was inferior effect in liquefaction by using CO_2 instead of N_2 for pressurization of 0.1wt% H_2O_2 solution, formation of peroxy-carbonic acid, a strongly oxidizing agent, was still unclear. As the same previous discussion in recoverable monosaccharides, the effect of peroxy-carbonic acid could not be confirmed yet for liquefaction of MCC. In hydrolysis case, it compared between hydrolysis without adding acid and hydrolysis with adding acid. These results demonstrated that hydrolysis with adding acid performed in yield of organic acids higher than hydrolysis without adding acid. Overall comparing condition between hydrolysis and oxidation, these results clearly pronounced the oxidation condition was performed on yields of organic acids higher than hydrolysis condition.

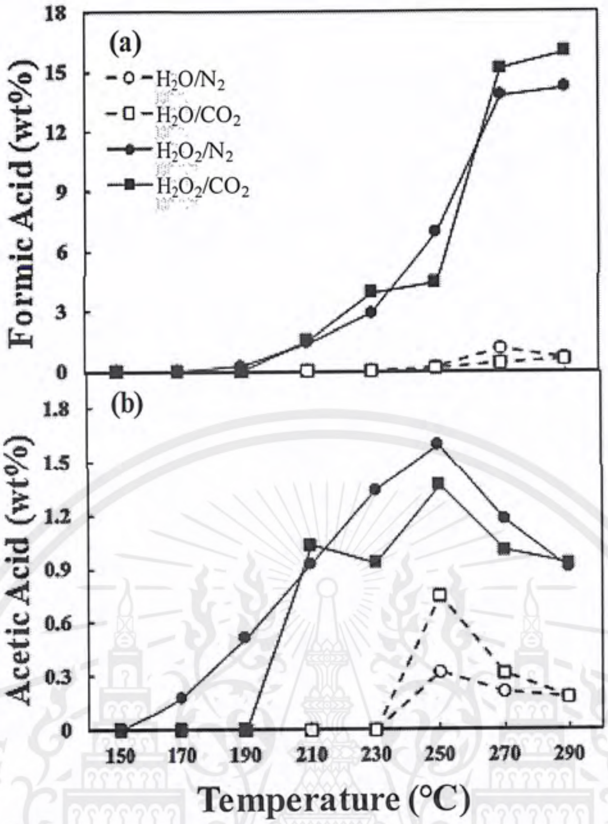


Figure 4.7 Yield of organic acids from MCC as treated by different hydrothermal method

4.4 Mass balance various products from microcrystalline cellulose

As seen in Fig.4.8, it showed the summarize yields of residue, various water-soluble compounds, such as saccharides, dehydrated compound and organic acids, from MCC as treated by hot-compressed water under pressurization of N_2, hot-compressed water under pressurization of CO_2, hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2 and hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2, respectively were different. The unknown was calculated from 100% - total of residue and water-soluble compounds. Moreover, the yield of monosaccharides was observed the highest yields on hot-compressed 0.1wt% H_2O_2 solution under N_2. The yields of cello-oligosaccharides as treated by hydrolysis methods were higher than oxidation methods. Besides, the yields of organic acids as treated by oxidation methods were higher than hydrolysis ones. The unknowns were represented the other unidentified compounds and gaseous products that couldn't identify. It increased when the degree of liquefaction was intensified. Conversely, the water-soluble compound, which could not be identified products, decreases when degree of liquefaction was intensified due to high temperature. It demonstrates that increasing degree of liquefaction provides more the number of the gaseous than lower temperature. The yield of formic acid which obtained from oxidation methods was higher than hydrolysis ones. It demonstrated that formic acid could be expected product where oxidation reaction was dominant.

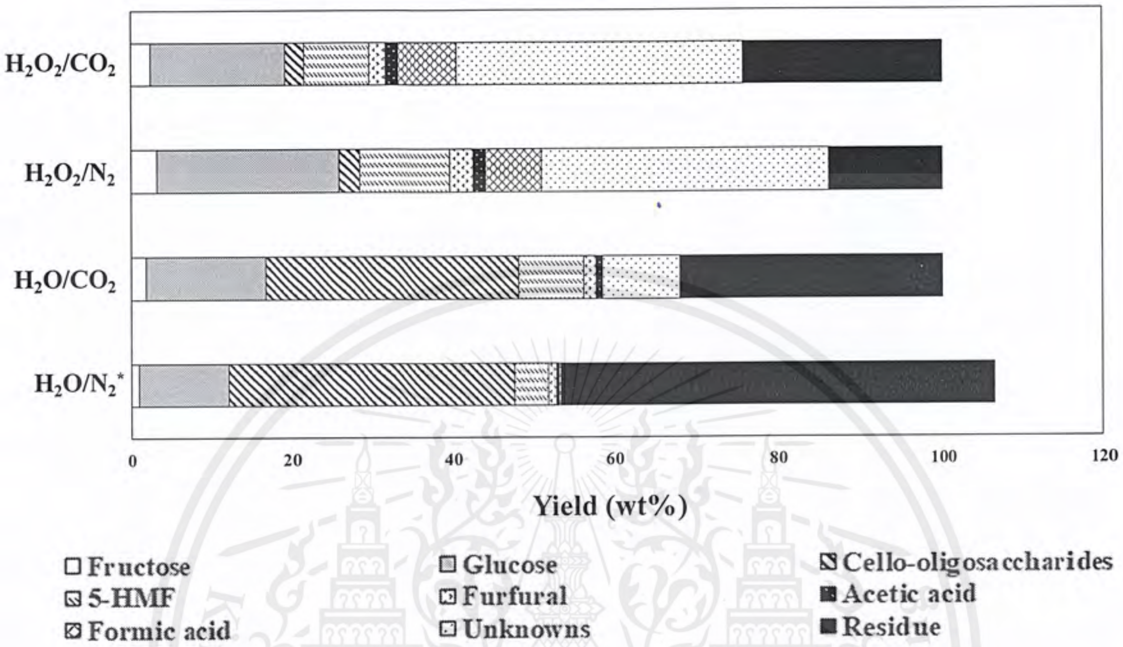


Figure 4.8 Summary of various products produced from MCC as treated by different hydrothermal methods at 250°C/5 MPa. The asterisk (*) marked on the result of hot-compressed under N_2 indicates that total yield is over 100wt%, caused by error from analysis and calculation.

