Comparative Study on Liquefaction Behaviors of Xylan as treated by Different Hydrothermal Methods

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การศึกษาเชิงเปรียบเทียบพฤติกรรมการกลายเป็นผลิตภัณฑ์ของเหลวของไซลานด้วยวิธีการไฮโดรเทอร์มัลที่ต่างกัน

รวิภาส ฉิมพาลี

ปริญญานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิศวกรรมศาสตรบัณฑิต
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Title	Comparative Study on Liquefaction Behaviors of Xylan as treated by Different Hydrothermal Methods
By	Mr.Ravipas Chimpalee
Field of Study	Petrochemical Engineering
Advisor	Dr.Natthanon Phaiboonsilpa

Accepted by the Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang in Partial Fulfillment of the Requirements for the Degree of Bachelor of Engineering (Petrochemical Engineering).

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Abstract

The aim of this research is to investigate liquefaction behaviors of xylan isolated from corn core. A comparative study on six hydrothermal methods, i.e. hot-compressed water under pressurization of nitrogen or carbon dioxide, hot-compressed 0.01 and 0.1wt% hydrogen peroxide solutions under pressurization of nitrogen or carbon dioxide were performed. The experiments were conducted over the treatment temperature range of 110-250°C for 0 min in 10-ml batch-type reactor. Xylan was found to be readily liquefied in to hot-compressed water and hot-compressed hydrogen peroxide solutions. As hydrolyzed products, not only xylose and xylo-oligosaccharides, but also arabinose, glucose and acetic acid were obtained from other hemicellulosic components remaining in xylan structure used in this study. Decomposed compounds such as furans and organic acids were also found. The treatment temperature, at which the highest yield of xylose was attained, for all hydrothermal methods were the same at 210°C except for the method of 0.1wt% hydrogen peroxide solution under pressurization of carbon dioxide, of which the such temperature was at 190°C. The highest hydrated xylose yield of 61.63wt% were found in the hydrothermal method using 0.01wt% hydrogen peroxide under pressurization of nitrogen. Hot-compressed water treatment under carbon dioxide produced more xylose in comparison with the treatment under nitrogen due to the acid-catalytic effect of carbonic acid formed during the carbon dioxide treatment at elevated temperature. As for the treatment in the presence of hydrogen peroxide, in most cases, a higher yield of xylose could be realized at the lower temperature range of 150-210°C than those of the hot-compressed water treatments. In contrast, decomposition of xylose was found to be intensified as indicated by an increase in formations of furans and formic acid as well as unknowns, leading to a lower recoverable saccharide yield. Such decomposition was more pronounced when carbon dioxide was used as the reaction atmosphere, which peroxy carbonic acid, a strong oxidizing agent, occurred. Under oxidation-dominated conditions, moreover, arabinose and acetic acid were remarkably founded to be highly liberated from arabinose and acetyl residues linked to the xylan backbone. Through these lines of this comparative study, it would help provide a clear perception on different liquefaction behaviors of xylan under different hydrothermal treatment conditions. Their appropriate applications would be consequently revealed by considering a variety of liquefied products obtained under different hydrothermal conditions.

Keywords: decomposition, dehydration, hydrogen peroxide, hydrothermal liquefaction, xylan, xylo-saccharide

เรื่อง การศึกษาเชิงเปรียบเทียบพฤติกรรมการกลายเป็นผลิตภัณฑ์ของเหลวของไซลาน ด้วยวิธีการไฮโดรเทอร์มัลที่ต่างกัน
โดย นายรวิภาส ฉิมพาลี
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บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาพฤติกรรมการกลายเป็นผลิตภัณฑ์ของเหลวของไซลานที่สกัดจากซังข้าวโพดด้วยกระบวนการไฮโดรเทอร์มัลที่ต่างกัน 6 วิธี ได้แก่ น้ำร้อนอัดความดันภายใต้บรรยากาศไนโตรเจน หรือ คาร์บอนไดออกไซด์ สารละลายไฮโดรเจนเพอร์ออกไซด์ความเข้มข้นร้อยละ 0.01 และ 0.1 โดยมวล อัดวามดันภายใต้บรรยากาศไนโตรเจนหรือคาร์บอนไดออกไซด์ ทำการทดลองที่อุณหภูมิ 110-250 องศาเซลเซียส และเวลา 0 นาที โดยใช้เครื่องปฏิกรณ์แบบกะปริมาตร 10 มิลลิลิตร จากผลการทดลองพบว่าไซลานถูกทำให้กลายเป็นผลิตภัณฑ์ของเหลวภายใต้ภาวะน้ำร้อนอัดความดัน ผลิตภัณฑ์ที่ได้จากการไฮโดรไลซิสไม่ได้มีเพียงน้ำตาลไซโลสและไซโลโอลิโกแซ็กคาร์ไรด์ แต่ยังมีอะราบิโนส กลูโคส และกรดอะซิติกจากองค์ประกอบที่เป็นโซ่กิ่งของเฮมิเซลลูโลสซึ่งหลงเหลืออยู่ในโครงสร้างของไซลานที่ใช้ในโครงงานนี้ นอกจากนี้ยังพบสารประกอบที่ได้จากการสลายตัว เช่น ฟูแรน และกรดอินทรีย์ อุณหภูมิที่ทำให้เกิดผลได้ร้อยละของน้ำตาลไซโลสสูงสุดสำหรับวิธีการไฮโดรเทอร์มัลทั้งหมดพบว่ามีค่าเท่ากันคือ 210 องศาเซลเซียส ยกเว้นวิธีการที่ใช้สารละลายไฮโดรเจนเพอร์ออกไซด์ความเข้มข้นร้อยละ 0.1 โดยมวลอัดก๊าซคาร์บอนไดออกไซด์ซึ่งมีค่าเท่ากับ 190 องศาเซลเซียส ร้อยละผลได้โดยมวลสูงสุดของน้ำตาลไซโลส 61.63 ได้จากปฏิริยาไฮโดรเทอร์มัลที่ใช้สารละลายไฮโดรเจนเพอร์ออกไซด์ความเข้มข้นร้อยละ 0.01 โดยมวลอัดก๊าซไนโตรเจน จากการเปรียบเทียบวิธีการที่ใช้น้ำร้อนอัดก๊าซคาร์บอนไดออกไซด์สามารถผลิตไซโลสได้มากกว่าวิธีการที่ใช้น้ำร้อนอัดก๊าซไนโตรเจน เนื่องจากผลของตัวเร่งปฏิกิริยาคือกรดคาร์บอนิกที่เกิดในระบบ สำหรับวิธีการที่ใช้สารละลายไฮโดรเจนเพอร์ออกไซด์ พบว่าร้อยละผลได้ของไซโลสมีค่าเพิ่มขึ้นในช่วงอุณหภูมิที่ต่ำลงตั้งแต่ 150-210 องศาเซลเซียส เปรียบเทียบกับวิธีการที่ใช้น้ำร้อนอัดความดัน ในทางกลับกันภายใต้ภาวะดังกล่าวมีการพบว่าน้ำตาลไซโลสมีการสลายตัวมากขึ้นโดยบ่งชี้ได้จากการเกิดขึ้นของฟูแรน กรดฟอร์มิก และสารประกอบอื่นๆ ซึ่งส่งผลให้ร้อยละผลได้คืนมาของน้ำตาลโดยรวมลดต่ำลง การสลายตัวจะถูกพบมากขึ้นเมื่อใช้ก๊าซคาร์บอนไดออกไซด์เป็นบรรยากาศของการทำปฏิริยาซึ่งก่อให้เกิดกรดเพอร์ออกซีคาร์บอนิกที่เป็นสารออกซิไดซ์ที่รุนแรง นอกจากนี้ยังพบว่าอะราบิโนสและหมู่อะซิติกที่เป็นโซ่กิ่งเกาะอยู่กับโครงสร้างของไซลานถูกจะผลิตออกมาได้มากจากภาวะการทดลองที่มีปฏิกิริยาออกซิเดชันรุนแรง การศึกษาเชิงเปรียบเทียบนี้ช่วยอธิบายพฤติกรรมการกลายเป็นผลิตภัณฑ์ของเหลวของไซลาน

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Ravipas Chimpalee

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CHAPTER I

INTRODUCTION

1.1 Background

In recent years, global energy consumption, mainly from fossil fuels, is increasing due to economic and population growths. Fluctuations of fuel price, energy security and uncertainty of fossil fuels are issue to be concerned. Excessive consumption of fossil fuels, such as petroleum, natural gas and coal, has been claimed to be one of the reasons to emit large amount of carbon dioxide, leading to a blanket traps heat in earth's atmosphere, so-called greenhouse effect. Due to the energy crisis and environmental problems, the world's attention has greatly turned to renewable energy for decades. Renewable energy is used on purpose to reinforce energy security and reduce energy consumption from fossil fuels.

Renewable energy refers to energy from natural resources such as solar energy, hydro energy, wind energy, geothermal energy and biomass energy. Among those renewable energy resources, biomass is considered as a carbon-neutral source via the plant photosynthesis which reduces carbon dioxide accumulation in atmosphere. In other words, biomass is organic substances obtained from plants and animal such as agricultural residues and manure. Lignocelluloses are the most abundant biomass available on earth. They have a high potential to be used as a resource for biochemical and biofuel production. Cellulose, hemicelluloses and lignin are the major components of plant cell wall, existing in lignocelluloses.

Xylan and glucomannan are the main structures of hemicelluloses. Their compositions differently varied by plant species. Chemical composition of hemicellulose agricultural residues, which are mainly obtained from monocotyledons, is xylan. The chemical structure of the major hemicellulose in monocotyledonous agricultural residues is the polysaccharides with xylan backbone linked-a number of xylose molecules by β-(1→4)-glycosidic bonds and branched with its moeities such as arabinose, acetic acid, glucose and mannose. In view of its chemical structure, xylan hemicellulose, therefore, can be considered as a substrate to produce xylo- and mono-saccharides as treated by an appropriate decomposition technique (Phaiboonsilapa et al., 2011).

Hydrothermal treatment is widely used for liquefaction of lignocelluloses. This technique is efficient for convert hemicellulosic and cellulosic portions to reducing sugars. Hydrolysis reaction plays an important role in liquefaction process. Principle of hydrolysis is a cleavage of chemical bonds by the addition of water, then OH^- and H^+ ion of water molecule will attach to the hydrolyzed chemical bonds. Liquefaction techniques can be classified into catalytic and non-catalytic hydrolysis. Catalytic hydrolysis is using acid or alkaline pretreatment to increase yield of reducing sugars but its acidity or basicity cause a poison and corrosion in the system. Non-catalytic hydrolysis, such as super/subcritical water, steam explosion and hot-compressed water, become interesting techniques in present because yield and recovery of saccharides are high without drawbacks of acid or base catalyst.

In the previous study by our research group member, study hydrolysis of sugarcane bagasse as treated 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 acidative condition, higher yields of mono-saccharides 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 pathway during liquefaction of lignocelluloses were not clarified yet due to coexistence of various saccharides and other compounds in hydrolysate from liquefaction of these cell wall components. Moreover, the recoverable yield of xylo-saccharides was relatively low. It was reported that only 33.46wt% of recovery yield from xylan were obtained by hot-compressed 1wt% H_2O_2 solution under pressurization of CO_2. This might be attributed to an excessive concentration of H_2O_2 solution, which promoted too much oxidation and ended up with organic acids rather than saccharides.

In this present study, therefore, xylan was used as a reagent to study liquefaction behaviors as treated by different hydrothermal methods. The interference of cellulose and lignin could then be avoided. The decomposition pathway of xylan hemicellulose was expected to be clarified. In addition, concentration of H_2O_2 solution was varied to explore the appropriate conditions for higher recovery yield of xylo-saccharides from xylan. The results from this study would provide more insights into the understanding in chemical conversion of lignocelluloses and their utilizations for bio-fuels and bio-chemicals.

1.2 Objectives

1.2.1 To study liquefaction behaviors of xylan as treated by six different hydrothermal methods

1.2.2 To obtain appropriate conditions of those hydrothermal methods for liquefaction of xylan with higher saccharides yields

1.3 Scopes of the Research

1.3.1 To study chemical composition of xylan isolated from corn cob

1.3.2 To study liquefaction behaviors of xylan 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 0.01 and 0.1wt% H_2O_2 solutions under pressurization of N_2
- Hot-compressed 0.01 and 0.1wt% H_2O_2 solutions under pressurization of CO_2

1.3.3 To explore effect of hydrogen peroxide concentrations, i.e.0.01, 0.1wt%, and temperatures, i.e.,110-250°C, in liquefaction of xylan as treated by six different hydrothermal methods

1.3.4 To quantitatively and qualitatively analyze various products from xylan isolated from corn cob

1.3.5 To investigate decomposition pathway of xylan as treated by six different hydrothermal methods

1.4 Benefits of this Study

1.4.1 Appropriate conditions for each hydrothermal method in terms of the highest yield of xylo-saccharides or xylose

1.4.2 A novel hydrothermal technique to chemically covert xylan to xylo-saccharides by hot-compressed H_2O_2 solution under pressurization of N_2 and CO_2

1.4.3 Mechanism of xylan decomposition under the oxidation reaction studied

1.4.4 Application of the obtained appropriate hydrothermal treatment conditions to chemically convert xylan in lignocellulosic materials for the production of saccharides

CHAPTER II

THEORY AND RITERATURE REVIEWS

In this chapter, chemical compositions of lignocellulose were described, which its component are cellulose, hemicelluloses and lignin. In addition, chemical conversion technique, solubility equilibria of carbon dioxide, oxidation reaction of saccharides are explained. Moreover, some theory and related literature are review as an approach to this research.

2.1 Lignocelluloses

Lignocelluloses are organic compound which contain in cell wall of plants, which cellulose, hemicelluloses and lignin are the main chemical components. In general, proportion of chemical components in lignocellulose are 40% cellulose, 30% hemicelluloses, 20% lignin different and others 10% are ash, extractives, starch and proteins, which can be different depends on species of plants.

Table 2.1 Compositions of main components in lignocellulose (Rabemanolontsa and Saka, 2013)

Lignocellulose	Component (wt%)			
	Cellulose	Hemicelluloses	Lignin	Others*
Cupressaceae (Softwoods)				
- Japanese Cedar	38.67	23.16	33.78	4.39
Fagacceae (Hardwoods)				
- Japanese beech	43.94	28.43	24.02	3.60
Poaceae (Grass)				
- Bamboo	39.80	31.41	20.81	7.98
- Rice straw	34.53	21.82	20.22	23.42
- Corn cob	34.61	33.1	18.16	14.13
- Sugarcane bagasse	40.92	33.01	22.33	3.74

Remarks: Others* are protein, starch, extractives and ash

2.1.1. Cellulose

Cellulose is biopolymer which composed of glucose monomer repeating about 10,000 unit connect with β-(1,4) glyosidic linkage, molecular weight is about 200,000-400,000. The structure of cellulose composes of microfibril connect by hydrogen bond. Cellulose structure composes of crystalline region and para-crystalline region. However, para-crystalline region can easily be depolymerized compared to crystallin region.

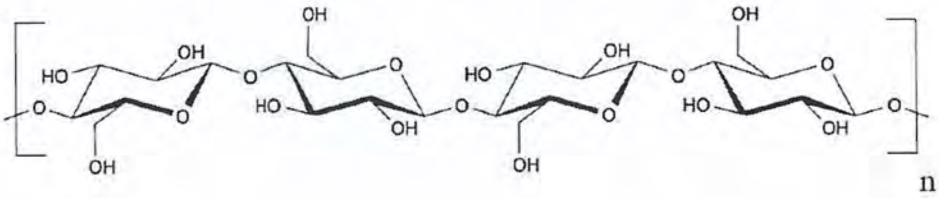


Figure 2.1 Chemical structure of cellulose (Laine, 2005)

2.1.2. Hemicelluloses

Hemicelluloses is heteropolymer which composed of pentose and hexose such as xylose, arabinose, glucose, galactose and mannose. Molecule of hemicelluloses compose of 200 repeating unit of monomer. In general, the structure of hemicelluloses is branch, which can be easily decomposed due to its para- crystalline. However, hemicelluloses will attach with lignin, so delignification is required.

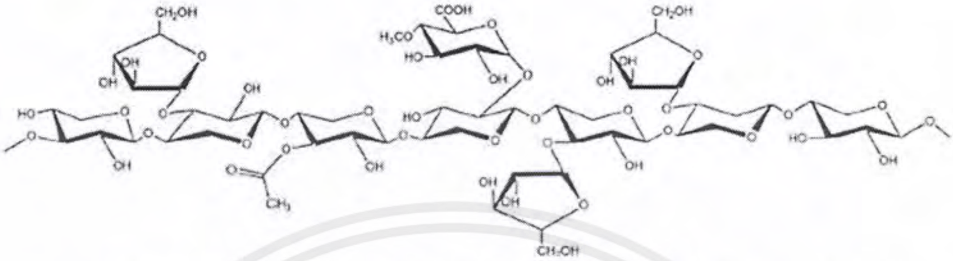


Figure 2.2 Chemical structure of O-acetyl-4-O-methylglucuronoarabinoxylan (Phaiboonsilapa et al., 2011)

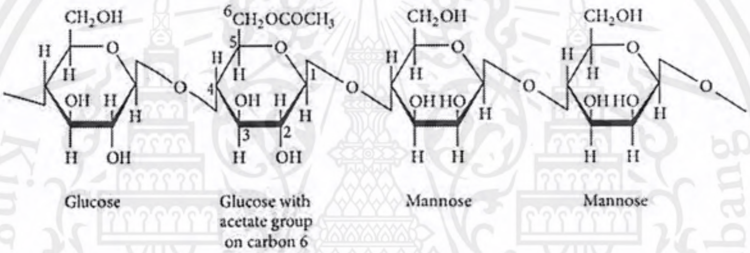


Figure 2.3 Chemical structure of Acetyl-glucomannan (Joyce K. Keithley et al., 2013)

2.1.3. Lignin

Lignin is aromatic polymer which exist in cell wall of plants. Function of lignin is preventing degradation of cellulose from microorganism enzyme. There are three types of lignin monomer, which are coumaryl alcohol, coniferyl alcohol, and synapyl alcohol, different of its structure is number of methoxy group (OMe). These chemical compositions can be different depend on plant species

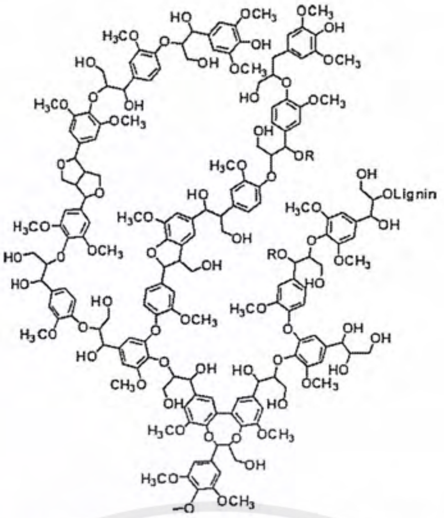


Figure 2.4 Chemical structure of lignin (Lignin, 2015)

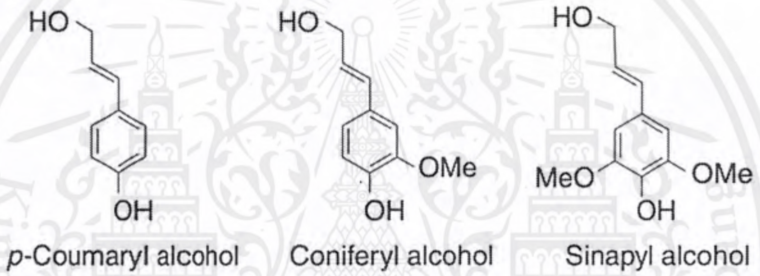


Figure 2.5 Chemical structure of three lignin monomers (Joffres et al., 2013)

2.2 Chemical Conversion of Lignocelluloses

Lignocelluloses are biomass which can be used as substrate to produce biochemical or biofuels. However, chemical compositions of lignocelluloses have to be analyzed before do the experiment.

2.2.1. Acid Hydrolysis

There are inorganic acid or mineral acid can be used in lignocellulose hydrolysis e.g. sulfuric acid, hydrochloric acid, nitric acid, formic acid and phosphoric acid, as well as organic acid such as acetic acid or formic acid can be used. However, concentration of acid is inverse variation to temperature for hydrolysis reaction, so acid is used as catalyst to reduce reaction temperature. Sulfuric acid is commonly used in hydrolysis reaction because its cheap price and good productivity of reducing sugar. Moreover, products from acid hydrolysis can be furfural and hydroxy methyl furfural.

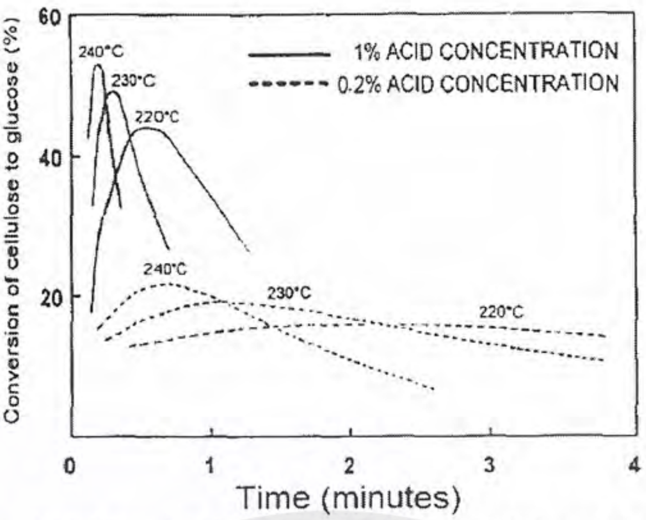


Figure 2.6 Glucose yield from hydrolysis reaction using 0.2 and 1wt% sulfuric acid at different temperature and time (Fagan et al., 1971)

2.2.2. Enzymatic Hydrolysis

Enzymatic hydrolysis can produce reducing sugar without by product such as furfural and hydroxy methyl furfural which inhibit fermentation reducing sugar to be ethanol. Essential enzyme using in enzymatic hydrolysis are cellulase, endocellulase and exocellulase, enzyme using to decomposition of cellulose is cellulase, enzyme using to break hydrogen bond between glucan chains in cellulose structure is endocellulase, exocellulase is used to shorten glucan chains to be cellobiose, as well as cellobioses are hydrolyze using β-glycosidase enzyme (Yu et al., 2008).

2.2.3. Steam Explosion

Principle of steam explosion is saturated lignocelluloses with steam under condition which high temperature and high pressure, then immediate decrease pressure, causing evaporation of water out of structure of lignocelluloses. As a result of lignocelluloses steam explosion, cellulose fibers are separated, as well as some of hemicelluloses are convert to reducing sugar (Ragg and Fields, 1987).

2.2.4. CO_2 Explosion

Carbon dioxide gas dissolves into water to be carbonic acid which is catalyst in hydrolysis reaction, this method is called carbon dioxide explosion. This method can eliminate enzyme deactivation inhibitor but productivity of reducing sugar are lower compared to steam explosion. (Ragg and Fields, 1987).

2.2.5. Wet Oxidation

Air and oxygen gas are used as intermediate in this method, also bio-fermentation tank is used under conditions of 170-200 °C and 1.0-1.2 MPa for 10-15 min (Ogbonna et al., 2001). As a result of wet oxidation (Mashima et al., 2006)., more cellulose was found in solid residues which come from hydrolysis of hemicelluloses and lignin. Moreover, this method also used to produce ethanol as a simultaneous saccharification and fermentation (SSF).

2.2.6. Liquid Hot-compressed Water

This method used water to hydrolyze lignocelluloses under temperature of 160-240 °C and pressure more than 5 MPa. As a result of this method, products are reducing sugar and oligosaccharides. Addition of acid as a catalyst in hydrolysis reaction can cause of 88-89wt% of lignocelluloses, as well as aggregation of reducing sugar to polymer is reduced (Mosier et al. 2005). However, this method can produce furfural, hydroxy methyl furfural and carboxylic acid which are microorganism growth inhibitor.

In Figure 2.7 O-acetyl-4-O-methylglucuronoxylan is used as substrate in decomposition reaction by hot-compressed water methods. The reaction is carry out at 230°C/10 MPa for 15 min, product of this method can be xylose, glucuronic acid and acetic acid which are from hydrolysis reaction. Moreover, furfural, glycolaldehyde, methyglyoxal and other products can be obtained from dehydration and fragmentation reaction.

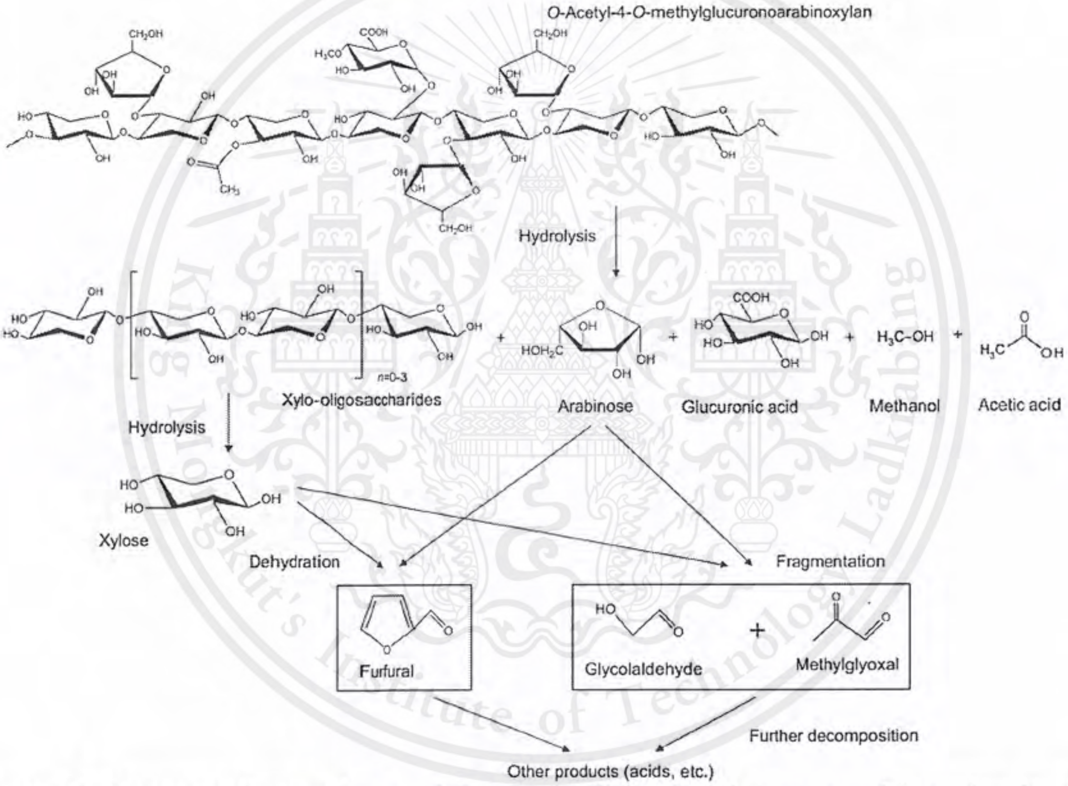


Figure 2.7 Decomposition pathway of O-acetyl-4-O-methylglucuronoarabinoxylan in nipa frond as treated in a semi-flow reactor with two-step hot-compressed water (Phaiboonsilpa et al., 2011)

2.2.7. Water under Pressurization of CO_2

Carbon dioxide gas with pressure more than 5 MPa is compressed into water to be carbonic acid which act as catalyst in hydrolysis reaction. As a result of carbonic acid, polysaccharides can be hydrolyzed to mono saccharides at 150-230 °C, as well as xylose yield from hydrolysis of xylan using this method is higher when compared to liquid hot-compressed water method (Van Walsum et al., 2004; Miyazawa and Funazukuri, 2005). Moreover, this method is environmental friendly because acid and base are no need to be added.

2.2.8. Hydrogen Peroxide Solution under Pressurization of CO_2

This method is similar to water under pressurization of carbon dioxide but hydrogen peroxide is added so that carbon dioxide dissolved in solution will react with hydrogen peroxide to be peroxy carbonic acid which has stronger acidity than carbonic acid. Hydrogen peroxide solution was never being used in hydrolysis of lignocelluloses, but it was used in epoxy oxidation of natural rubber to modify hydroxyl group at 40-60 °C and 12 MPa (Thidarat et al. 2015). However, peroxy carbonic acid is unstable which it will decompose to carbon dioxide and hydrogen peroxide at room temperature and atmospheric pressure (Nolen et al. 2002).

2.3 Reducing Sugar

Reducing sugar is sugar which its functional is aldehyde or ketone. Monosaccharides e.g. arabinos, galactose, glucose, mannose and xylose are reducing sugar, including cellobiose, lactose and maltose which are disaccharides, as well as oligomer which has aldehyde or ketone as functional group from hydrolysis reaction of lignocelluloses. Therefore, sugar from hydrolyzed lignocelluloses in hydrolysates are reducing sugar which can be report in total reducing sugar form (Campbell and Farrell, 2012; Nelson, 1994; Miler, 1959).

2.4 Carbonic Acid in Water

Carbon dioxide can be dissolve in to water to be carbonic acid shown in equation 2.1 and 2.2. Carbonic acid is diprotic which shown in equation 2.3 and 2.4 as monoprotic and diprotic respectively (Carbonic acid and Carbonate Salts, 2017).

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

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

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

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

Acid ionization constant of monoprotic and diprotic of carbonic acid at 25°C are K_{a1} and K_{a2} which are 4.5×10^{-7} and 4.7×10^{-11} respectively (CRC Handbook of Chemistry and Physics, 2004). When increase pressure of system, carbon dioxide can be more dissolved into water, including lower solution pH. In contrast, when increase temperature, carbon dioxide can be less dissolve in to solution due to solubility equilibria of carbon dioxide in water depends on temperature (Science HSC, 2013).

2.5 Solubility Equilibria of CO_2 in Water

Considering close system consisting of two phases of carbon dioxide gas and water at room temperature, assume that evaporating rate of water is very low, so total pressure (P_{Total}) is equal to partial pressure of carbon dioxide (P_{CO2}). Solubility of car bon dioxide gas is depends on temperature and pressure of the system. Relationship between concentration of carbon dioxide gas in solution and partial pressure can be explained by Henry's law. From equation 2.5, H is Henry's constant, P_{CO2} is partial pressure of carbon dioxide gas and x_{CO2} is mole fraction of carbon dioxide in liquid (Smith et al.2005).

From assumption that partial pressure of carbon dioxide equal to total pressure, when increase temperature until water evaporates to gas, then total pressure is equal to partial pressure of carbon dioxide merge with partial pressure of water as shown in equation 2.6.

$$P_{CO2} = x_{CO2}H \tag{2.5}$$

$$P_{CO2} + P_{H2O} = P_{total}(y_{CO2} + y_{H2O}) = P_{total} \tag{2.6}$$

From Walsum (2001), study of solubility equilibria of carbon dioxide in water which depends on temperature, it was found that Henry's constant represents solubility of carbon dioxide in water at various temperature shown in figure 2.8, relationship between Henry's constant from experiment and temperature is parabolic function.

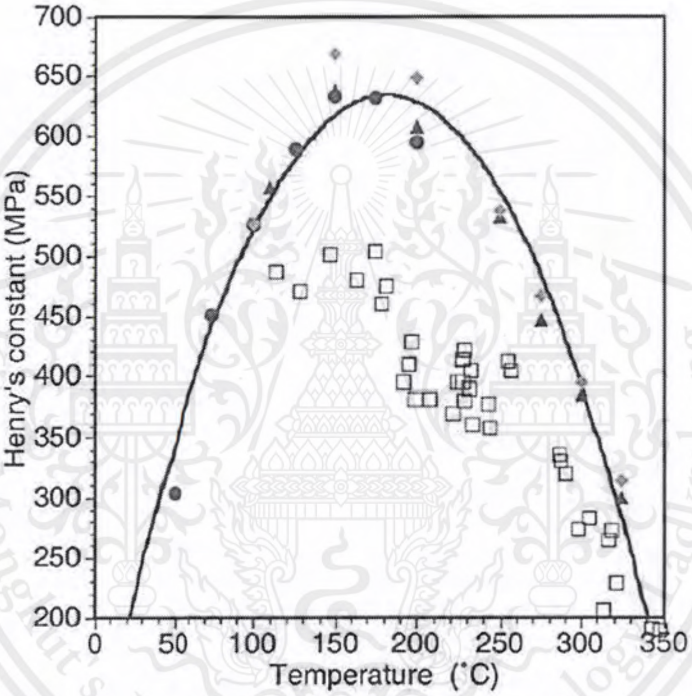


Figure 2.8 Henry's constant of carbon dioxide at different temperature (Van Walsum, 2001)

Equation 2.8 which is using to find Henry's constant represents parabolic function of temperature and Henry's constant, T is temperature (°C) and H is henry's constant (MPa)

$$H = -0.017037T^2 + 6.1553T + 78.227 \tag{2.7}$$

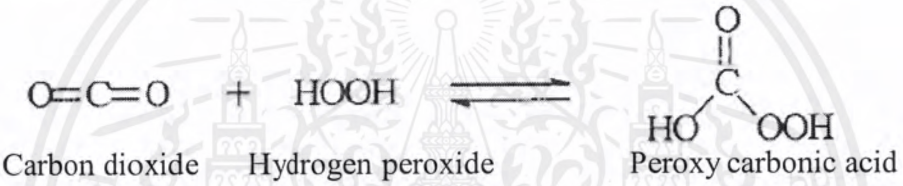
From Figure 2.8 and equation 2.7, at 150-200 °C henry's constant is about 630 MPa, if volume of dissolved carbon dioxide is to be increased then partial pressure of carbon dioxide is increased. In this research, batch reactor is used and pressure of carbon dioxide is 5 MPa at room temperature.

2.6 Peroxy Acid

Peroxy acid is divided into inorganic and organic peroxy acid which have -OOH as functional group. Theses acid are strong oxidizing agent e.g. peroxy monosulfuric acid (inorganic peroxy acid) which used to eliminate cyanide in mining industry (Jakob et al., 2012) and peroxy carboxylic (organic peroxy acid) which prepare from carboxylic acid. Stability of organic peroxy acid is increasing along with carbon atom in molecule (Brandsch and Piringer, 2000) but acid ionization constant will decrease because resonance instability of anion (Klenk et al., 2012).

$$RCO_2H + H_2O_2 \rightleftharpoons RCO_3H + H_2O \qquad (2.8)$$

Pressurization of hydrogen peroxide solution using carbon dioxide under 5-12 MPa can produce peroxy carbonic acid shown in equation 2.9. Peroxy carbonic acid is stronger oxidizing agent compared to hydrogen peroxide (Brandsch and Piringer, 2000), but it cannot be prepared as a pure substance because of its instability (Nolen et al., 2002).

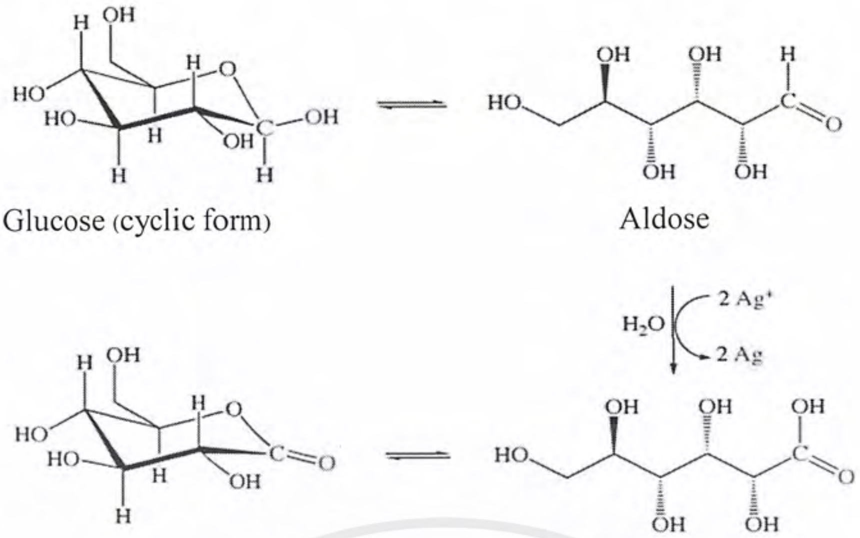


(2.9)

From research of Thidarat et al. (2015), study of preparation of modified natural rubber with hydroxyl group using 30wt% of hydrogen peroxide under pressurization of 12 MPa carbon dioxide at 60 °C, it was found that peroxy carbonic acid can oxidize natural rubber with hydroxyl group which has molecular weight of 1.9×10^4 g/mole to 4.2×10^3 g/mole. From molecule decomposability of peroxy carbonic, this research applies pressurization of hydrogen peroxide solution using carbon dioxide to hydrolysis of xylan in order to study effect of peroxy carbonic on reducing sugar production.