As seen in Fig.4.9, it elucidated the unknown products produced from MCC as treated by four different hydrothermal methods were more pronounced when treatment temperature increased. It demonstrated that the unknown products were temperature-dependence tend. The unknowns include other unidentified compounds and gaseous products where the treatment was intensified by hydrothermal methods. The oxidation methods were more intensify than hydrolysis ones. Therefore, the unknowns could be provided identified intensified liquefaction degree of MCC as treated by hydrothermal methods.

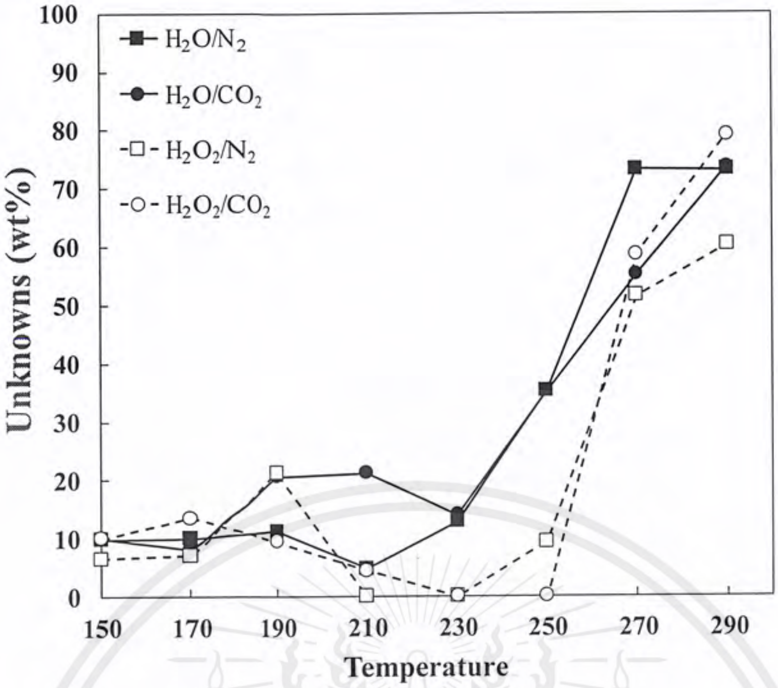


Figure 4.9 Unknowns products produced from MCC as treated by four different hydrothermal methods, the unknowns include other unidentified compounds and gaseous products.

4.5 Decomposition pathway of microcrystalline cellulose under the studied hydrothermal conditions

The consideration of the decomposition pathway, which is discussed above, could be elucidated that the hydrothermal methods may involve in three major reaction including hydrolysis, oxidation, and decomposition mechanism. The MCC was hydrolyzed or oxidized to glucose, oligosaccharides and cello-saccharides which could soluble in liquid. The cello-saccharides were hydrolyzed or oxidized to glucose. The glucose could be isomerized to fructose. When the reaction is prolonged and intensified, glucose is decomposed to 5-hydroxymethylfurfural and furfural, which was previously discuss, respectively. Moreover, if the treatment may involve with oxidation reaction and be more intensified condition, the decomposed compounds will be more decomposed to organic acids, which formic acid is the major production. Conversely the another partway of glucose or fructose were hydrolyzed to levulinic acid and then it could be oxidized to acetic acid. The involved study claims that the hydrolysis condition has oxidation involving, the oxidation will competitive relation with hydrolysis in performed products (Niu et al., 2014). The glucose can oxidize to formic acid, if the conditions are intensified. At high temperature, acetic acid would be oxidized into formic acid, which is the smallest one. If continuously increasing temperature the small molecule can convert to unknown products, which may be gaseous product.

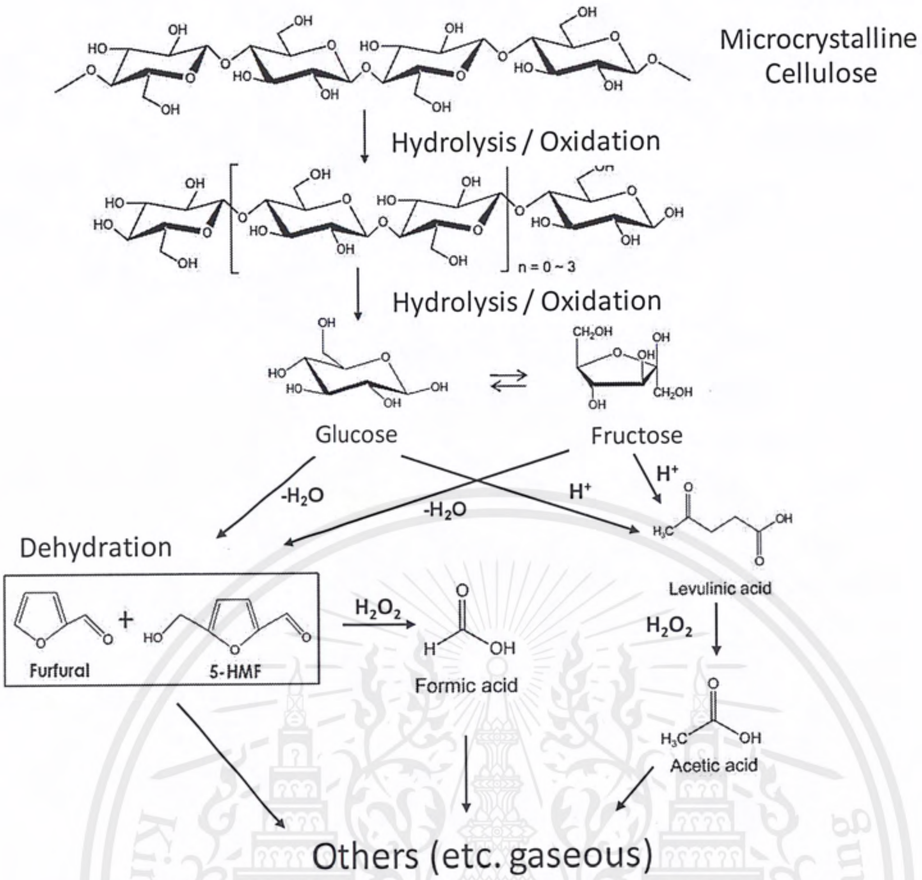


Figure 4.10 Decomposition pathway of MCC under the studied hydrothermal conditions (Lu et al., 2009, modified)

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study investigated liquefaction behavior treatment temperature of microcrystalline cellulose (MCC) as treated by four different hydrothermal methods, i.e. hot-compressed water under N_2 or CO_2, and hot-compressed 0.1wt% H_2O_2 solution under N_2 or CO_2. The experiments were carried out in the treatment temperature range of 150-290°C at 0 min by using 10-ml batch-type reactor. As a result, the appropriated conditions of hot-compressed water under pressurization of N_2 or CO_2 and hot-compressed 0.1wt% H_2O_2 under pressurization N_2 or CO2 were found to be at the same treatment temperature of 250°C, where the highest yield of cello-saccharides could be produced from liquefaction of MCC. Cello-saccharide yields of 61.1wt%, 68.8wt%, 57.1wt% and 42.8wt% were obtained, respectively.

In addition, the highest yields of recoverable monosaccharides of 13.5, 20.6, 28.8, and 21.4wt% were realized at the same temperature (250°C) under such hydrothermal conditions. The highest recoverable monosaccharide was attained by the treatment with hot-compressed 0.1wt% H_2O_2 solution under N_2. It was clearly demonstrated that the degree of MCC liquefaction was more pronounced by oxidation-dominated. Hydroxymethyl groups on glucose units were oxidized to carboxyl groups such the treatment. The obtained acid sites then acted as catalytic active centers for depolymerization of cellulose to glucose via hydrolysis reaction. As a consequence, the higher recovery yield of monosaccharides could be gained in comparison with the treatment with hydrolysis only help from the without oxidizing agent.

As for the production of cello-saccharides, their highest yield could be recovered at the same temperature of 250°C for all hydrothermal methods. In comparison, hot-compressed water treatment under CO_2, where carbonic acid could be formed in water inset at elevated temperature and high pressure, resulted in the highest recoverable yield of cello-saccharides than the other treatments. This could be attributed to the acid catalytic effect of carbonic acid in hydrolysis of MCC. The presence of carbonic acid by using CO_2 instead of N_2 in hot-compressed water treatment, moreover, helped promote hydrolysis of cello-oligosaccharides to monomer and ended up with more glucose proportion by its catalytic effect.

As seen by the lower recoverable yield of cello-saccharides, however, both liquefaction degree of MCC and decomposition of hydrolyzed products to dehydrated compounds and organic acids as well as gaseous products were intensified by the treatment with hot-compressed 0.1wt% H_2O_2 solution under N_2 or CO_2, where oxidation reaction became predominant. The major decomposed compound from glucose was 5-hydroxymethylfurfural, which could be subsequently dehydrated further to furfural. The obtained results clearly showed that the yield of 5-hydroxymethylfurfural was higher than furfural approximately 4 times. Besides, a drastic increase in organic acid production was more realized in the oxidation-dominated hydrothermal treatments. It was approximately 9 times higher compared to the hydrolysis ones. By this, the decomposition pathway starting from glucose to dehydrated compounds, then ending with organic acids or gaseous products could be confirmed.

Based on the obtained results, the decomposition pathway of MCC under the studied hydrothermal conditions could be established. The effects of hydrolysis- and/or oxidation-dominated treatment on the distributions of liquefied products were clearly explained. However, an inferior effect to saccharide yields and liquefaction by using CO_2 instead of N_2 for pressurization of 0.1wt% H_2O_2 solution, formation of peroxy-carbonic acid, a strongly oxidizing agent, was still unclear. It might be probably decomposed or instable under the studied conditions. Through these lines of this comparative study, it would help provide a clear perception on different liquefaction behaviors of MCC under various hydrothermal treatment conditions. Their appropriate applications, in addition, would be revealed by a variety of the liquefied products obtained.

5.2 Recommendation

5.2.1 An instrument for measured gas pressure should be installed to the batch reactor. In order to allow us to record the pressure after done the reaction. It would help to monitor and quantify gaseous products from the hydrothermal treatments of, MCC

5.2.2 The pH value of the obtained hydrolysates should be measured after the reaction to confirm and indicate the amount of organic acids, produced from the which would be mainly oxidation reaction. Analysis of more types of organic acids in addition to acetic and formic acids should be also performed to get more precise picture on decomposition pathway under oxidation-dominated conditions.

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APPENDIX

APPENDIX A

PREPARATIONS OF CHEMICALS AND EXAMPLES OF CALCULATIONS

1. Preparation of 0.1wt% hydrogen peroxide solution

Measure 0.25 ml of 30wt% hydrogen peroxide solution. Slightly pour it into 100-ml volumetric flask filled with a few of deionized water. Keep its temperature low while mixing by immersing the flask into an iced-water bath. Finally, add deionized water to bring the final volume to 100 ml

2. Preparation of 1 mg/ml sugar standard

Weight 0.006 g of sugar and dissolve in 6 ml of deionized water.

3.Preparation of 1 mg/ml dehydrated compound and organic acids standard

Weight 0.01 g of standard and dissolve in 10 ml of deionized water.

4.Calculated of chemical compositions in hydrolysates

Example 1 Calculation of the amount of glucose in hydrolysates obtained from hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2.

Peak area obtained from HPLC chromatogram was 300,183. From the calibration curve between peak area and concentration of glucose standard solution, as depicted in figure B.1, the relation was $Y = 5.2345 (X/10^{-6})$

Where Y = concentration of glucose standard solution (mg/ml)

X = peak area obtained HPLC chromatogram

Thus, $Y = 5.2345 \times (300{,}183/10^{-6})$

$Y = 1.5713$ mg/ml

According to the experiment procedure, the total liquid volume brought up to 6 ml for HPLC analysis

Thus, Amount of glucose = 1.5713 x 6

= 0.0094 g

APPENDIX B

RAW DATA

1.Calibration curves for calculations of the reducing sugar concentration and by-product concentration analyzed by HPLC