2.7 Oxidation Reaction of Saccharides

Glucose molecule can be converted from cyclic chain to straight chain which hydroxyl group at reducing end will convert to be aldehyde group as aldose sugar. Oxidation reaction of aldose can be occur using silver (Ag) as catalyst which convert aldehyde group to carboxylic group, as well as organic acid derivatives of glucose as shown in Figure 2.9



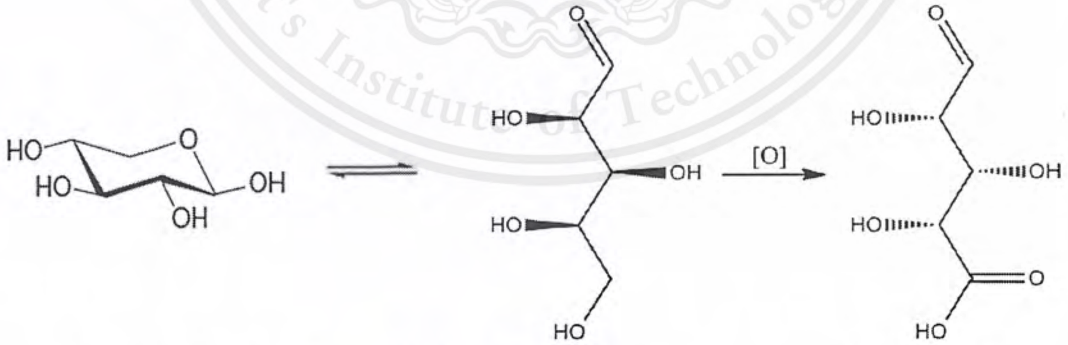
Glucose (cyclic form) Aldose

Ketose Organic acid

Figure 2.9 Isomerization and oxidation reaction of glucose (Shapley, 2012)

Structure of xylose molecule also can be converted from cyclic chain which is to straight chain which has aldehyde group. Oxidation reaction convert aldehyde group to be organic acid derivative of xylose using metal catalyst e.g. Au, Pd or Cu at 25-60 °C, xylose will be converted to xylonic acid and other products such as acetic acid, formic acid, threonic acid, trihydroxy acid, xylaric acid and xylitol

Figure 2.10 show isomerization reaction and oxidation reaction of xylose to xylonic acid, and Figure 2.11 show isomerization reaction and oxidation reaction of xylose to xylaric acid. There are many types of monosaccharide(s) from hydrolysis reaction of lignocelluloses e.g. glucose and xylose, if oxidizing agent is added into the reaction, monosaccharides can be oxidized to derivatives of organic acid.



Xylose (cyclic form) Xylose (acyclic form) Xylonic acid

Figure 2.10 Isomerization and oxidation reaction of xylose to xylonic acid (Hernandez, 2013)

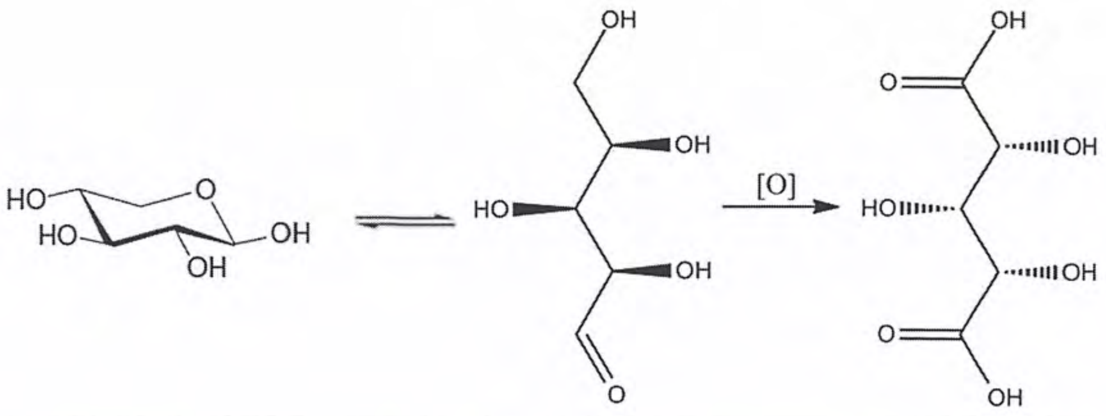


Figure 2.11 Isomerization and oxidation reaction of xylose to xylaric acid (Hernandez, 2013)

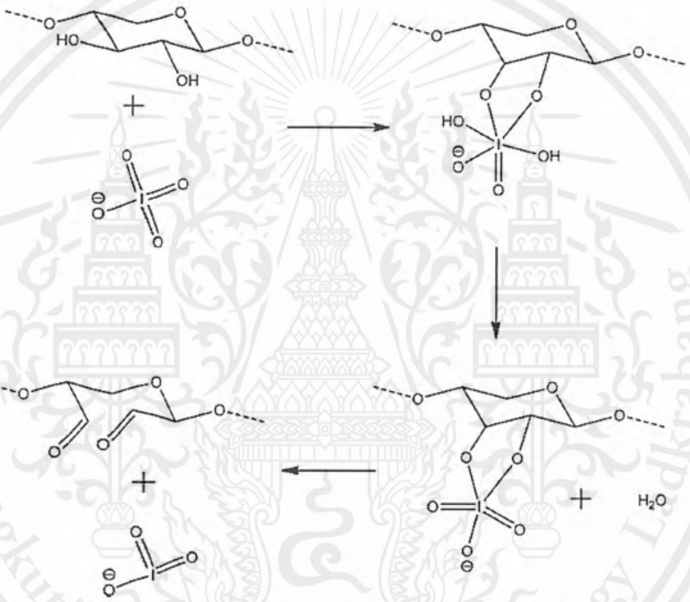


Figure 2.12 Mechanism of periodate oxidation on xylan to aldehyde (Chemin et al., 2016)

Periodate oxidation reaction using $NaIO_4$ as oxidizer which cause of open ring of xylose and form two aldehyde groups shown in Figure 2.12

2.8 Literature Reviews

In recently years, there many studies on lignocelluloses under non-catalytic reaction e.g. supercritical water method, hot-compressed water, steam explosion, including catalytic reaction using acid or base as catalyst. Objective of this research is comparative study on liquefaction behaviors of xylan as treated by different hydrothermal method.

Sluiter et al. (2010) studied chemical composition of biomass using water to decomposition and delignification using 72wt% of sulfuric to hydrolyzed biomass at room temperature and atmospheric pressure, then dilute it by add water to system and heat up temperature to 100-125 °C to convert polysaccharides to be monosaccharides. Hydrolysate from hydrolysis reaction will be analyzed to determine hemicelluloses and cellulose in biomass. Residues will be filtered using vacuum filter, weight of residue can be calculated to find quantity of lignin. This method is approved and wildly used to study chemical composition of lignocelluloses.

Phiboonsilpa et al. (2009;2011;2013) study chemical conversion of lignocelluloses as treated by two-step hydrolysis on japanese beech, japanese pine, rice straw and rice husk, including vascular plants. Flow-through reactor is used under 10 MPa for 60 min and flow rate of hot-compressed water is 10 ml./min, it was found that optimal conditions of first step second step are different, as well as optimal temperature for hydrolysis reaction of hemicelluloses is 230 °C and temperature for hydrolysis reaction of cellulose is 270-280 °C, almost of hemicelluloses and 70% of cellulose were converted to reducing sugar.

Walsum et al. (2001) studied the hydrolysis of xylanase from beech wood using carbonic acid. This experiment using 15 ml batch reactor, 1 g of xylan/L compressed and with carbon dioxide at 0-5.5 MPa. The reaction was carried out at 170-230 °C for 2-30 min, it was found that carbonic acid can used as catalyst to convert xylan to xylose for study temperature range. However, when compared to dilute sulfuric acid using as catalyst in hydrolysis reaction, it was found that the use of carbonic acid was less effective at 190 °C and 14.5 min g hydrolysis although pressured in reactor is 14 MPa.

Walsum et al. (2004) study on the using of carbonic acid to increase performance of corncob hydrolysis, particle size of the corncob is 0.5-1 mm., reactor type is batch reactor which volume is 15 ml. compressed with carbon dioxide at 5.5 MPa and temperature is 180-220 °C for 2-32 min. It was found that carbonic acid can be used as catalyst in hydrolysis reaction. As a result of using carbonic acid yield of xylose in the hydrolysate was increase 2 times compared to using hot-compressed water method.

Juttamalakul (2016) study on hydrolysis of sugarcane bagasse by using 1wt% H_2O_2 solution under pressurization of carbon dioxide, weight of sugarcane bagasse is 0.1 g, reactor using is 10-ml batch reactor, reaction carry out at 150-250°C for 0-30 min. It was found that H_2O_2 solution is strong oxidizing agent which increase yield of reducing sugars. Yield and recovery yield of xylo-saccharides from hemicelluloses are 10.03wt% and 33.46 wt% respectively.

This research is comparative study on liquefaction behaviors of xylan as treated by four different hydrothermal methods. Hydrothermal technique was explored using 0.01 and 0.1wt% H_2O_2 solution in order to study oxidation effect of peroxy carbonic acid and temperature in range of 150-250°C. It is expected that peroxy carbonic acid will increase yield of reducing sugar in hydrolysate, compared with hot-compressed water method. In addition, the liquid product is expected to be different due to effect of oxidation reaction.

CHAPTER III

EXPERIMENTAL

This research is comparative study on liquefaction behaviors of xylan using hot-compressed water, hydrogen peroxide solution under pressurization of carbon dioxide and hydrogen peroxide solution under pressurization of nitrogen.

3.1 Chemical Composition Analysis by Klason Lignin Determination Method

Chemical composition of xylan such as xylose, glucose and arabinose were quantitatively and qualitatively analyzed by using Klason lignin determination method as comparison of products yield from hydrothermal liquefaction

3.1.1 Chemicals and Materials

1. Xylan isolated from corn cob
2. 72wt% Sulfuric acid
3. Distilled water

3.1.2 Equipment

1. 100-ml amber glass bottle
2. 50-ml beaker
3. 10-ml glass pipette
4. Autoclave
5. Stirring rod
6. Vacuum filtration apparatus (vacuum pump, glass funnel, rubber ring, filter flask)
7. Filter paper (Whatman No.4)

3.1.3 Procedure

1. Dry xylan at 105 °C for 4 hours, cooling to room temperature in desiccator
2. Weight 0.2 g of oven-dried sample and put it into 50 milliliter beaker
3. Add 2 ml of 72wt % sulfuric acid into beaker using glass pipette, stir by stirring rod, and keep the reaction at room temperature for 2 hours
4. Measure 75 ml of deionized water into a separated beaker. After 2 hours, add 10 ml distilled water into beaker in step 3 in order to dilute concentration of sulfuric acid and terminate the reaction
5. Rinse beaker several times with 60 milliliter distilled water and carefully transfer sample and sulfuric acid to prevent losing of mass, total volume of sulfuric acid is 77 milliliters and its concentration is 3wt%
6. Close a cap bottle from step 5 and cover it with aluminum foil and place in autoclave at 121 °C for 30-60 min
7. Cooling sample from autoclave at room temperature
8. Filter product from step 7 using vacuum filter to separate hydrolysate and residues
9. Quantitatively and qualitatively analyze hydrolysate using high performance liquid chromatography (HPLC). The obtained xylose yield is hemicelluloses.

3.2 Hot-compressed Water under Pressurization of N_2

In this experiment, study on effect of temperature at 150-250 °C and heat up time for 30 min using 10-ml batch reactor under pressurization of 5 MPa N_2 at room temperature.

3.2.1 Chemicals and Materials

1. Xylan isolated from corn cob
2. 99wt% pure N_2 gas

3.2.2 Equipment

1. 10-ml batch reactor
2. Heater and controller experimental set-up
3. 10-ml glass pipette

3.2.3 Procedure

1. Load 0.025 g of xylan into 10-ml batch reactor
2. Add 6 ml. deionized water into reactor and tighten reactor cap.
3. Pressurize N_2 gas at 5 MPa at room temperature into reactor and check leakage
4. Install the batch reactor to heater and controller board, set the desired temperature, and switch on the system
5. Heat up the reactor 30 min to desired temperature, then cool the reactor temperature down by quenching in iced-water bath for 30 min
6. Open gas valve to release pressure, then open reactor cap and take hydrolysate.
7. Quantitative and qualitative analyze hydrolysate by high performance liquid chromatography (HPLC) technique

3.3 Hot-compressed Water under Pressurization of CO_2

The details of the study and the experimental procedure are the same as previous method described in 3.2, but these treatment CO_2 was used instead of N_2 to in order to study effect of carbonic acid on reducing sugar yield.

3.4 Hot-compressed 0.01 and 0.1wt% H_2O_2 Solution under Pressurization of N_2

In this experiment, study on effects of temperature at 150-250 °C and concentration of 0.01% and 0.1wt% H_2O_2 solution, heat up time for 30 min using 10-ml batch reactor under pressurization of 5 MPa N_2 at room temperature.

3.4.1 Chemicals and Materials

1. Xylan isolated from corn cob
2. 99wt% pure N_2 gas
3. 0.01 and 0.1wt% H_2O_2

3.4.2 Equipment

1. 10-ml batch reactor
2. Heater and controller experimental set-up
3. 10-ml glass pipette

3.4.3 Procedure

1. Load 0.025 g of xylan into 10-ml batch reactor
2. Add 0.002 ml H_2O_2 (0.01wt%) and 0.020 ml H_2O_2 (0.1wt%) into reactor then add deionized water to adjust volume to be 6 ml., tighten reactor cap.
3. Pressurize N_2 gas at 5 MPa at room temperature into reactor and check leakage
4. Install the batch reactor to heater and controller board, set the desired temperature, and switch on the system
5. Heat up the reactor 30 min to desired temperature, then cool the reactor temperature down by quenching in iced-water bath for 30 min
6. Open gas valve to release pressure, then open reactor cap and take hydrolysate.
7. Quantitative and qualitative analyze hydrolysate by high performance liquid chromatography (HPLC) technique

3.5 Hot-compressed 0.01 and 0.1wt% H_2O_2 Solution under Pressurization of CO_2

The details of the study and the experimental procedure are the same as previous method described in 3.4, CO_2 is used instead of N_2 to in order to study effect of peroxy carbonic acid to reducing sugar yield.

3.6 Analytical Methods

3.6.1 Analyses and Quantification of Liquid Products

Reducing sugars and other products are quantitatively and qualitatively analyzed by high performance liquid chromatography (HPLC), but only monosaccharides can be analyzed. Therefore, 1.25 µl of 98wt% H_2SO_4 is added into 1 ml. of hydrolysate to obtained 3wt% H_2O_2 solution, then conduct hydrolysis reaction in autoclave at 121°C for 30 min to hydrolyzed polysaccharides to be monosaccharides this method is called post hydrolysis. Yield of sugar from post hydrolysis is equal to total reducing sugar, quantity of polysaccharides can be calculated by total reducing sugar minus by monosaccharides from hydrolysate before conduct post hydrolysis.

Analysis of mono- and oligo-saccharides in hydrolysate from four different hydrothermal liquefaction methods and Klason lignin using high performance liquid chromatography with conditions detail as follows:

- Analysis column (Aminex HPX-87H, Bio-rad)

- 5 mM of sulfuric acid as carrier	- Carrier flow rate of 0.5 ml / min
- 65 °C of column temperature	- Refractive index detector (RID)

Make calibration curve with a standard sugar solution of xylose and glucose with known concentration at least two values to find the relationship between concentration and area under the chromatogram graph of each standard sugar solution. The standard graph is used to calculate the amount of sugar in the hydrolysate from the area under the chromatogram graph of the sugar in the hydrolysate analyzed by high performance liquid chromatography. And reported as a percent yield relative to weight of xylan dried-basis.

3.6.2 Removal of H_2O_2 from Hydrolysates

Hydrogen peroxide could be used in this study to increase yield of mono- and oligo-saccharides. However, recovery yield of oligo-saccharides was found to be decreased because of oxidation reaction become dominant, lead to elimination of hydrogen peroxide. 2-ml of hydrolysate will be heated to 80°C for 60 min, then its volume will be adjusted to 10-ml, after that, divide hydrolysate into two portions in order to conduct post-hydrolysis by adds 1 and 3 wt% H_2SO_4 solution.

3.6.3 Quantitative of Oligo-saccharides by Post-hydrolysis

To quantify oligo-saccharides, 1 and 3wt% of H_2SO_4 will be added into hydrolysate, then the hydrolysate will be put into autoclave at 121°C for 30 min. Hydrolysate from post-hydrolysis will be analyses by high performance liquid chromatography (HPLC) according to 3.6.1. Amount of oligo-saccharides can be calculated from

$$\boldsymbol{Oligosaccharides} = (Mono - saccharides\ in\ Post - Hydrolysis) - (Mono - saccharides\ in\ as\ recieve\ sample)$$

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the experimental results were discussed including, (4.1) production of hydrolyzed products by different hydrothermal methods, (4.2) proportional yield of xylose, (4.3) decomposition of hydrolyzed products, (4.4) mass balance and (4.5) decomposition pathway. Xylan isolated from corn core was liquefied using water under pressurization of nitrogen or carbon dioxide, liquefaction using hot-compressed 0.01 and 0.1wt% hydrogen peroxide to produce xylo-saccharides. The experiment was conduct at a temperature of 110-250 ˚C to explore effects of temperature and concentration of hydrogen peroxide on yield of xylo-saccharide.

4.1 Production of Hydrolyzed Products by Different Hydrothermal Methods

4.1.1 Hemicellulosic saccharides and acetic acid

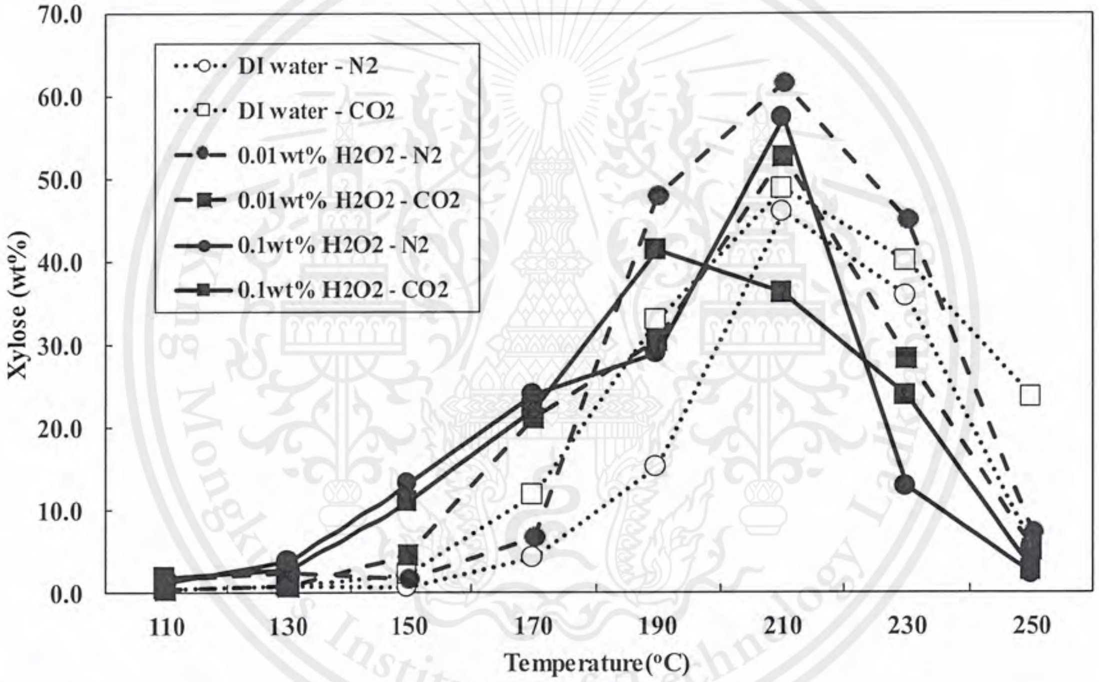


Figure 4.1 Xylose from liquefaction of xylan as treated by different hydrothermal methods at various temperature

According to Figure 4.1, yield of xylose increases in the temperature range of 170-210˚C because the degree of liquefaction increased as a consequence of increases in treatment temperature, while the xylose yield decreases at temperature higher than 210˚C because of high degree of decomposition. The appropriate temperature for xylo-saccharides production is the same at 210˚C for all hydrothermal treatment except that method using 0.1wt% of hydrogen peroxide because the high concentration of hydrogen peroxide lead to the high degree of oxidation, ends up with lower yield of xylose compared to the other methods.

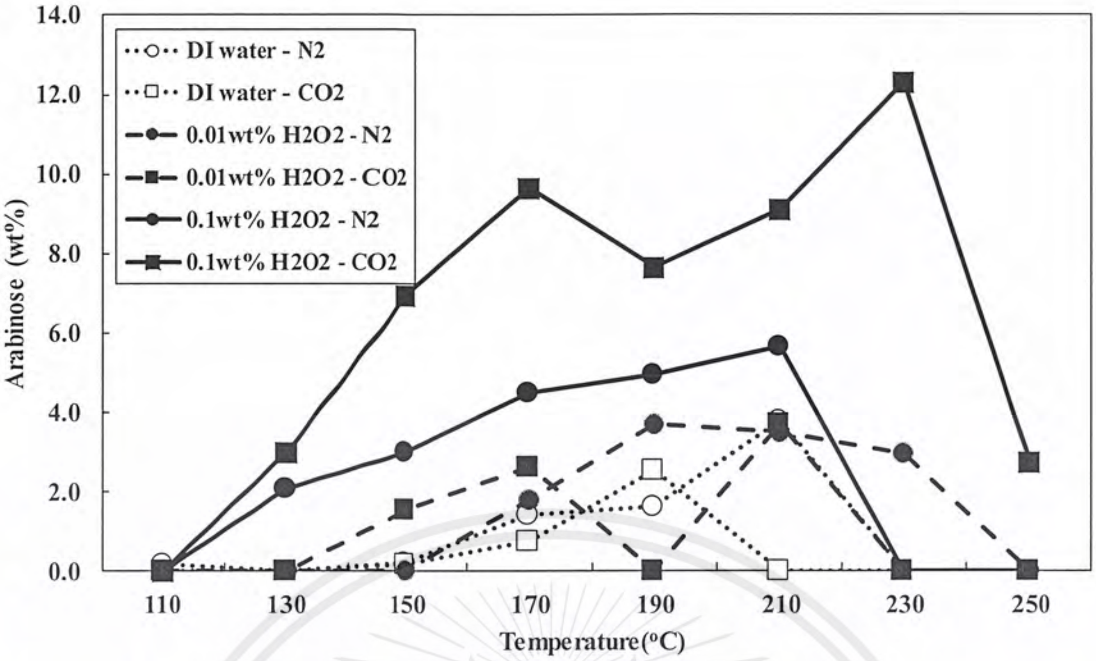


Figure 4.2 Arabinose from liquefaction of xylan as treated by different hydrothermal methods at various temperature

Based on the obtained result, it implies that yield of arabinose increased as the temperature increases, then decreases at the high temperature because of high intensity of decomposition. As for the treatment with addition of hydrogen peroxide solution, yield of arabinose is higher compared to the treatment without addition of hydrogen peroxide.

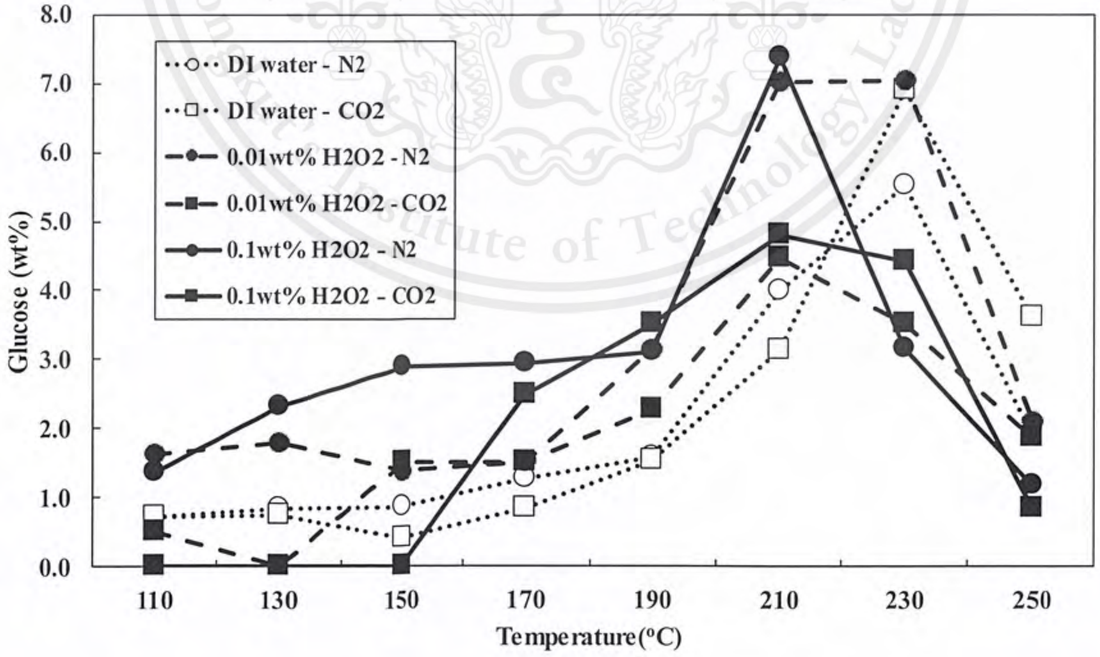


Figure 4.3 Glucose from liquefaction of xylan as treated by different hydrothermal methods at various temperature

Despite xylan is used as substrate in the experiment, glucose also can be produce because glucomannan is minor composition in hemicelluloses. From the Figure 4.2, yield of glucose is increased as the temperature increases, but then yield of glucose decreases at the temperature over 230˚C for xylan treated by hot-compressed water because of glucose decomposition as the temperature increases. However, yield of glucose is decrease at the temperature over 210 ˚C for xylan treated by hydrogen peroxide solution because of high degree of oxidation.

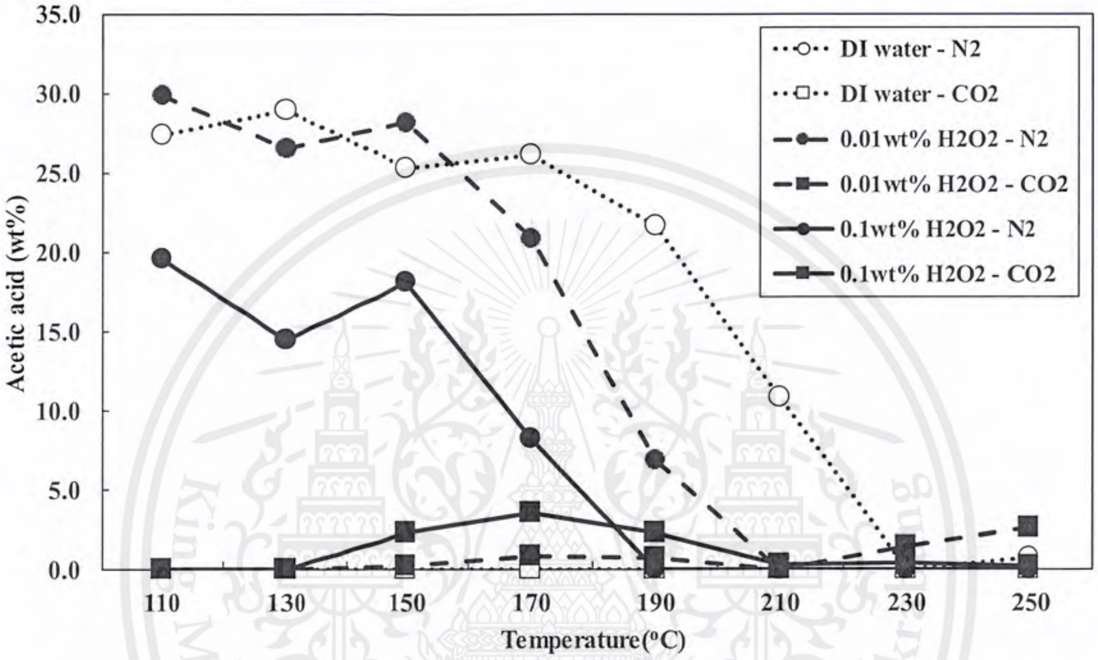


Figure 4.4 Acetic acid from liquefaction of xylan as treated by different hydrothermal methods at various temperature

From the experimental result, it was found that yields of acetic acid are high in the temperature range of 110-170˚C, then yield of acetic acid decreases as temperature increases because the high intensity of decomposition, for xylan liquefaction using hot-compressed water and hydrogen peroxide solution under pressurization of nitrogen. However, yields of acetic acid obtained from xylan treated by hot-compressed water and hydrogen peroxide solution under pressurization of carbon dioxide are lower compared to those obtained from solution under pressurization of nitrogen, because there are carbonic acid and peroxy carbonic acid that increases degree of decomposition.

4.1.2 Proportion of mono- and oligomeric xylo-saccharides

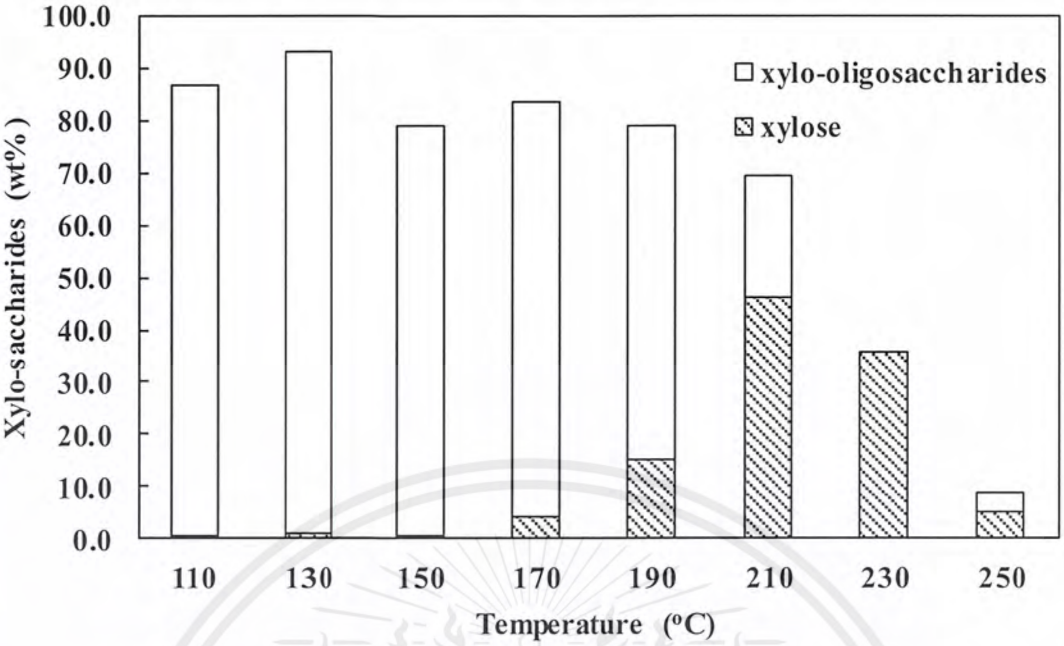


Figure 4.5 Proportions of mono- and oligomeric xylo-saccharides from liquefaction of xylan using water under pressurization of nitrogen

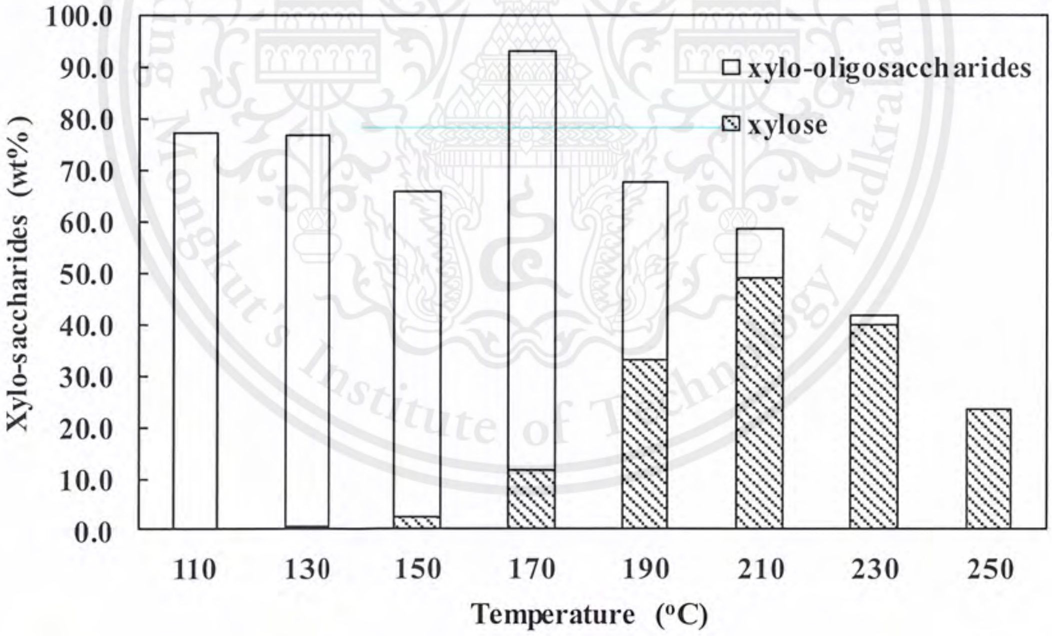


Figure 4.6 Proportions of mono- and oligomeric xylo-saccharides from liquefaction of xylan using water under pressurization of carbon dioxide

Figure 4.5 and 4.6 shows the production of xylo-saccharides from xylan treated by water under pressurization of nitrogen and water under pressurization of carbon dioxide respectively, it was found that hydrolysis reaction was started at temperature of 170°C, including the appropriate condition of these 2 methods were the same at temperature of 210°C. However, yield of xylose from xylan treated by water under pressurization of carbon dioxide is 48.83wt% which higher than 46.09wt% those obtained from using water under pressurization of nitrogen because of carbonic acid which act as catalyst for hydrolyzed xylo-oligosaccharides to be xylo-saccharides dissolved in water. In the temperature range over 210°C yield of xylo-saccharide drastically decrease because of high degree of decomposition.

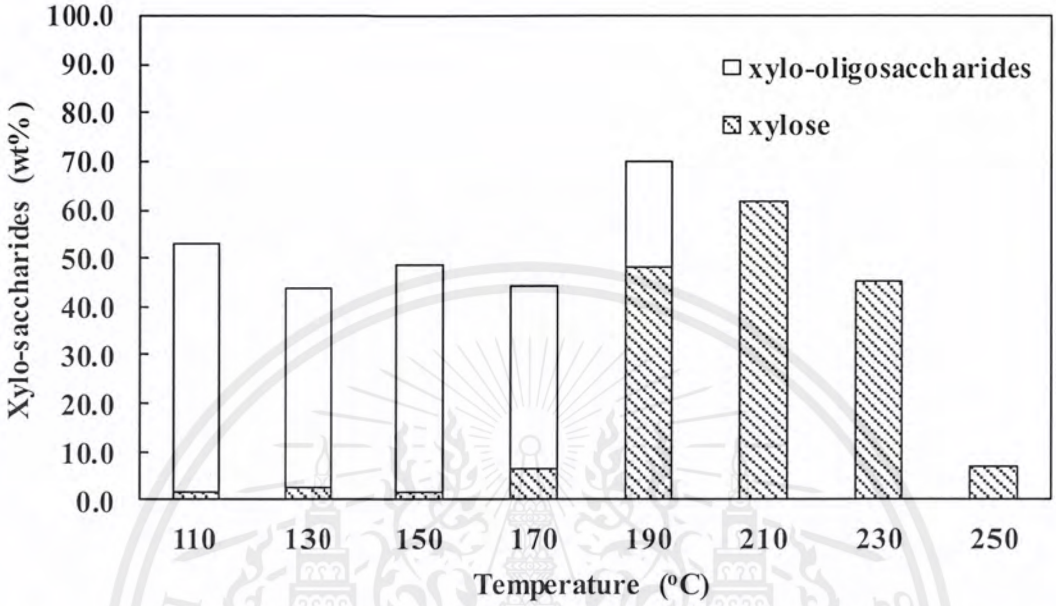


Figure 4.7 Proportions of mono- and oligomeric xylo-saccharides from liquefaction of xylan using hot-compressed 0.01wt% of hydrogen peroxide under pressurization of nitrogen

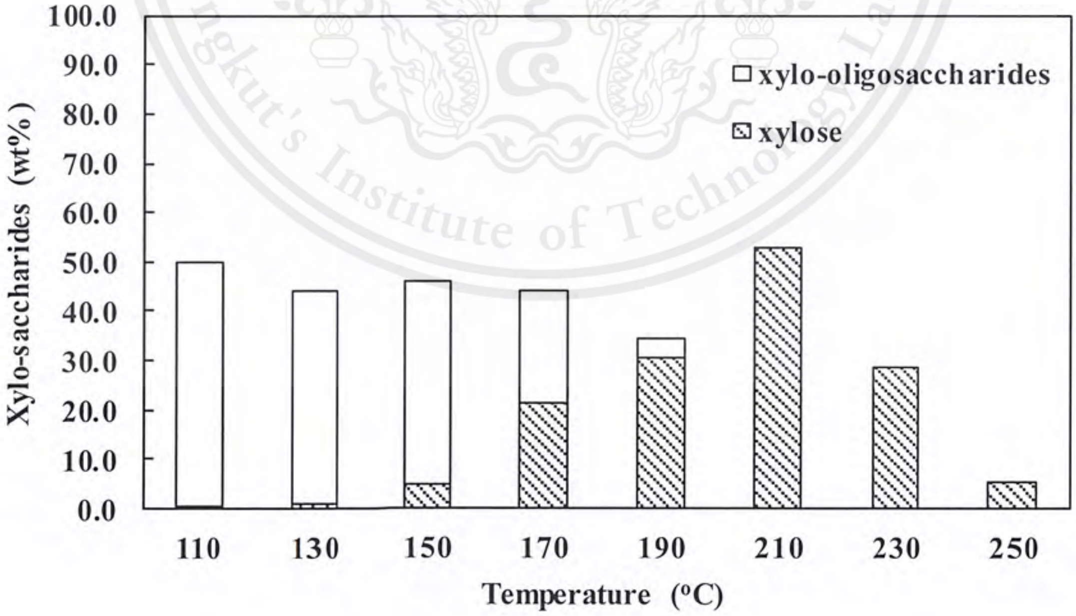


Figure 4.8 Proportions of mono- and oligomeric xylo-saccharides from liquefaction of xylan using hot-compressed 0.01wt% of hydrogen peroxide under pressurization of carbon dioxide

From the obtained experimental result as shown in Figure 4.7 and 4.8, it was found that yield of xylo-saccharide increases at the temperature range of 170-210°C, then decrease at the temperature over 210°C because of high degree of decomposition and oxidation. Recoverable yield of xylo-oligosaccharides is low because hydrogen peroxide and peroxy carbonic acid which are oxidant, for xylose to be organic acid presents in the hydrolysate. The appropriate temperature for theses 2 methods is the same at 210°C, as well as yield of xylo-saccharide from xylan treated by hydrogen peroxide solution under nitrogen is 61.63wt% which higher than 52.89% those obtained from using carbon dioxide, because xylose was oxidized ends up with lower yield of xylose.