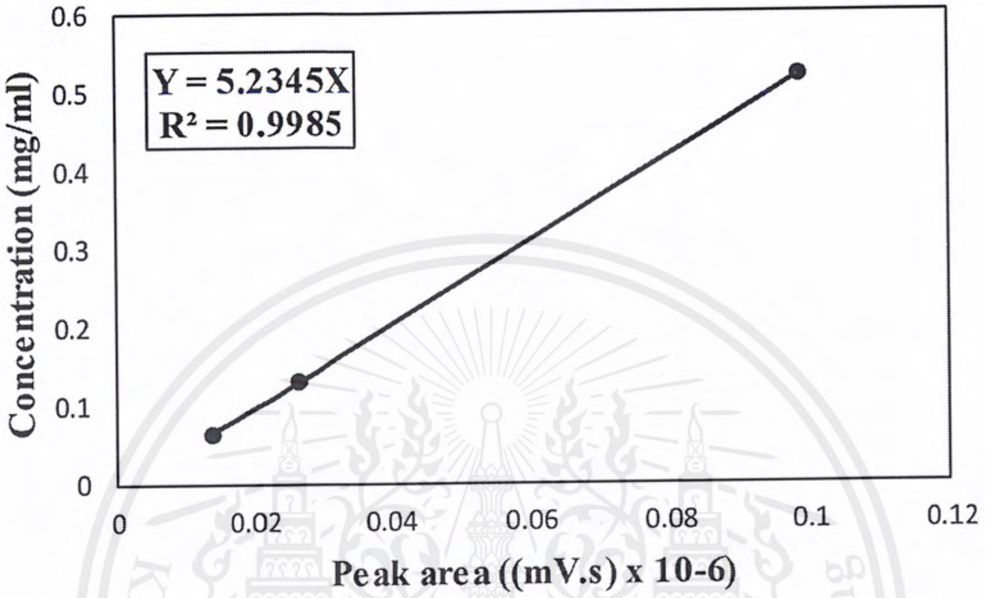

Figure B.1 Calibration curve of HPLC chromatogram peak area and concentration of glucose standard solutions

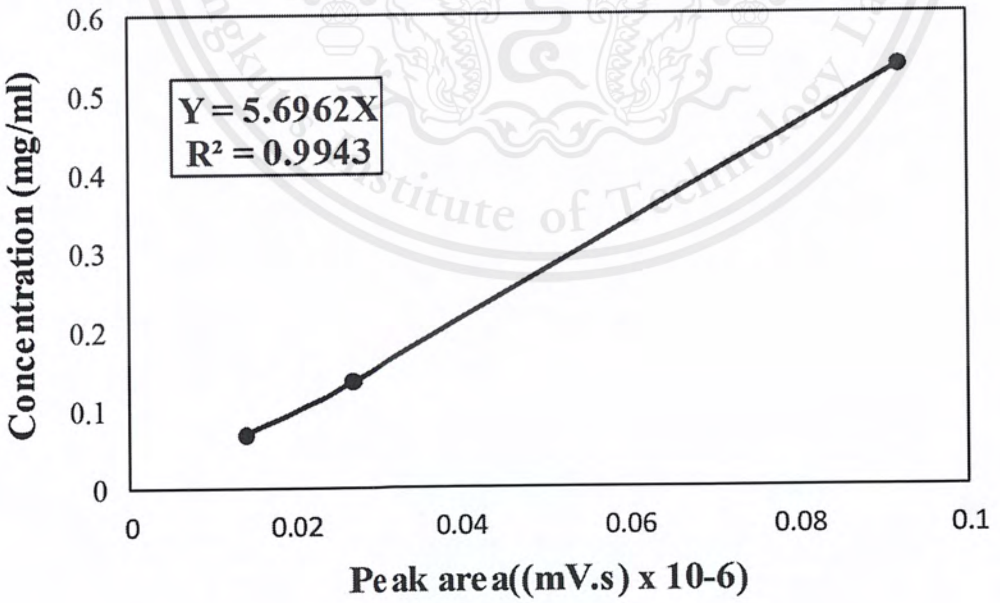

Figure B.2 Calibration curve of HPLC chromatogram peak area and concentration of xylose standard solutions

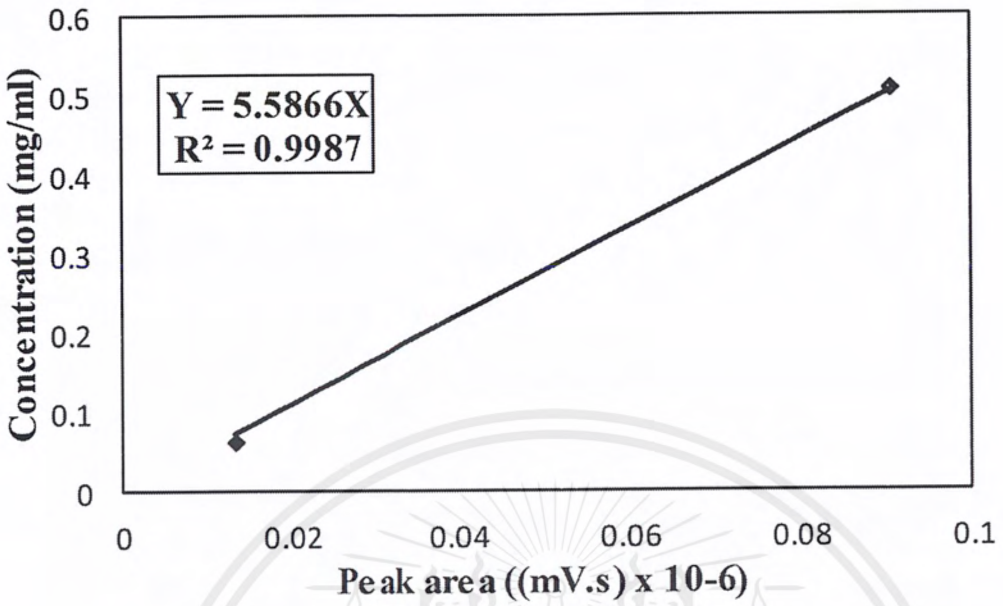

Figure B.3 Calibration curve of HPLC chromatogram peak area and concentration of arabinose standard solutions

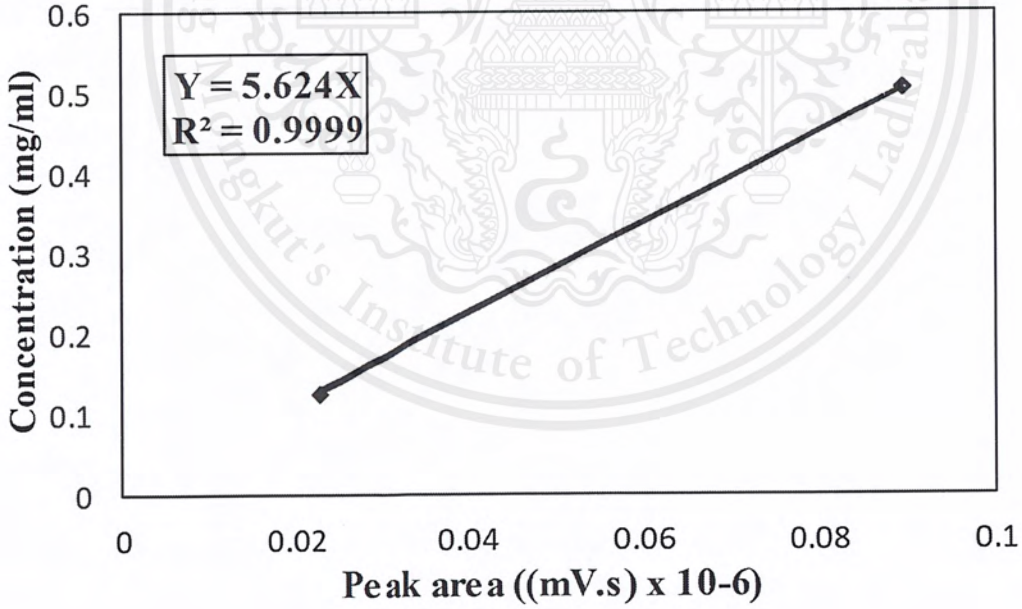

Figure B.4 Calibration curve of HPLC chromatogram peak area and concentration of fructose standard solutions