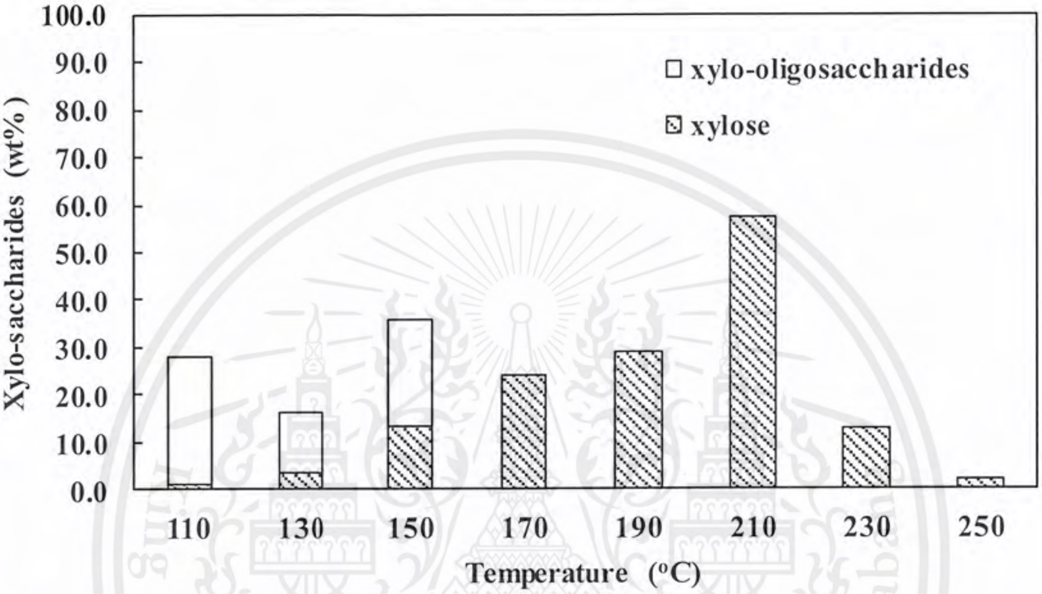


Figure 4.9 Proportions of mono- and oligomeric xylo-saccharides from liquefaction of xylan using 0.1wt% of hydrogen peroxide under pressurization of nitrogen

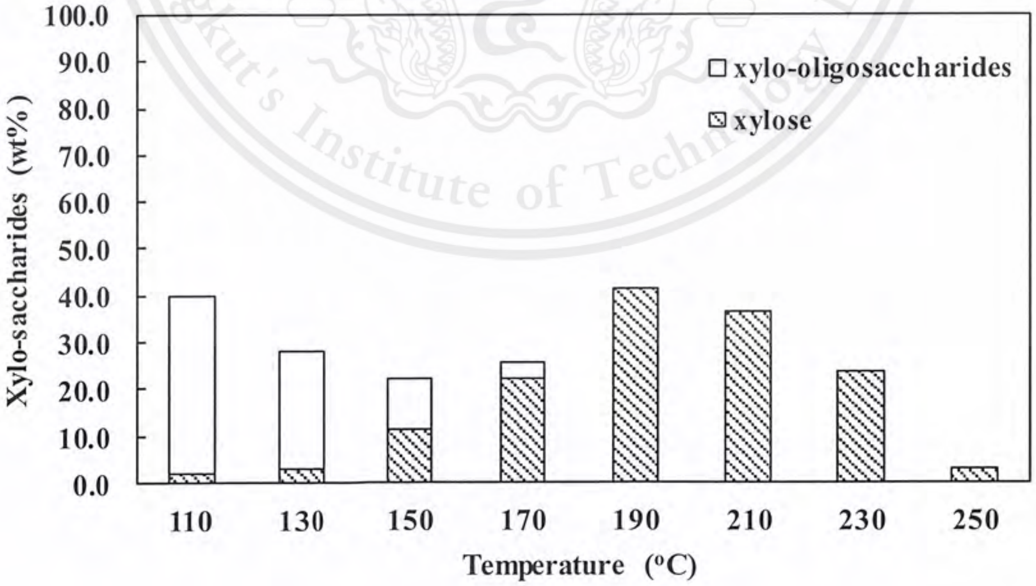


Figure 4.10 Proportions of mono- and oligomeric xylo-saccharides from liquefaction of xylan using 0.1wt% of hydrogen peroxide under pressurization of carbon dioxide

As for the treatment using 0.1wt% of hydrogen peroxide, yield of xylo-saccharides is lower than the previous hydrogen peroxide treatment. Recoverable yield of xylo-oligosaccharides is low because xylose was oxidized by hydrogen peroxide and peroxy carbonic acid. The highest yield of xylo-saccharides is 57.44wt% for xylan treated by hydrogen peroxide under pressurization of nitrogen, when using carbon dioxide instead of nitrogen, the xylose yield is 41.39wt%. Likewise, the appropriate temperature for the treatment using nitrogen is at 210°C, when the treatment using carbon dioxide instead of nitrogen the appropriate temperature is at 190°C because the presence of an excess amount of hydrogen peroxide and peroxy carbonic acid.

Table 4.1 Proportional yield of xylose and xylo-oligosaccharides from liquefaction of xylan as treated by different hydrothermal methods

Temp. (°C)	Yield of Xylo-saccharides (wt%)											
	H_2O/N_2		H_2O/CO_2		0.01wt%H_2O_2/N_2		0.01wt% H_2O_2/CO_2		0.1wt%H_2O_2/N_2		0.1wt%H_2O_2/CO_2	
	Xylose	Xylo-oligosacc.	Xylose	Xylo-oligosacc.	Xylose	Xylo-oligosacc.	Xylose	Xylo-oligosacc.	Xylose	Xylo-oligosacc.	Xylose	Xylo-oligosacc.
110	0.42 (0.48%)*	86.42 (99.52%)	0.34 (0.44%)	76.86 (99.56%)	1.57 (2.98%)	51.22 (97.02%)	0.49 (0.99%)	49.57 (99.01%)	1.28 (4.56%)	26.73 (95.44%)	1.91 (4.78%)	38.06 (95.22%)
130	0.85 (0.91%)	92.06 (99.09%)	0.83 (1.08%)	75.98 (98.92%)	2.44 (5.56%)	41.43 (94.44%)	0.92 (2.07%)	43.33 (97.93%)	3.80 (23.26%)	12.52 (76.74%)	2.88 (10.19%)	25.36 (89.81%)
150	0.73 (0.92%)	78.05 (99.08%)	2.32 (3.52%)	63.71 (96.48%)	1.67 (3.44%)	46.87 (96.56%)	4.64 (10.12%)	41.19 (89.88%)	13.16 (36.88%)	22.52 (63.12%)	11.09 (50.07%)	11.06 (49.93%)
170	4.22 (5.06%)	79.21 (94.94%)	11.78 (12.65%)	81.34 (87.35%)	6.54 (14.80%)	37.69 (85.20%)	21.18 (48.03%)	22.92 (51.97%)	24.05 (100%)	0.00	22.18 (86.11%)	3.58 (13.89%)
190	15.23 (19.31%)	63.65 (80.69%)	33.03 (48.73%)	34.75 (51.27%)	48.04 (68.93%)	21.66 (31.07%)	30.61 (89.16%)	3.72 (10.84%)	28.99 (100%)	0.00	41.39 (100%)	0.00
210	46.09 (66.57%)	23.15 (33.43%)	48.83 (83.09%)	9.94 (16.91%)	61.63 (100%)	0.00	52.89 (100%)	0.00	57.44 (100%)	0.00	36.18 (100%)	0.00
230	35.82 (100%)	0.00	40.03 (95.87%)	1.72 (4.13%)	45.14 (100%)	0.00	28.53 (100%)	0.00	12.87 (77.66%)	3.70 (22.34%)	23.83 (100%)	0.00
250	5.35 (61.06%)	3.41 (38.94%)	23.60 (100%)	0.00	7.23 (100%)	0.00	5.15 (100%)	0.00	2.18 (42.86%)	2.91 (57.14%)	2.72 (100%)	0.00

*Number in parentheses indicate ratio of mono- or oligo-saccharides to total saccharides in hydrolysate

According to the obtained result from this table, proportional yield is ratio of mono- or oligo-saccharides to total saccharides in hydrolysate. The equipment that used for analysis saccharides in this project is High Performance Liquid Chromatography (HPLC). Mono-saccharides was obtained from the experiment, while oligo-saccharides obtained from calculation after conduct post-hydrolysis, because analytical column in theses experiment was only used for saccharides analysis. Post-hydrolysis is methods to identify total saccharides in product, oligomer can be quantified by subtract monomer from experiment out of total saccharides. As for the treatment using hot-compressed water it was found that proportion of xylose for treatment using carbon dioxide is higher than those obtained using nitrogen because carbonic that occurred reinforces degree of liquefaction. On the other hand, for the treatment using hot-compressed 0.01 and 0.1wt% hydrogen peroxide solution, proportion of xylose for treatment using nitrogen is higher than those obtained from carbon dioxide because xylose from the treatment under pressurization of carbon dioxide lead to the presence of hydrogen peroxide and peroxy carbonic acid which are cause of xylose oxidation.

4.2 Decomposition of Hydrolyzed Products under Different Hydrothermal Conditions

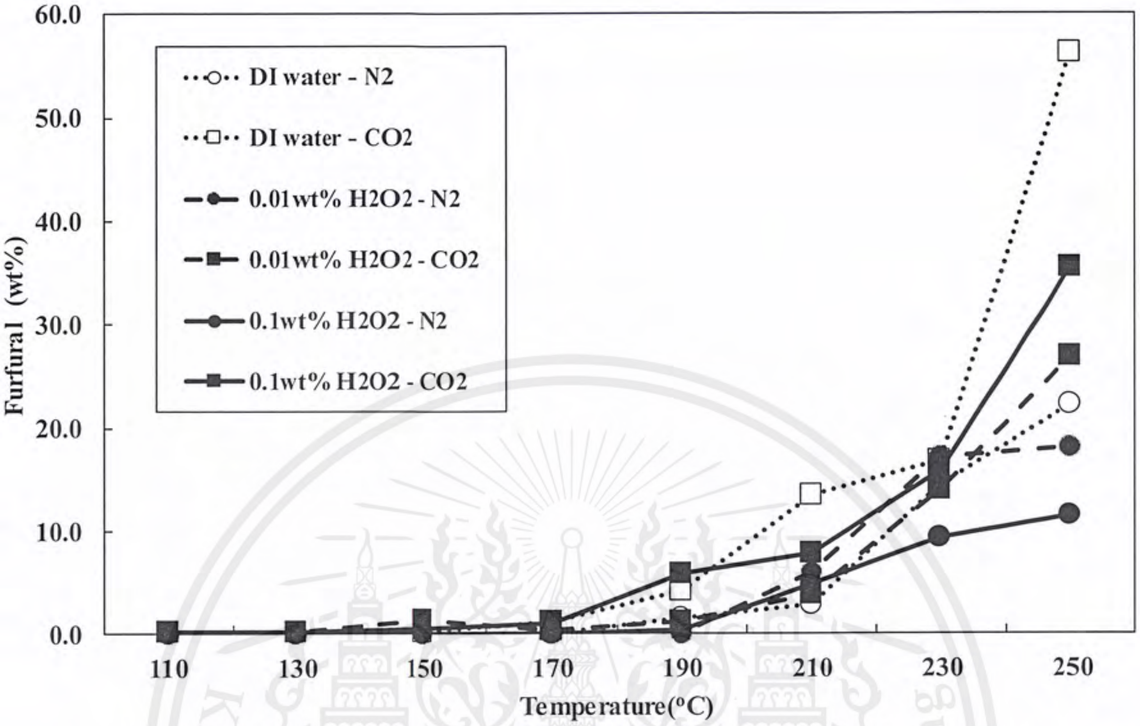


Figure 4.11 Furfural from liquefaction of xylan as treated by different hydrothermal methods at various temperature

Furfural is dehydrated product from 5-carbon monosaccharides that occurs at high temperature because water is drain out of the structure or molecule. From figure 4.11, it was found that yield of furfural increases at the temperature over 170°C. In case of the liquefaction of xylan as treated by hot-compressed water and hydrogen peroxide under pressurization of carbon dioxide, it was revealed that yield of furfural is higher than those obtained from treatment under pressurization of nitrogen, because the high proportion of mono-saccharides at 190°C so that the occurred mono-saccharides can be easily dehydrated compared to oligo-saccharide.

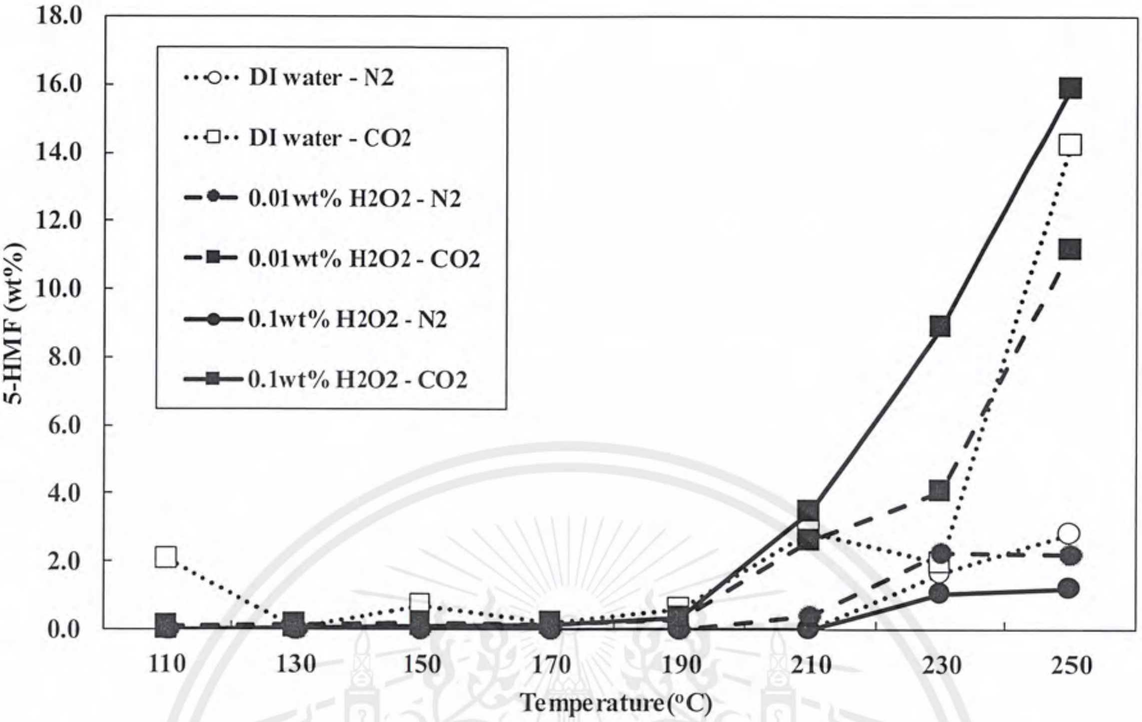


Figure 4.12 5-HMF from liquefaction of xylan as treated by different hydrothermal methods at various temperature

5-HMF is dehydrated product from 6-carbon saccharides that occurs at the high temperature. As for the treatment using hot-compressed water and hydrogen peroxide under pressurization of carbon dioxide or nitrogen, it was found that yield of 5-MHF increases at the temperature over 190°C. The experimental result revealed that yield of 5-HMF produced for the treatment under the pressurization of carbon dioxide is higher than those obtained from treatment under pressurization of nitrogen, because of the high proportion of mono-saccharides that can be easier dehydrate than oligo-saccharides.

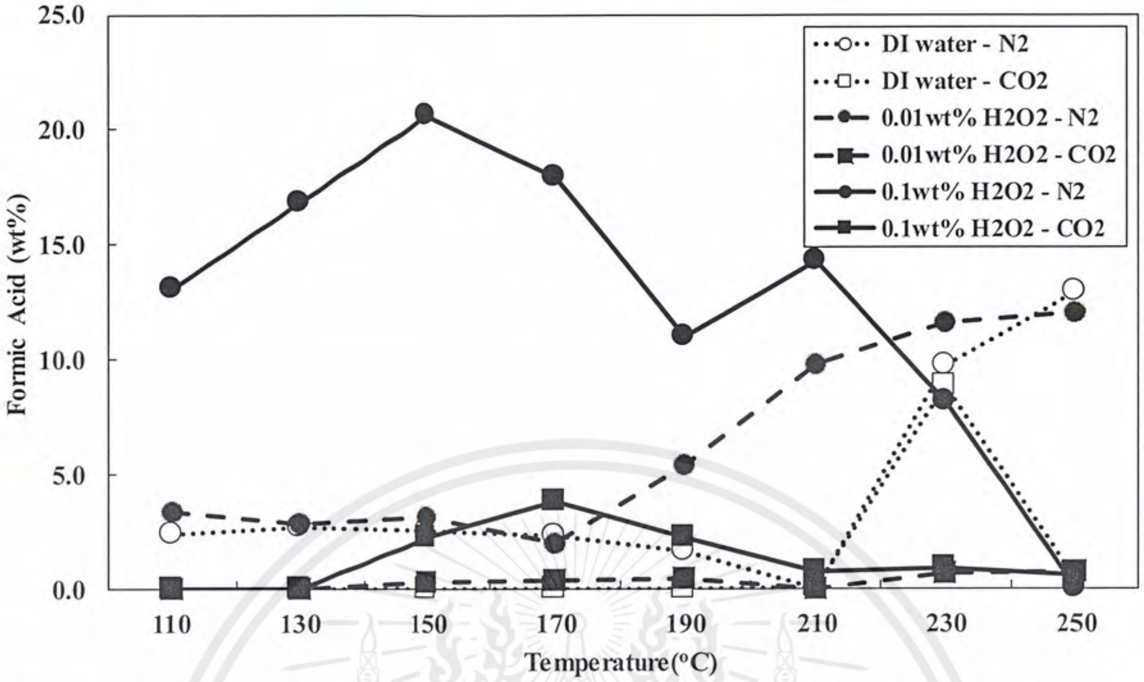


Figure 4.13 Formic acid from liquefaction of xylan as treated by different hydrothermal methods at various temperature

Formic acid is product that obtained from hydrolysis of acetic acid. According to Figure 4.4 and 4.13, yield of formic acid is increased as the decreases of acetic yield. Based on the experimental result, it was found that yield of xylo-saccharides was high for the liquefaction of xylose as treated by hot-compressed water and hydrogen peroxide under pressurization of nitrogen because acetic acid occurred was high compared to those obtained from the treatment under pressurization of carbon dioxide. On the on the hand, the treatment under pressurization of carbon dioxide revealed that yield of acetic acid is low so that there is no acetic acid to be converted to formic acid.

4.3 Mass Balance on various products from xylan as treated by different hydro thermal methods

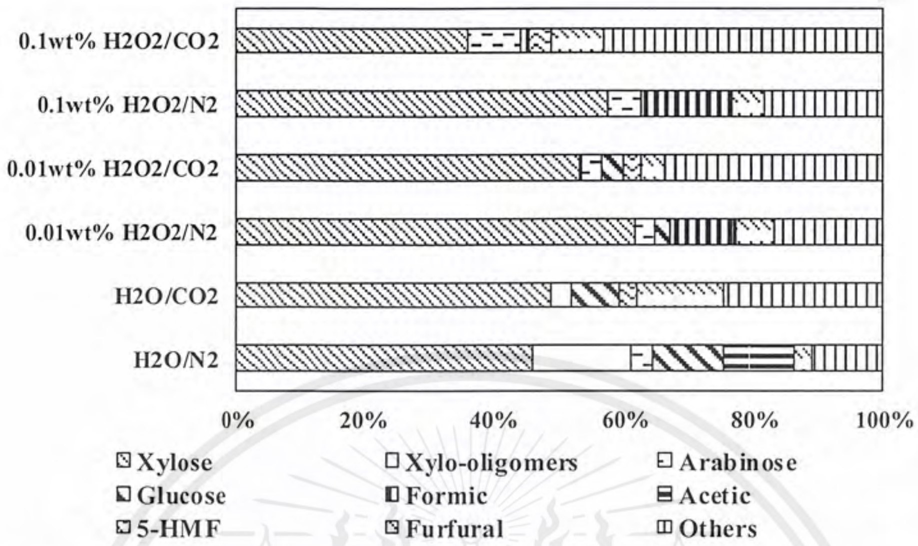


Figure 4.14 Mass balance of all products from xylan as treated by different hydrothermal methods at 210 °C

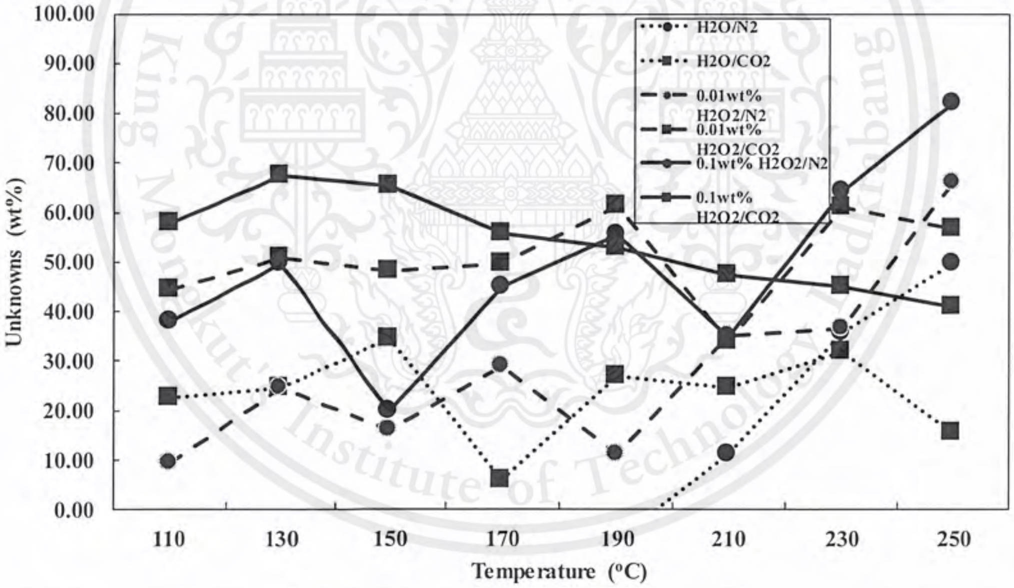


Figure 4.15 Unknowns from liquefaction of xylan as treated by different hydrothermal methods at various temperature

According to Figure 4.14, it was found that formic acid was increased as the increases of hydrogen peroxide concentration, because oxidation reaction becomes dominated. The unknowns in Figure 4.15, which can be unidentified compounds and gaseous products, were increased as the temperature and concentration of hydrogen peroxide increase, led to the formation of peroxy carbonic acid, a strong oxidizing agent, so that the severe degree of oxidation could be the cause of higher yields of unknowns.

4.4 Decomposition Pathway of Xylan under the Studied Hydrothermal Methods

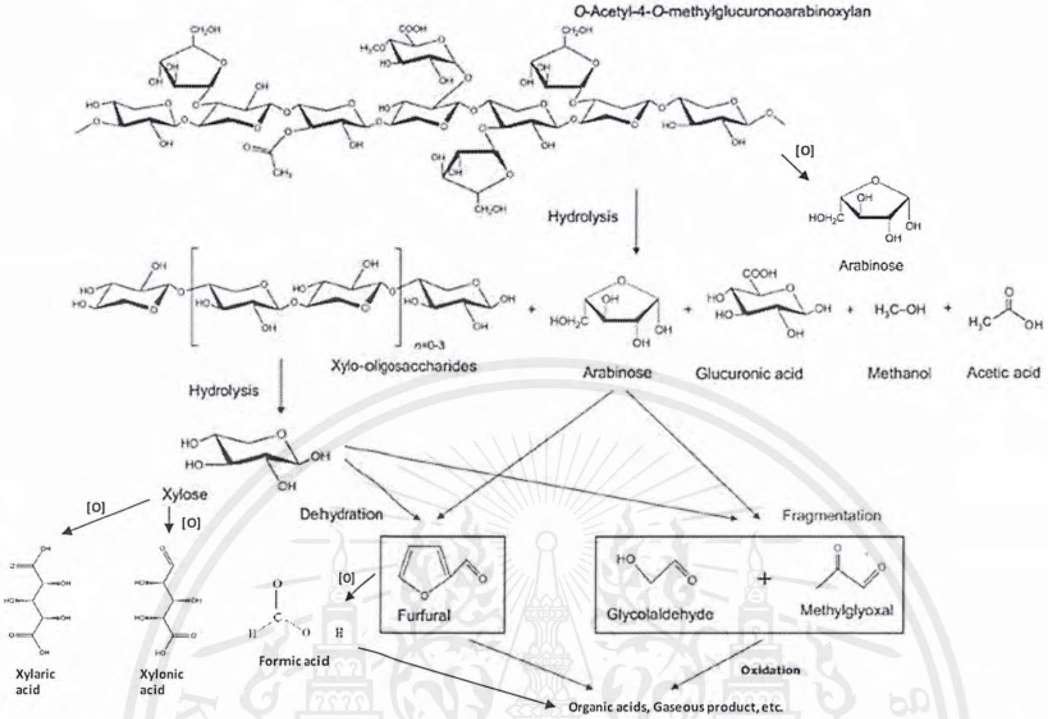


Figure 4.16 Decomposition pathway of O-Acetyl-4-O-methylglucuronoarabinoxylanas as treated by different hydrothermal methods in this research (Phaiboonsilapa et al.,2011; modified)

Phaiboonsilapa et al. (2011) revealed decomposition path way of hemicelluloses from nipa frond as shown in Figure 4.16, when sugarcane bagasse was hydrolyzed by liquid hot-compressed water method, xylan which could be the main structure of O-Acetyl-4-O-methylglucuronoarabinoxylan (hemicellulose) was hydrolyzed to be xylo-saccharides as soluble product. As the continuity of the hydrolysis reaction, xylo-saccharide will be hydrolyzed to be xylo-oligosaccharides and xylose respectively, as well as arabinose and glucuronic acid will be in monomer form. However, the monomer and mono saccharides can be converted to other by-product such as furfural, glycolaldehyde, methylglyoxal and organic acid and gaseous because of high degree of decomposition.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

From a comparative study on liquefaction of xylan as treated by six different hydrothermal methods over the temperature range of 110-250°C, it could be concluded that xylan was liquefied to xylose and xylo-oligosaccharides, also arabinose, glucose and acetic acid from other hemicellulosic components remaining in xylan structure used in this study. Decomposed compounds such as furans and organic acids were also found. The appropriate temperature, at which the highest xylo-saccharides was attained, for all hydrothermal methods were the same at 210°C, except for the method using 0.1wt% hydrogen peroxide which the highest yield was at 190°C. At this temperature, the obtained xylose yields were 46.09, 61.63 and 57.44wt% as treated by water, hot-compressed 0.01wt% hydrogen peroxide, and 0.1wt% hydrogen peroxide under pressurization of nitrogen, respectively. On the other hand, when using carbon dioxide as the atmosphere, the xylose yields were 48.83, 52.9 and 41.39wt%, respectively.

Among six different hydrothermal methods it was found that yield of xylo-saccharides obtained from the methods using hot-compressed water under pressurization of carbon dioxide is higher than those obtained from the methods using hot-compressed water under pressurization of nitrogen due to the acid-catalytic effect of carbonic acid formed during the carbon dioxide treatment at elevated temperature. As for the method using hot-compressed 0.01 and 0.1wt% hydrogen peroxide solutions under pressurization of carbon dioxide, it was found that yield of xylo-saccharides was lower than those obtained from the method using hydrogen peroxide under solutions pressurization of nitrogen because the presence of peroxy carbonic, a strong oxidizing agent, led to the severe degree of oxidation, ended up with lower yield of xylo-saccharides.

In addition, yields of hydroxy methylfurfural, furfural and formic were found to be increased because of high intensity of decomposition and dehydration. The production of decomposed compounds was more pronounced in the treatment with addition of hydrogen peroxide. Under oxidation-dominated conditions, arabinose and acetic acid were remarkably founded to be highly liberated from arabinose and acetyl residues linked to the xylan backbone. Base on the obtained results, the decomposition pathway of xylan under the studied hydrothermal conditions could be established. The effect of hydrolysis- and/or oxidation-dominated treatment on the distribution of liquefied products were clearly explained. Through these lines of this comparative study, it would help provide a clear perception on different liquefaction behaviors of xylan under different hydrothermal treatment conditions. Their appropriate applications would be consequently revealed by considering a variety of liquefied products obtained under different hydrothermal conditions.

5.2 Recommendation

5.2.1 Researcher recommends to study for the appropriate concentration of hydrogen peroxide, because high concentration of hydrogen peroxide led to the excessive degree of oxidation and ended up with lower yield of xylo-saccharides.

5.2.2 Researcher recommends to identify chemical compositions of xylan by using an appropriate method which could give a precise and accurate result rather than

Klason lignin determination in order to calculated recoverable yield of xylo-saccharides correctly.

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Appendix

Appendix A

Calculation

1. Calculation of Chemical Composition in Xylan

Example 1 Calculate amount of xylose and xylo-saccharides obtained from liquefaction of xylan using hot-compressed water under pressurization of CO_2 at 210 °C volume 6 ml

Area under chromatogram obtained from analysis of hydrolysate and hydrolysate from post-hydrolysis is 925,559 and 111,399 respectively. Calibration curve show relationship between area under chromatogram and concentration of xylose in figure B.2 is $Y = 2.6210X$

where Y is concentration of xylose (mg/ml)
X is area under chromatogram
substitution $Y = 2.6210 \times (925{,}559 \times 10^{-6})$
$Y = 2.4259$ mg/ml
Amount of xylose in 6 ml of hydrolysate $= 2.4259 \times 6$ mg
$= 14.5553$ mg
$= 0.0146$ g
Therefore, amount of xylose in hydrolysate is 0.0146 g

Amount of xylo-saccharides was determined from amount of xylose in 10-time diluted hydrolysate from post-hydrolysis

substitution $Y = 2.6210 \times (111{,}399 \times 10^{-6}) \times 10$
$Y = 2.920$ mg/ml
Amount of xylose in 6 ml of hydrolysate $= 2.920 \times 6$ mg
$= 17.5186$ mg
$= 0.0175$ g
Therefore, amount of xylo-saccharides in hydrolysate is 0.0175 g

2. Calculation of Yield and Recovery of Xylose

$$\text{\% Yield of xylose} = \frac{\text{Amount of analyzed xylose(g)}}{\text{Initial amount of xylan(g)}} \times 100$$

$$\text{\% Recovery of xylose} = \text{Yield of xylose(wt\%)} \times 0.88$$

Example 2 Calculate yield and recovery of xylose from hydrolysate from liquefaction of xylan using hot-compressed water under pressurization of CO_2 at 210°C. The initial amount of xylan is 0.0255 g

$$\text{\% Yield of xylose} = \frac{0.0150}{0.0255} \times 100 = 58.78 \text{ wt\%}$$

$$\text{\% Recovery of xylose} = 58.78 \times 0.88 = 51.72 \text{ wt\%}$$

Appendix B

Raw Data

1. Calibration curve for calculate concentration of reducing sugar and by-product from chromatogram

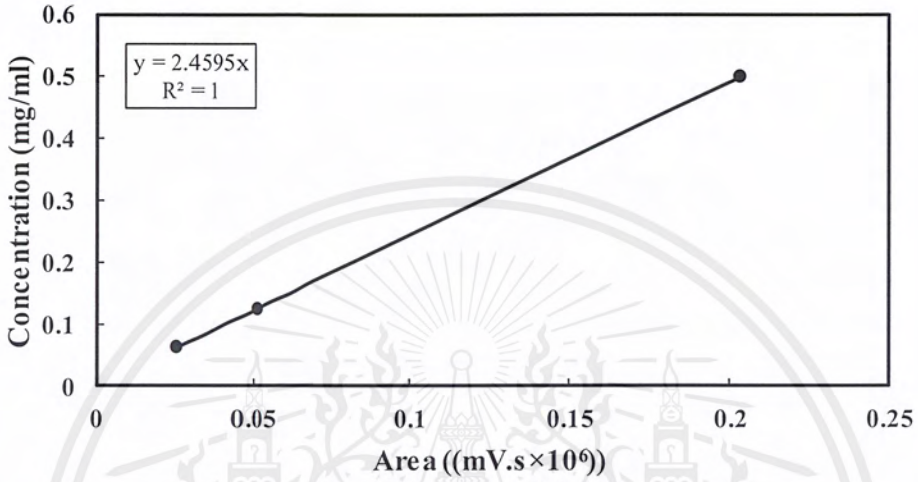

Figure B.1 Calibration curve of HPLC chromatogram peak area and concentration of glucose

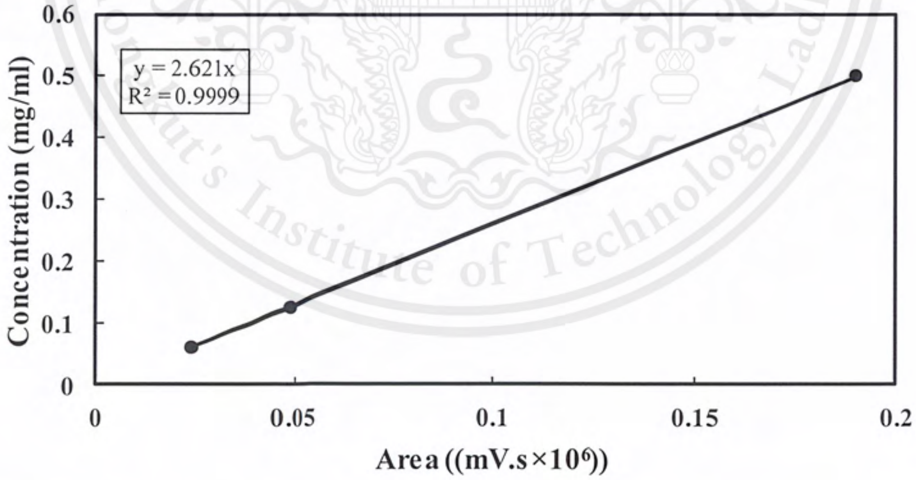

Figure B.2 Calibration curve of HPLC chromatogram peak area and concentration of xylose

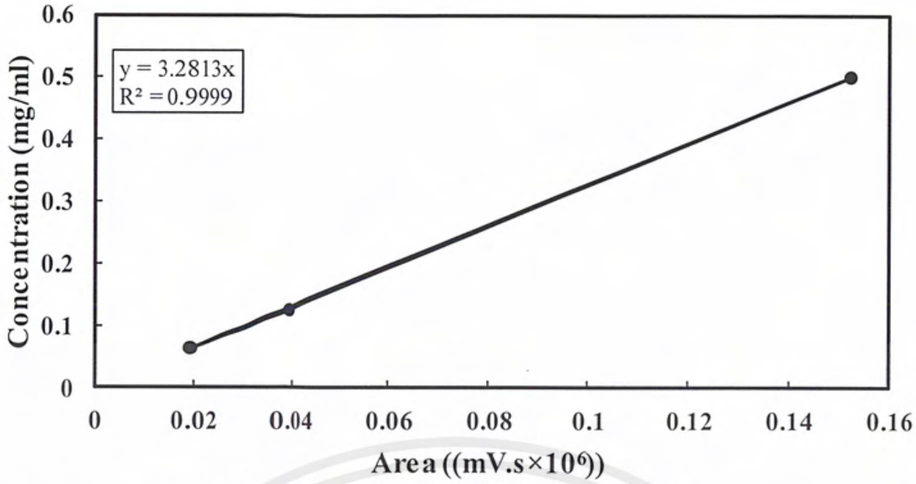

Figure B.3 Calibration curve of HPLC chromatogram peak area and concentration of arabinose

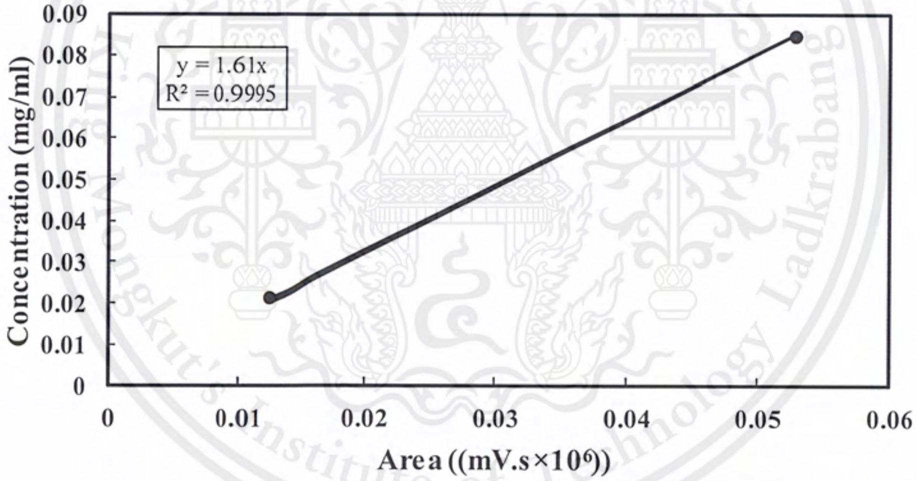

Figure B.4 Calibration curve of HPLC chromatogram peak area and concentration of formic