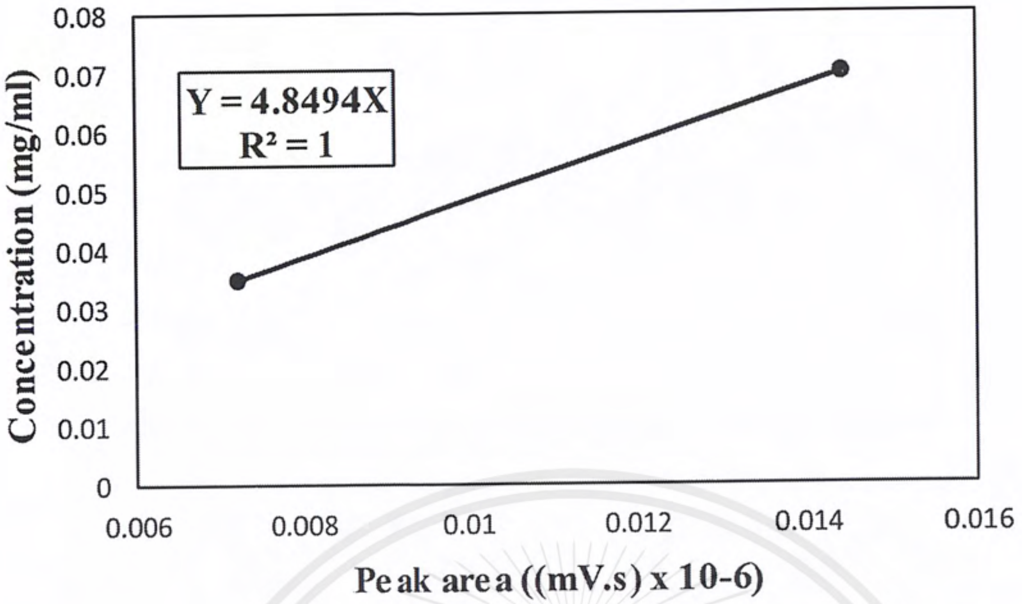

Figure B.5 Calibration curve of HPLC chromatogram peak area and concentration of furfural standard solutions

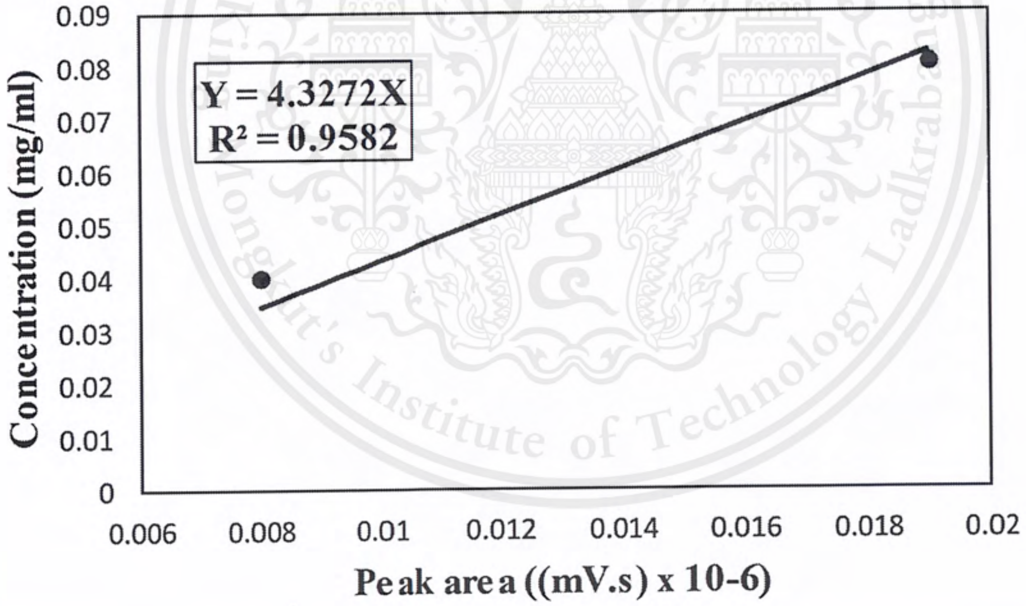

Figure B.6 Calibration curve of HPLC chromatogram peak area and concentration of 5-hydroxymethylfurfural standard solutions

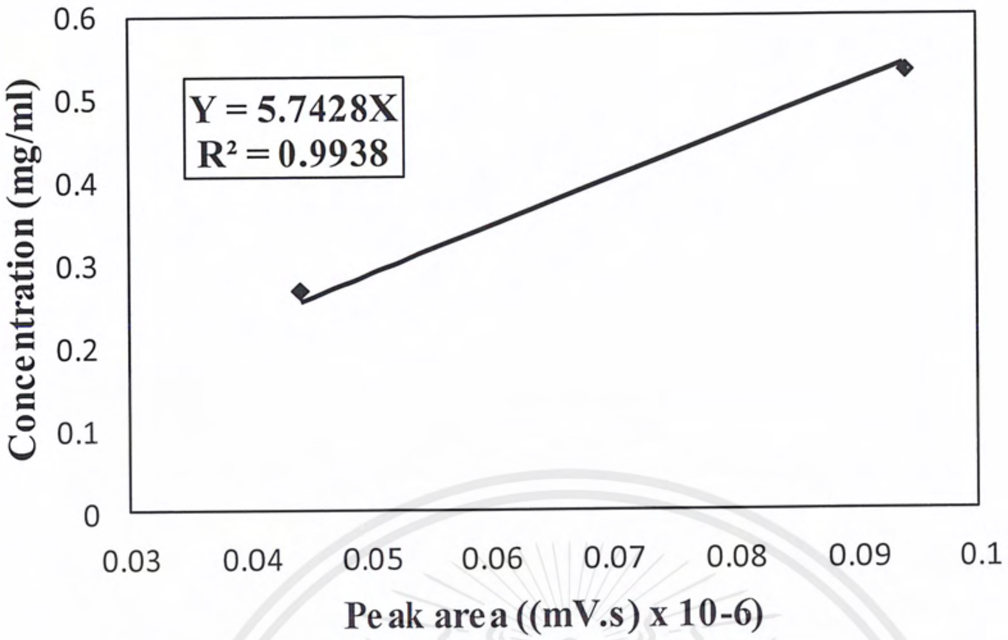

Figure B.7 Calibration curve of HPLC chromatogram peak area and concentration of acetic acid standard solutions

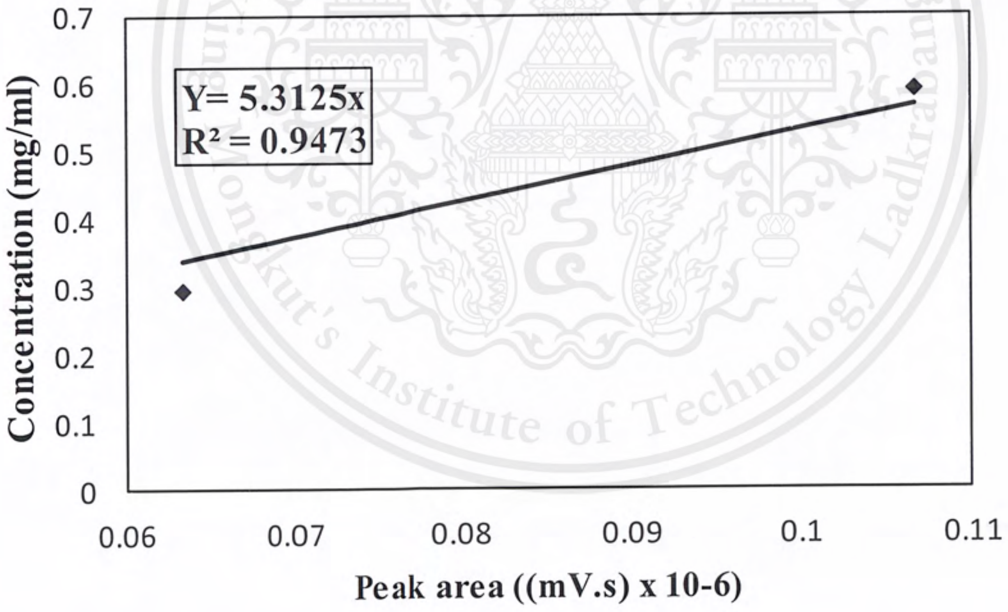

Figure B.8 Calibration curve of HPLC chromatogram peak area and concentration of formic acid standard solutions

2.Peak area of HPLC chromatogram

Table B.1 HPLC chromatogram peak areas of standard solutions and theirs corresponding concentrations

Standard	Concentration (mg/ml)	Peak area							
		Glucose	Fructose	Xylose	Arabinose	Furfural	5-HMF	Acetic acid	Formic acid
Glucose	0.5200	98,614	-	-	-	-	-	-	-
	0.0650	13,965	-	-	-	-	-	-	-
Fructose	0.5050	-	89,664	-	-	-	-	-	-
	0.1263	-	22,958	-	-	-	-	-	-
Xylose	0.5333	-	-	92,139	-	-	-	-	-
	0.0667	-	-	14,149	-	-	-	-	-
Arabinose	0.5083	-	-	-	90,696	-	-	-	-
	0.0635	-	-	-	13,379	-	-	-	-
Furfural	0.0700	-	-	-	-	14,427	-	-	-
	0.0350	-	-	-	-	7,233	-	-	-
5-HMF	0.0800	-	-	-	-	-	19,007	-	-
	0.0400	-	-	-	-	-	8,012	-	-
Acetic acid	0.5333	-	-	-	-	-	-	93,970	-
	0.2667	-	-	-	-	-	-	44,091	-
Formic acid	0.5917	-	-	-	-	-	-	-	106,756
	0.2958	-	-	-	-	-	-	-	63,455

Table B.2 Peak area of glucose and cello-saccharides that obtained from MCC as treated by different hydrothermal methods

Temperature (°C)	hot-compressed water under pressurization of N_2		hot-compressed water under pressurization of CO_2		hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2		hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2	
	Glucose	Cello-saccharides	Glucose	Cello-saccharides	Glucose	Cello-saccharides	Glucose	Cello-saccharides
150	0	0	0	0	0	0	16,239	43
170	0	0	0	0	898	0	11,062	232
190	0	0	7,545	0	12,403	0	10,454	244
210	0	0	12,084	12,115	30,831	0	42,249	2,652
230	22,650	17,399	49,753	17,499	109,516	2,747	79,632	2,832
250	404,770	70,164	759,311	104,779	411,290	8,753	300,183	6,550
270	50,674	16,092	145,409	23,209	28,716	555	11,342	0
290	3,897	0	3,181	0	0	179	19,258	291

Table B.3 Peak area of fructose that obtained from MCC as treated by different hydrothermal methods

Temperature (°C)	hot-compressed water under pressurization of N_2	hot-compressed water under pressurization of CO_2	hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2	hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2
	Fructose	Fructose	Fructose	Fructose
150	0	0	0	0
170	0	0	0	0
190	0	14,578	14,019	8,303
210	0	43,887	24,665	26,609
230	26,212	85,405	31,610	26,612
250	30,898	51,346	54,933	41,021
270	35,584	37,983	9,333	0
290	22,444	37,983	0	0

Table B.4 Peak area of furfural and 5-HMF that obtained from MCC as treated by different hydrothermal methods

Temperature (°C)	hot-compressed water under pressurization of N_2		hot-compressed water under pressurization of CO_2		hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2		hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2	
	Furfural	5-HMF	Furfural	5-HMF	Furfural	5-HMF	Furfural	5-HMF
150	83,893	7,284	29,141	33,426	0	0	0	0
170	56,381	27,986	221,047	293,380	0	509	0	0
190	137,591	108,314	615,379	342,488	0	0	0	0
210	668,922	920,349	1,768,346	2,238,947	0	2,047	0	3,060
230	5,653,198	7,320,986	9,158,226	15,028,403	4,163	20,375	0	10,807
250	39,582,851	117,020,630	33,745,339	209,139,391	50,900	222,717	34,524	159,664
270	146,348,975	374,327,284	75,851,085	397,404,167	81,335	334,987	65,595	287,841
290	110,856,517	303,492,744	95,510,744	283,077,103	65,615	129,819	91,573	286,681