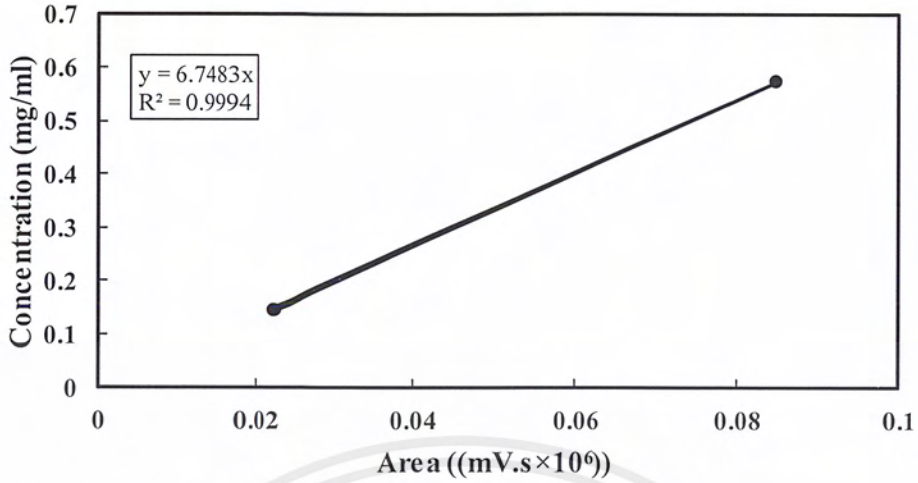

Figure B.5 Calibration curve of HPLC chromatogram peak area and concentration of acetic acid

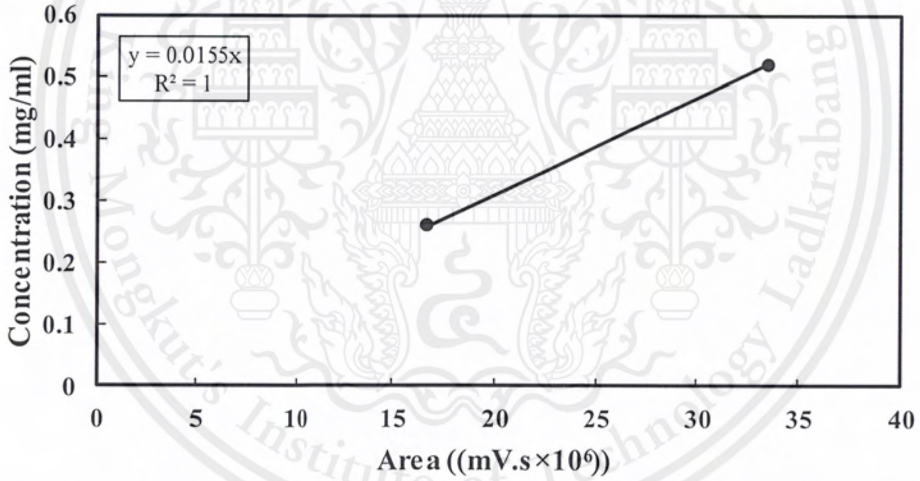

Figure B.6 Calibration curve of HPLC chromatogram peak area and concentration of furfural

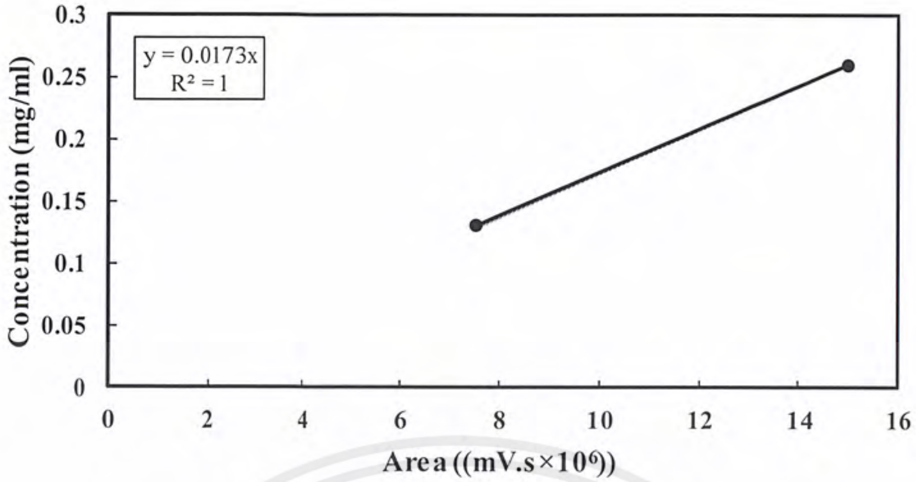

Figure B.7 Calibration curve of HPLC chromatogram peak area and concentration of hydroxy methylfurfural

2. Area under chromatogram

Table B.1 HPLC chromatogram peak area of standard solutions and their corresponding concentrations

Standard solution	Concentration (mg/ml)	Area under chromatogram						
		Glucose	Xylose	Arabinose	Formic	Acetic acid	Furfural	Hydroxy methyl furfural
Glucose	0.5000	203,201	-	-	-	-		-
	0.1250	51,057	-	-	-	-	-	-
	0.0625	25,694	-	-	-	-	-	-
Xylose	0.5000	-	190,347	-	-	-	-	-
	0.1250	-	49,001	-	-	-	-	-
	0.0625	-	24,479	-	-	-	-	-
Arabinose	0.5000	-	-	152,116	-	-	-	-
	0.1250	-	-	39,153	-	-	-	-
	0.0625	-	-	18,954	-	-	-	-
Formic	0.0850	-	-	-	52,936	-	-	-
	0.0213	-	-	-	12,606	-	-	-
Acetic acid	0.5750	-	-	-	-	84,930	-	-
	0.1438	-	-	-	-	22,353	-	-
Furfural	0.5200	-	-	-	-	-	33,475,843	-
	0.2600	-	-	-	-	-	16,774,804	-
Hydroxy methyl furfural	0.2600	-	-	-	-	-	-	14,981,235
	0.1300	-	-	-	-	-	-	7,522,690

Table B.2 HPLC chromatogram peak area of glucose and cello-saccharides from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of nitrogen

Temperature (˚C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Glucose	Cello-saccharides	Glucose	Cello-saccharides	Glucose	Cello-saccharides
110	5,802	10,409	13,455	1,821	11,069	-
130	6,834	10,978	14,383	-	18,754	-
150	6,995	9,849	11,169	1,303	23,884	956
170	10,446	11,073	12,480	-	24,137	-
190	12,913	9,483	25,761	-	25,669	2,199
210	32,490	10,028	57,945	2,140	59,311	-
230	44,723	7,246	56,648	1,090	25,549	-
250	15,711	3,466	16,715	-	9,539	-

Table B.3 HPLC chromatogram peak area of glucose and cello-saccharides from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of carbon dioxide

Temperature (˚C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Glucose	Cello-saccharides	Glucose	Cello-saccharides	Glucose	Cello-saccharides
110	14,962	16,702	10,297	2,525	-	-
130	15,271	16,861	-	2,057	-	-
150	8,490	14,660	26,469	-	-	-
170	16,968	22,838	22,531	-	43,698	-
190	31,069	14,153	33,881	-	61,627	-
210	64,022	16,772	92,848	2,982	96,449	-
230	53,723	9,356	53,457	-	90,789	-
250	73,130	7,009	28,899	-	16,860	-

Table B.4 HPLC chromatogram peak area of xylose and xylo-saccharides from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of nitrogen

Temperature (˚C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Xylose	Xylo-saccharides	Xylose	Xylose-saccharides	Xylose	Xylo-saccharides
110	3,064	64,029	13,133	13,133	3,212	6,806
130	6,429	70,406	10,576	10,576	3,966	3,966
150	5,391	58,318	11,797	11,797	8,878	8,878
170	31,872	62,982	11,005	11,005	5,880	5,880
190	114,995	59,551	8,041	8,570	6,231	6,231
210	345,204	51,858	9,000	10,261	9,422	9,535
230	267,229	25,956	6,640	6,640	2,045	4,044
250	40,506	6,634	405	405	402	1,237

Table B.5 HPLC chromatogram peak area of xylose and xylo-saccharides from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of carbon dioxide

Temperature (˚C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Xylose	Xylo-saccharides	Xylose	Xylose-saccharides	Xylose	Xylo-saccharides
110	6,475	148,597	9,255	12,118	35,892	9,713
130	15,639	145,000	17,300	10,795	53,890	6,836
150	44,041	125,162	76,102	11,357	181,175	5,466
170	219,715	173,724	307,883	10,675	365,277	6,408
190	616,198	126,448	441,342	8,244	681,647	3,505
210	925,559	111,399	1,018,228	12,594	672,279	7,403
230	298,772	31,163	421,272	2,194	453,337	1,248
250	442,061	22,823	76,999	-	51,184	-

Table B.6 HPLC chromatogram peak area of arabinose and total arabinose from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of nitrogen

Temperature (˚C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Arabinose	Total arabinose	Arabinose	Total arabinose	Arabinose	Total arabinose
110	1,374	-	-	-	-	-
130	-	-	-	-	15,341	-
150	1,477	-	-	-	22,501	-
170	10,752	-	13,327	-	33,344	-
190	12,270	-	27,547	-	37,070	-
210	28,256	-	26,317	-	41,598	-
230	-	-	21,569	-	-	-
250	-	-	-	-	-	-

Table B.7 HPLC chromatogram peak area of arabinose and total arabinose from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of carbon dioxide

Temperature (˚C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Arabinose	Total arabinose	Arabinose	Total arabinose	Arabinose	Total arabinose
110	-	-	-	-	-	-
130	-	4,696	-	-	46,751	-
150	2,946	-	20,230	-	90,491	-
170	11,546	-	42,477	-	127,020	-
190	39,973	-	-	-	100,674	-
210	-	-	59,997	-	141,904	-
230	-	-	-	-	195,660	-
250	-	-	-	-	43,325	-

Table B.8 HPLC chromatogram peak area of organic acids from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of nitrogen

Temperature (˚C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Formic	Acetic acid	Formic	Acetic acid	Formic	Acetic acid
110	18,514	215,537	27,172	241,442	102,882	154,181
130	21,533	233,698	22,324	207,807	132,682	114,644
150	19,786	199,502	24,621	222,829	166,694	146,360
170	18,590	210,704	16,119	168,866	143,579	65,723
190	13,108	174,558	42,844	54,560	88,763	-
210	-	86,153	78,861	-	112,723	-
230	76,957	-	91,619	-	64,767	-
250	104,266	5,960	93,683	-	-	-

Table B.9 HPLC chromatogram peak area of organic acids from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of carbon dioxide

Temperature (˚C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Formic	Acetic acid	Formic	Acetic acid	Formic	Acetic acid
110	-	-	-	-	-	-
130	-	-	-	-	-	-
150	-	-	7,204	1,524	59,540	14,881
170	-	-	27,794	5,556	101,628	22,875
190	-	-	36,765	4,968	60,622	14,415
210	9,323	-	-	-	77,945	26,471
230	63,610	-	57,848	10,672	99,526	32,181
250	39,109	-	64,684	18,862	67,183	14,170

Table B.10 HPLC chromatogram peak area of dehydrated compounds from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of nitrogen

Temperature (°C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Furfural	Hydroxy methyl furfural	Furfural	Hydroxy methyl furfural	Furfural	Hydroxy methyl furfural
110	-	-	-	-	-	-
130	-	-	-	-	-	-
150	-	-	-	-	-	-
170	-	-	-	-	-	-
190	13,900	-	-	-	3,122	-
210	25,046	-	53,071	4,114	41,843	-
230	126,263	16,418	148,430	21,929	80,673	10,134
250	198,225	28,080	154,930	21,439	99,548	11,704

Table B.11 HPLC chromatogram peak area of dehydrated compounds from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of carbon dioxide

Temperature (°C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Furfural	Hydroxy methyl furfural	Furfural	Hydroxy methyl furfural	Furfural	Hydroxy methyl furfural
110	525,337	2,885,242	314,537	104,941	498,686	-
130	637,198	84,077	370,576	199,262	570,267	68,534
150	494,614	935,533	3,889,966	536,245	1,589,162	187,275
170	2,960,646	284,226	3,357,152	355,542	3,002,613	338,493
190	11,326,857	818,795	12,149,116	812,886	16,083,518	894,682
210	36,786,973	3,920,138	10,712,653	3,635,713	20,918,751	4,686,655
230	141,852	16,270	149,377,155	10,982,095	43,575,912	12,272,721
250	152,323,452	19,306,856	290,980,190	30,447,910	96,736,920	21,673,718

3. Mass balance on various products and amount of reducing sugar and by-product from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of nitrogen or carbon dioxide

Table B.12 Summary of various products from xylan as treated by hot-compressed water under pressurization of nitrogen

Temp. (˚C)	Hydrolyzed saccharides			Organic acids		Dehydrated compounds		Total*	Unknowns
	Cello-saccharide	Xylo-saccharide	Arabinose	Formic	Acetic	5-HMF	Furfural		
110	11.68	76.42	0.17	2.36	27.44	0.00	0.00	118.05	-18.05
130	11.98	81.76	0.00	2.67	28.94	0.00	0.00	125.35	-25.35
150	11.00	69.33	0.18	2.51	25.29	0.00	0.00	108.31	-8.31
170	12.13	73.42	1.27	2.31	26.20	0.00	0.00	115.33	-15.33
190	10.39	69.42	1.44	1.63	21.70	0.00	1.57	106.16	-6.16
210	11.07	60.92	3.35	0.00	10.80	0.00	2.85	88.99	11.01
230	8.03	30.61	0.00	9.69	0.00	1.67	14.41	64.41	35.59
250	3.78	7.70	0.00	12.92	0.74	2.81	22.27	50.23	49.77

The asterisk (*) marked on total indicates that total yield is over 100wt% cause by error from analysis and calculation.

Table B.13 Summary of various products from xylan as treated by hot-compressed water under pressurization of carbon dioxide

Temp. (°C)	Hydrolyzed saccharides			Organic acids		Dehydrated compounds		Total	Unknowns
	Cello-saccharide	Xylo-saccharide	Arabinose	Formic	Acetic	5-HMF	Furfural		
110	7.22	67.93	0.00	0.00	0.00	2.07	0.19	77.41	22.59
130	7.43	67.59	0.00	0.00	0.00	0.06	0.23	75.32	24.68
150	6.44	58.11	0.16	0.00	0.00	0.68	0.18	65.58	34.42
170	10.19	81.95	0.65	0.00	0.00	0.21	1.10	94.10	5.90
190	6.32	59.65	2.26	0.00	0.00	0.60	4.20	73.02	26.98
210	7.37	51.72	0.00	0.08	0.00	2.85	13.42	75.44	24.56
230	4.05	36.74	0.00	8.79	0.00	1.96	16.75	68.28	31.72
250	3.11	10.72	0.00	0.36	0.00	14.20	56.21	84.61	15.39

According to the table B.12 and B.13, liquefaction of xylose as treated by hot-compressed water under pressurization of carbon dioxide or nitrogen was revealed that xylo-saccharides is the highest product from these treatments. As the increases of temperature, it was found that the total product is decreased because of high degree of decomposition, so that the product that occurred in gas phase was not be identified in this experiment.

Table B.14 Summary of various products from xylan as treated by hot-compressed 0.01wt% of hydrogen peroxide solution under pressurization of nitrogen

Temp. (°C)	Hydrolyzed saccharides			Organic acids		Dehydrated compounds		Total	Unknowns
	Cello-saccharide	Xylo-saccharide	Arabinose	Formic	Acetic	5-HMF	Furfural		
110	1.99	55.51	0.00	3.37	29.90	0.00	0.00	90.77	9.23
130	0.00	46.13	0.00	2.85	26.56	0.00	0.00	75.54	24.46
150	1.46	51.05	0.00	3.12	28.25	0.00	0.00	83.88	16.12
170	0.00	46.52	1.56	2.00	20.91	0.00	0.00	70.99	29.01
190	0.00	73.30	3.27	5.37	6.84	0.00	0.00	88.77	11.23
210	2.34	43.37	3.09	9.77	0.00	0.41	5.96	64.94	35.06
230	1.22	28.73	2.59	11.62	0.00	2.25	17.07	63.48	36.52
250	0.00	1.77	0.00	12.03	0.00	2.23	18.03	34.06	65.94

Table B.15 Summary of various products from xylan as treated by hot-compressed 0.01wt% of hydrogen peroxide solution under pressurization of carbon dioxide

Temp. (˚C)	Hydrolyzed saccharides			Organic acids		Dehydrated compounds		Total	Unknowns
	Cello-saccharide	Xylo-saccharide	Arabinose	Formic	Acetic	5-HMF	Furfural		
110	2.83	52.64	0.00	0.00	0.00	0.08	0.12	55.67	44.33
130	2.29	46.53	0.00	0.00	0.00	0.15	0.14	49.10	50.90
150	0.00	48.19	1.36	0.27	0.24	0.22	1.40	51.68	48.32
170	0.00	46.38	2.31	0.34	0.79	0.13	0.32	50.26	49.74
190	0.00	36.10	0.00	0.45	0.71	0.31	1.17	38.74	61.26
210	3.25	53.23	3.28	0.00	0.00	2.60	3.85	66.22	33.78
230	0.00	18.76	0.00	0.70	1.49	4.07	14.00	39.02	60.98
250	0.00	1.84	0.00	0.77	2.61	11.14	26.96	43.33	56.67

According to the table B.14 and B.15, liquefaction of xylose as treated by hot-compressed 0.01wt% of hydrogen peroxide under pressurization of carbon dioxide or nitrogen was revealed that xylo-saccharides is the highest product from these treatments. As the increases of temperature, it was found that the total product is decreased because of high degree of decomposition, so that the product that occurred in gas phase was not be identified in this experiment. The treatment under pressurization of carbon oxide revealed that the unknown products were higher compared to those obtained from the treatment under pressurization of nitrogen, because of the high in intensity of liquefaction.