Table B.5 Peak area of formic acid and acetic acid that obtained from MCC as treated by different hydrothermal methods

Temperature (°C)	hot-compressed water under pressurization of N_2		hot-compressed water under pressurization of CO_2		hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2		hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2	
	Formic acid	Acetic acid	Formic acid	Acetic acid	Formic acid	Acetic acid	Formic acid	Acetic acid
150	0	0	0	0	0	0	0	0
170	0	0	0	0	0	2602	0	0
190	0	0	0	0	4,198	7556	0	0
210	0	0	0	0	22,346	13,591	24,736	15,251
230	0	0	0	0	45,580	19,608	61,880	13,579
250	18,571	49,480	29,527	112,064	111,584	23,688	69,890	20,050
270	107,960	32,923	81,629	45,569	217,767	17,163	241,717	14,812
290	148,450	27,965	124,427	27,317	224,537	13,205	259,341	13,939

3.Among of yield of recoverable saccharides, dehydrated compounds and organic acids from liquefaction of microcrystalline cellulose as treated by different hydrothermal methods

Table B.6 Yield of recoverable monosaccharides and cello-saccharides from MCC as treated by different hydrothermal methods

Temperature (°C)	hot-compressed water under pressurization of N_2 (%)		hot-compressed water under pressurization of CO_2 (%)		hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2 (%)		hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2 (%)	
	recoverable mono-saccharides	Cello-saccharides	recoverable mono-saccharides	Cello-saccharides	recoverable mono-saccharides	Cello-saccharides	recoverable mono-saccharides	Cello-saccharides
150	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.14
170	0.00	0.00	0.00	0.00	0.05	0.00	0.67	0.74
190	0.00	0.00	0.62	10.69	1.70	0.00	1.20	0.80
210	0.00	4.17	1.75	22.65	3.57	0.00	4.36	8.64
230	1.66	36.54	3.18	28.74	8.94	9.05	6.76	9.35
250	13.52	47.60	20.61	48.17	28.79	28.34	21.37	21.50
270	2.69	22.17	5.02	27.52	2.41	1.83	0.70	0.00
290	0.68	0.00	1.09	23.28	0.00	0.59	1.17	0.93

Table B.7 Yield of furfural and 5-HMF from MCC as treated by different hydrothermal methods

Temperature (°C)	hot-compressed water under pressurization of N_2 (%)		hot-compressed water under pressurization of CO_2 (%)		hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2 (%)		hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2 (%)	
	Furfural	5-HMF	Furfural	5-HMF	Furfural	5-HMF	Furfural	5-HMF
150	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00
170	0.00	0.00	0.01	0.01	0.00	0.03	0.00	0.00
190	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00
210	0.02	0.03	0.08	0.08	0.00	0.11	0.00	0.16
230	0.15	0.29	0.43	0.61	0.24	1.05	0.00	0.56
250	0.96	4.27	1.57	8.04	2.89	11.27	1.99	8.19
270	3.54	13.57	3.64	15.74	4.70	17.26	3.75	14.68
290	5.08	11.47	4.49	10.97	3.78	6.67	5.14	14.37

Table B.8 Yield of formic acid and acetic acid from MCC as treated by different hydrothermal methods

Temperature (°C)	hot-compressed water under pressurization of N_2 (%)		hot-compressed water under pressurization of CO_2 (%)		hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2 (%)		hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2 (%)	
	Formic acid	Acetic acid	Formic acid	Acetic acid	Formic acid	Acetic acid	Formic acid	Acetic acid
150	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
170	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.00
190	0.00	0.00	0.00	0.00	0.26	0.51	0.00	0.00
210	0.00	0.00	0.00	0.00	1.41	0.93	1.55	1.03
230	0.00	0.00	0.00	0.00	2.88	1.34	3.92	0.93
250	0.19	0.32	0.13	0.74	6.93	1.59	4.40	1.37
270	1.12	0.21	0.38	0.31	13.77	1.17	15.14	1.00
290	0.66	0.18	0.56	0.18	14.17	0.90	15.96	0.93

4. Residue of microcrystalline cellulose

Table B.9 Residue of MCC as treated by different hydrothermal methods

Temperature (°C)	Residue (%)			
	hot-compressed water under pressurization of N_2 (%)	hot-compressed water under pressurization of CO_2 (%)	hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2 (%)	hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2 (%)
150	89.88	93.49	90.12	89.43
170	86.50	92.90	91.68	88.29
190	90.60	60.35	78.66	86.42
210	91.40	77.21	76.44	82.55
230	80.95	74.80	71.43	73.96
250	53.04	32.04	13.84	24.31
270	1.83	1.00	6.15	2.36
290	3.63	0.39	0.40	1.35

5.Temperature profile

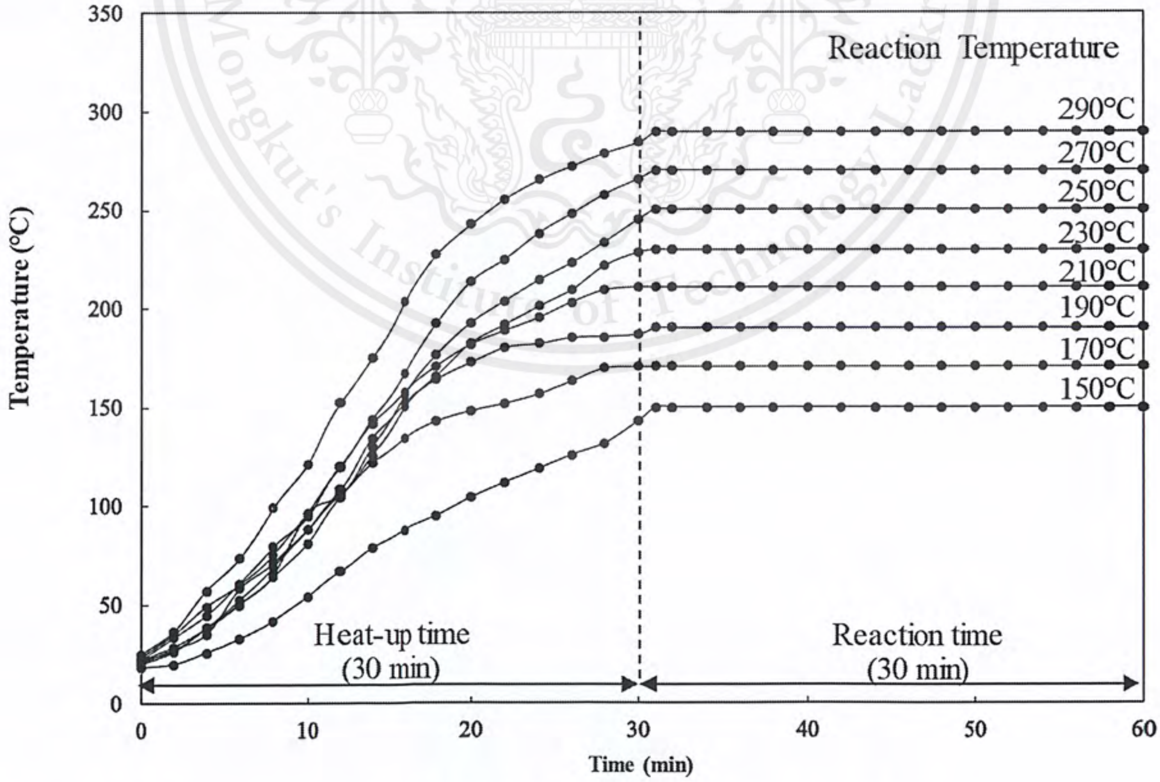

Figure B.9 Temperature profiles of the batch-type reaction in this study

6.Summary of various products produced from MCC as treated by different hydrothermal methods

Table B.10 Summary of various products produced from MCC as treated by hot-compressed water under pressurization of N_2

Temperatures (°C)	Residue (wt%)	Water-Soluble Compound (wt%)							Total	Unknown
		Saccharides			Dehydrated Compounds		Oraganic Acids			
		Fructose	Glucose	Cello-oligosaccharides	5-HMF	Fufural	Acetic Acid	Formic Acid		
150	89.88	0.00	0.00	0.00	0.00	0.09	0.00	0.00	89.97	10.03
170	86.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	86.50	13.50
190	90.60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	90.61	9.39
210	91.40	0.00	0.00	4.17	0.03	0.02	0.00	0.00	95.62	4.38
230	80.95	0.81	0.68	35.05	0.29	0.15	0.00	0.00	117.93	0.00
250	53.04	0.89	11.29	35.42	4.27	0.96	0.32	0.19	106.38	0.00
270	1.83	1.01	1.41	19.75	13.57	3.54	0.21	0.11	41.44	58.56
290	3.63	0.53	0.08	-0.61	11.47	5.08	0.18	0.66	21.01	78.99

Table B.11 Summary of various products produced from MCC as treated by hot-compressed water under pressurization of CO_2

Temperatures (°C)	Residue (wt%)	Water-Soluble Compound (wt%)							Total	Unknown
		Saccharides			Dehydrated Compounds		Oraganic Acids			
		Fructose	Glucose	Cello-oligosaccharides	5-HMF	Fufural	Acetic Acid	Formic Acid		
150	93.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	93.49	6.51
170	92.90	0.00	0.00	0.00	0.01	0.01	0.00	0.00	92.92	7.08
190	68.06	0.33	0.17	10.19	0.01	0.02	0.00	0.00	78.78	21.22
210	78.69	0.95	0.46	21.23	0.08	0.08	0.00	0.00	101.50	0.00
230	74.80	1.03	1.55	26.17	0.61	0.43	0.00	0.00	104.59	0.00
250	32.04	1.83	14.86	31.48	8.04	1.57	0.74	0.13	90.70	9.30
270	1.00	1.13	2.93	23.46	15.74	3.64	0.31	0.38	48.59	51.41
290	0.39	0.82	0.06	22.40	10.97	4.49	0.18	0.56	39.87	60.13

Table B.12 Summary of various products produced from MCC as treated by hot-compressed 0.1wt% H_2O_2 solution under pressurization of N_2

Temperatures (°C)	Residue (wt%)	Water-Soluble Compound (wt%)							Total	Unknown
		Hydroly			Dehydrated Compounds		Oraganic Acids			
		Fructose	Glucose	Cello-oligosaccharides	5-HMF	Fufural	Acetic Acid	Formic Acid		
150	90.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	90.12	9.88
170	91.68	0.00	0.05	-0.05	0.03	0.00	0.17	0.00	91.88	8.12
190	78.66	0.84	0.69	-1.53	0.00	0.00	0.51	0.26	79.44	20.56
210	76.44	1.48	1.73	-3.21	0.11	0.00	0.93	1.41	78.88	21.12
230	71.43	1.90	6.14	1.01	1.05	0.24	1.34	2.88	86.00	14.00
250	13.84	3.25	22.66	2.43	11.27	2.89	1.59	6.93	64.86	35.14
270	6.15	0.56	1.61	-0.34	17.26	4.70	1.17	13.77	44.88	55.12
290	0.40	0.00	0.00	0.59	6.67	3.78	0.90	14.17	26.51	73.49

Table B.13 Summary of various products produced from MCC as treated hot-compressed 0.1wt% H_2O_2 solution under pressurization of CO_2

Temperatures (°C)	Residue (wt%)	Water-Soluble Compound (wt%)							Total	Unknown
		Saccharides			Dehydrated Compounds		Oraganic Acids			
		Fructose	Glucose	Cello-oligosaccharides	5-HMF	Fufural	Acetic Acid	Formic Acid		
150	89.43	0.00	0.90	-0.76	0.00	0.00	0.00	0.65	90.23	9.77
170	88.29	0.00	0.60	0.14	0.00	0.00	0.00	0.94	89.97	10.03
190	86.42	0.50	0.58	-0.28	0.00	0.00	0.00	1.53	88.74	11.26
210	82.55	1.58	2.34	4.71	0.16	0.00	1.03	2.88	95.25	4.75
230	73.96	1.61	4.47	3.27	0.56	0.00	0.93	2.41	87.20	12.80
250	24.31	2.46	16.77	2.27	8.19	1.99	1.37	7.39	64.74	35.26
270	2.36	0.00	0.63	-0.63	14.68	3.75	1.00	5.11	26.91	73.09
290	1.35	0.00	1.05	-0.12	14.37	5.14	0.93	4.24	26.97	73.03

BIOGRAHPY

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