Table B.16 Summary of various products from xylan as treated by hot-compressed 0.1wt% of hydrogen peroxide solution under pressurization of nitrogen

Temp. (˚C)	Hydrolyzed saccharides			Organic acids		Dehydrated compounds		Total	Unknowns
	Cello-saccharide	Xylo-saccharide	Arabinose	Formic	Acetic	5-HMF	Furfural		
110	0.00	29.45	0.00	13.05	19.55	0.00	0.00	62.05	37.95
130	0.00	17.16	1.84	16.83	14.54	0.00	0.00	50.37	49.63
150	1.04	37.53	2.64	20.66	18.13	0.00	0.00	79.99	20.01
170	0.00	25.05	3.94	17.93	8.20	0.00	0.00	55.12	44.88
190	2.40	26.34	4.35	11.00	0.00	0.00	0.35	44.43	55.57
210	0.00	41.26	4.99	14.30	0.00	0.00	4.81	65.36	34.64
230	0.00	17.43	0.00	8.18	0.00	1.04	9.24	35.89	64.11
250	0.00	5.35	0.00	0.00	0.00	1.20	11.45	18.00	82.00

Table B.17 Summary of various products from xylan as treated by hot-compressed 0.1wt% of hydrogen peroxide solution under pressurization of carbon dioxide

Temp. (°C)	Hydrolyzed saccharides			Organic acids		Dehydrated compounds		Total	Unknowns
	Cello-saccharide	Xylo-saccharide	Arabinose	Formic	Acetic	5-HMF	Furfural		
110	0.00	42.03	0.00	0.00	0.00	0.00	0.18	42.21	57.79
130	0.00	29.70	2.63	0.00	0.00	0.05	0.21	32.59	67.41
150	0.00	23.28	6.10	2.24	2.34	0.08	0.58	34.62	65.38
170	0.00	27.09	8.50	3.79	3.58	0.14	1.08	44.16	55.84
190	0.00	29.63	6.73	2.26	2.25	0.36	5.78	47.01	52.99
210	0.00	32.42	8.04	0.72	0.35	3.48	7.78	52.78	47.22
230	0.00	18.17	10.82	0.89	0.42	8.89	15.83	55.02	44.98
250	0.00	4.46	2.42	0.61	0.19	15.88	35.56	59.12	40.88

According to the table B.16 and B.17, liquefaction of xylose as treated by 0.1wt% of hydrogen peroxide under pressurization of carbon dioxide or nitrogen was revealed that xylo-saccharides is the highest product from these treatments. As the increases of temperature, it was found that the total product is decreased because of high degree of decomposition, so that the product that occurred in gas phase was not be identified in this experiment. The treatment under pressurization of carbon oxide revealed that the unknown products were higher compared to those obtained from the treatment under pressurization of nitrogen, because of the high in intensity of liquefaction and oxidation, ends up with the low yield of xylo-saccharides.

Table B.18 Proportional yield of glucose, cello-oligosaccharides and cello-saccharides from liquefaction of xylan using hot-compressed water under pressurization of carbon nitrogen

Temperature (°C)	Glucose (% recovery)	Cello-oligosaccharides (% recovery)	Cello-saccharides (% recovery)
110	0.72 (5.57%)	12.25 (94.43%)	12.97 (100%)
130	0.83 (6.23%)	12.48 (93.77%)	13.31 (100%)
150	0.87 (7.10%)	11.36 (92.90%)	12.23 (100%)
170	1.2716 (9.43%)	12.21 (90.57%)	13.48 (100%)
190	1.57 (13.62%)	9.97 (86.38%)	11.54 (100%)
210	3.99 (32.40%)	8.32 (67.60%)	12.30 (100%)
230	5.51 (61.72%)	3.42 (38.28%)	8.92 (100%)
250	1.91 (45.33%)	2.30 (54.67%)	4.20 (100%)

Table B.19 Proportional yield of glucose, cello-oligosaccharides and cello-saccharides from liquefaction of xylan using hot-compressed water under pressurization of carbon dioxide

Temperature (°C)	Glucose (% recovery)	Cello-oligosaccharides (% recovery)	Cello-saccharides (% recovery)
110	0.72 (8.96%)	7.31 (91.04%)	8.02 (100%)
130	0.75 (9.06%)	7.51 (91.04%)	8.26 (100%)
150	0.41 (5.79%)	6.74 (94.21%)	7.15 (100%)
170	0.84 (7.43%)	10.48 (92.57%)	11.32 (100%)
190	1.54 (21.95%)	5.48 (78.05%)	7.02 (100%)
210	3.12 (38.17%)	5.06 (61.83%)	8.18 (100%)
230	6.89 (100%)	0.00	6.89 (100%)
250	3.61 (100%)	0.00	3.61 (100%)

Table B.20 Proportional yield of glucose, cello-oligosaccharides and cello-saccharides from liquefaction of xylan using hot-compressed 0.01wt% hydrogen peroxide under pressurization of nitrogen

Temperature (˚C)	Glucose (% recovery)	Cello-oligosaccharides (% recovery)	Cello-saccharides (% recovery)
110	1.63 (73.89%)	0.58 (26.11%)	2.21 (100%)
130	1.80 (100%)	0.00	1.80 (100%)
150	1.39 (85.72%)	0.23 (14.28%)	1.62 (100%)
170	1.51 (100%)	0.00	1.51 (100%)
190	3.16 (100%)	0.00	3.16 (100%)
210	7.03 (100%)	0.00	7.03 (100%)
230	7.03 (100%)	0.00	7.03 (100%)
250	2.10 (100%)	0.00	2.10 (100%)

Table B.21 Proportional yield of glucose, cello-oligosaccharides and cello-saccharides from liquefaction of xylan using hot-compressed 0.01wt% hydrogen peroxide pressurization of carbon dioxide

Temperature (˚C)	Glucose (% recovery)	Cello-oligosaccharides (% recovery)	Cello-saccharides (% recovery)
110	0.51 (16.16%)	2.64 (83.84%)	3.15 (100%)
130	0.00 (0%)	2.54 (100%)	2.54 (100%)
150	1.51 (100%)	0.00	1.51 (100%)
170	1.50 (100%)	0.00	1.50 (100%)
190	2.28 (100%)	0.00	2.28 (100%)
210	4.46 (100%)	0.00	4.46 (100%)
230	3.51 (100%)	0.00	3.51 (100%)
250	1.88 (100%)	0.00	1.88 (100%)

Table B.22 Proportional yield of glucose, cello-oligosaccharides and cello-saccharides from liquefaction of xylan using 0.1wt% hydrogen peroxide pressurization under pressurization of nitrogen

Temperature (˚C)	Glucose (% recovery)	Cello-oligosaccharides (% recovery)	Cello-saccharides (% recovery)
110	1.37 (100%)	0.00	1.37 (100%)
130	2.33 (100%)	0.00	2.33 (100%)
150	2.90 (100%)	0.00	2.90 (100%)
170	2.95 (100%)	0.00	2.95 (100%)
190	3.11 (100%)	0.00	3.11 (100%)
210	7.36 (100%)	0.00	7.36 (100%)
230	3.16 (100%)	0.00	3.16 (100%)
250	1.18 (100%)	0.00	1.18 (100%)

Table B.23 Proportional yield of glucose, cello-oligosaccharides and cello-saccharides from liquefaction of xylan using 0.1wt% hydrogen peroxide pressurization under pressurization of carbon dioxide

Temperature (˚C)	Glucose (% recovery)	Cello-oligosaccharides (% recovery)	Cello-saccharides (% recovery)
110	0.00	0.00	0.00
130	0.00	0.00	0.00
150	0.00	0.00	0.00
170	2.49 (100%)	0.00	2.49 (100%)
190	3.51 (100%)	0.00	3.51 (100%)
210	4.80 (100%)	0.00	4.80 (100%)
230	4.41 (100%)	0.00	4.41 (100%)
250	0.83 (100%)	0.00	0.83 (100%)

Table B.24 Proportional yield of xylose, xylo-oligosaccharides and xylo-saccharides from liquefaction of xylan using hot-compressed water under pressurization of nitrogen

Temperature (˚C)	Xylose (% recovery)	Xylo-oligosaccharides (% recovery)	Xylo-saccharides (% recovery)
110	0.42 (0.48%)	86.42 (99.52%)	86.84 (100%)
130	0.85 (0.91%)	92.06 (99.09%)	92.91 (100%)
150	0.73 (0.92%)	78.05 (99.08%)	78.78 (100%)
170	4.22 (5.06%)	79.21 (94.94%)	83.43 (100%)
190	15.23 (19.31%)	63.65 (80.69%)	78.89 (100%)
210	46.09 (66.57%)	23.15 (33.43%)	69.23 (100%)
230	35.82 (100%)	0.00	35.82 (100%)
250	5.35 (61.06%)	3.41 (38.94%)	8.75 (100%)

Table B.25 Proportional yield of xylose, xylo-oligosaccharides and xylo-saccharides from liquefaction of xylan using hot-compressed water under pressurization of carbon dioxide

Temperature (˚C)	Xylose (% recovery)	Xylo-oligosaccharides (% recovery)	Xylo-saccharides (% recovery)
110	0.34 (0.44%)	76.86 (99.56%)	77.19 (100%)
130	0.83 (1.08%)	75.98 (98.92%)	76.81 (100%)
150	2.32 (3.52%)	63.71 (96.48%)	66.04 (100%)
170	11.78 (12.65%)	81.34 (87.35%)	93.12 (100%)
190	33.03 (48.73%)	34.75 (51.27%)	67.78 (100%)
210	48.83 (83.09%)	9.94 (16.91%)	58.78 (100%)
230	40.03 (95.87%)	1.72 (4.13%)	41.75 (100%)
250	23.60 (100%)	0.00	23.60 (100%)

Table B.26 Proportional yield of xylose, xylo-oligosaccharides and xylo-saccharides from liquefaction of xylan using hot-compressed 0.01wt% hydrogen peroxide solution under pressurization of nitrogen

Temperature (˚C)	Xylose (% recovery)	Xylo-oligosaccharides (% recovery)	Xylo-saccharides (% recovery)
110	1.57 (2.98%)	51.22 (97.02%)	52.79 (100%)
130	2.44 (5.56%)	41.43 (94.44%)	43.87 (100%)
150	1.67 (3.44%)	46.87 (96.56%)	48.54 (100%)
170	6.54 (14.80%)	37.69 (85.20%)	44.23 (100%)
190	48.04 (68.93%)	21.66 (31.07%)	69.70 (100%)
210	61.63 (100%)	0.00	61.63 (100%)
230	45.14 (100%)	0.00	45.14 (100%)
250	7.23 (100%)	0.00	7.23 (100%)

Table B.27 Proportional yield of xylose, xylo-oligosaccharides and xylo-saccharides from liquefaction of xylan using hot-compressed 0.01wt% hydrogen peroxide solution under pressurization of carbon dioxide

Temperature (˚C)	Xylose (% recovery)	Xylo-oligosaccharides (% recovery)	Xylo-saccharides (% recovery)
110	0.49 (0.99%)	49.57 (99.01%)	50.06 (100%)
130	0.92 (2.07%)	43.33 (97.93%)	44.24 (100%)
150	4.64 (10.12%)	41.19 (89.88%)	45.83 (100%)
170	21.18 (48.03%)	22.92 (51.97%)	44.10 (100%)
190	30.61 (89.16%)	3.72 (10.84%)	34.33 (100%)
210	52.89 (100%)	0.00	52.89 (100%)
230	28.53 (100%)	0.00	28.53 (100%)
250	5.15 (100%)	0.00	5.15 (100%)

Table B.28 Proportional yield of xylose, xylo-oligosaccharides and xylo-saccharides from liquefaction of xylan using 0.1wt% hydrogen peroxide solution under pressurization of nitrogen

Temperature (˚C)	Xylose (% recovery)	Xylo-oligosaccharides (% recovery)	Xylo-saccharides (% recovery)
110	1.28 (4.56%)	26.73 (95.44%)	28.01 (100%)
130	3.80 (23.26%)	12.52 (76.74%)	16.32 (100%)
150	13.16 (36.88%)	22.52 (63.12%)	35.69 (100%)
170	24.05 (100%)	0.00	23.82 (100%)
190	28.99 (100%)	0.00	28.99 (100%)
210	57.44 (100%)	0.00	57.44 (100%)
230	12.87 (77.66%)	3.70 (22.34%)	16.57 (100%)
250	2.18 (42.86%)	2.91 (57.14%)	5.09 (100%)

Table B.29 Proportional yield of xylose, xylo-oligosaccharides and xylo-saccharides from liquefaction of xylan using 0.1wt% hydrogen peroxide solution under pressurization of carbon dioxide

Temperature (˚C)	Xylose (% recovery)	Xylo-oligosaccharides (% recovery)	Xylo-saccharides (% recovery)
110	1.91 (4.78%)	38.06 (95.22%)	39.97 (100%)
130	2.88 (10.19%)	25.36 (89.81%)	28.24 (100%)
150	11.09 (50.07%)	11.06 (49.93%)	22.14 (100%)
170	22.18 (86.11%)	3.58 (13.89%)	25.76 (100%)
190	41.39 (100%)	0.00	41.39 (100%)
210	36.18 (100%)	0.00	36.18 (100%)
230	23.83 (100%)	0.00	23.83 (100%)
250	2.72 (100%)	0.00	2.72 (100%)

Table B.30 Proportional yield of arabinose and total arabinose from liquefaction of xylan using hot-compressed water under pressurization of nitrogen

Temperature (°C)	Arabinose (% recovery)	Arabinose in form of xylan branch (% recovery)	Total arabinose (% recovery)
110	0.19 (100%)	0.00	0.19 (100%)
130	0.00	0.00	0.00
150	0.20 (100%)	0.00	0.20 (100%)
170	1.44 (100%)	0.00	1.44 (100%)
190	1.64 (100%)	0.00	1.64 (100%)
210	3.81 (100%)	0.00	3.81 (100%)
230	0.00	0.00	0.00
250	0.00	0.00	0.00

Table B.31 Proportional yield of arabinose and total arabinose from liquefaction of xylan using hot-compressed water under pressurization of carbon dioxide

Temperature (°C)	Arabinose (% recovery)	Arabinose in form of xylan branch (% recovery)	Total arabinose (% recovery)
110	0.00	0.00	0.00
130	0.00	2.98 (100%)	2.98 (100%)
150	0.19 (100%)	0.00	0.19 (100%)
170	0.74 (100%)	0.00	0.74 (100%)
190	2.56 (100%)	0.00	2.56 (100%)
210	0.00	0.00	0.00
230	0.00	0.00	0.00
250	0.00	0.00	0.00

Table B.32 Proportional yield of arabinose and total arabinose from liquefaction of xylan using hot-compressed 0.01wt% hydrogen peroxide under pressurization of nitrogen

Temperature (˚C)	Arabinose (% recovery)	Arabinose in form of xylan branch (% recovery)	Total arabinose (% recovery)
110	0.00	0.00	0.00
130	0.00	0.00	0.00
150	0.00	0.00	0.00
170	1.78 (100%)	0.00	1.78 (100%)
190	3.71 (100%)	0.00	3.71 (100%)
210	3.51 (100%)	0.00	3.51 (100%)
230	2.94 (100%)	0.00	2.94 (100%)
250	0.00	0.00	0.00

Table B.33 Proportional yield of arabinose and total arabinose from liquefaction of xylan using hot-compressed 0.01wt% hydrogen peroxide pressurization of carbon dioxide

Temperature (˚C)	Arabinose (% recovery)	Arabinose in form of xylan branch (% recovery)	Total arabinose (% recovery)
110	0.00	0.00	0.00
130	0.00	0.00	0.00
150	1.54 (100%)	0.00	1.54 (100%)
170	2.62 (100%)	0.00	2.62 (100%)
190	0.00	0.00	0.00
210	3.73 (100%)	0.00	3.73 (100%)
230	0.00	0.00	0.00
250	0.00	0.00	0.00

Table B.34 Proportional yield of arabinose and total arabinose from liquefaction of xylan using 0.1wt% hydrogen peroxide pressurization under pressurization of nitrogen

Temperature (°C)	Arabinose (% recovery)	Arabinose in form of xylan branch (% recovery)	Total arabinose (% recovery)
110	0.00	0.00	0.00
130	2.09 (100%)	0.00	2.09 (100%)
150	3.00 (100%)	0.00	3.00 (100%)
170	4.48 (100%)	0.00	4.48 (100%)
190	4.94 (100%)	0.00	4.94 (100%)
210	5.68 (100%)	0.00	5.68 (100%)
230	0.00	0.00	0.00
250	0.00	0.00	0.00

Table B.35 Proportional yield of arabinose and total arabinose from liquefaction of xylan using 0.1wt% hydrogen peroxide pressurization under pressurization of carbon dioxide

Temperature (°C)	Arabinose (% recovery)	Arabinose in form of xylan branch (% recovery)	Total arabinose (% recovery)
110	0.00	0.00	0.00
130	2.99 (100%)	0.00	2.99 (100%)
150	6.93 (100%)	0.00	6.93 (100%)
170	9.66 (100%)	0.00	9.66 (100%)
190	7.65 (100%)	0.00	7.65 (100%)
210	9.13 (100%)	0.00	9.13 (100%)
230	12.30 (100%)	0.00	12.30 (100%)
250	2.76 (100%)	0.00	2.76 (100%)

Table B.36 Yield (wt%) of formic and acetic acid from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of nitrogen

Temperature (°C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Formic	Acetic acid	Formic	Acetic acid	Formic	Acetic acid
110	2.36	27.44	3.37	29.90	13.05	19.55
130	2.67	28.94	2.85	26.56	16.83	14.54
150	2.51	25.29	3.12	28.25	20.66	18.13
170	2.31	26.20	2.00	20.91	17.93	8.20
190	1.63	21.70	5.37	6.84	11.00	0.00
210	0.00	10.80	9.77	0.00	14.30	0.00
230	9.69	0.00	11.62	0.00	8.18	0.00
250	12.92	0.74	12.03	0.00	0.00	0.00

Table B.37 Yield (wt%) of formic and acetic acid from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of carbon dioxide

Temperature (°C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Formic	Acetic acid	Formic	Acetic acid	Formic	Acetic acid
110	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00	0.00	0.00
150	0.00	0.00	0.27	0.24	2.24	2.34
170	0.00	0.00	0.34	0.79	3.79	3.58
190	0.00	0.00	0.45	0.71	2.26	2.25
210	0.08	0.00	0.00	0.00	0.72	0.35
230	8.79	0.00	0.70	1.49	0.89	0.42
250	0.36	0.00	0.77	2.61	0.61	0.19

Table B.38 Yield (wt%) of furfural and hydroxy methyl furfural from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of nitrogen

Temperature (˚C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Furfural	Hydroxy methyl furfural	Furfural	Hydroxy methyl furfural	Furfural	Hydroxy methyl furfural
110	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00	0.00	0.00
150	0.00	0.00	0.00	0.00	0.00	0.00
170	0.00	0.00	0.00	0.00	0.00	0.00
190	1.57	0.00	0.00	0.00	0.35	0.00
210	2.85	0.00	5.96	0.41	4.81	0.00
230	14.41	1.67	17.07	2.25	9.24	1.04
250	22.27	2.81	18.03	2.23	11.45	1.20

Table B.39 Yield (wt%) of furfural and hydroxy methyl furfural from liquefaction of xylan using hot-compressed water, hot-compressed 0.01 and 0.1wt% hydrogen peroxide under pressurization of carbon dioxide

Temperature (˚C)	Hot-compressed water		Hot-compressed 0.01wt% Hydrogen peroxide solution		Hot-compressed 0.1wt% Hydrogen peroxide solution	
	Furfural	Hydroxy methyl furfural	Furfural	Hydroxy methyl furfural	Furfural	Hydroxy methyl furfural
110	0.19	2.07	0.12	0.08	0.00	0.18
130	0.23	0.06	0.14	0.15	0.05	0.21
150	0.18	0.68	1.40	0.22	0.08	0.58
170	1.10	0.21	0.32	0.13	0.14	1.08
190	4.20	0.60	1.17	0.31	0.36	5.78
210	13.42	2.85	3.85	2.60	3.48	7.78
230	16.75	1.96	14.00	4.07	8.89	15.83
250	56.21	14.20	26.96	11.14	15.88	35.56