Department of Chemical Engineering

Mechanism and Kinetics of Cellobiose Decomposition in Hot-Compressed Water

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Declaration

To the best of my knowledge and belief this thesis contain no material previously published by any other person except where due acknowledgement has been made.

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Signature: .....

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To my beloved family

ABSTRACT

Conversion of biomass or biomass-derived liquids in HCW is considered to be a promising technology for the sustainable production of renewable fuels and green chemicals which are currently synthesised from petroleum. However, the yields of target products are low due to the lack of knowledge on fundamental reaction chemistry. Cellulose, as a major model compound of biomass, primarily decomposes in HCW into glucose and its oligomers at various degree of polymerisation. These primary products subsequently experience decomposition reactions into other products. However, apart from glucose, the decomposition of glucose oligomers is still largely unknown. Therefore, the present study aims to understand the fundamental mechanism of glucose oligomers under various conditions, using cellobiose as a model compound.

Firstly, cellobiose decomposition in hot-compressed water (HCW) was investigated at a temperature range of 225−275 °C using a continuous reactor system. The liquid products were characterised by high-performance anion exchange chromatography with pulsed amperometric detection and mass spectrometry (HPAEC-PAD/MS). The importance of isomerisation reactions to form two cellobiose isomers (i.e., cellobiulose and glucosyl-mannose) as the primary reaction products is clearly demonstrated under the reaction conditions. The results also confirm another two primary reactions take place during cellobiose decomposition in HCW: retro-aldol condensation reaction to produce glucosyl-erythrose (GE) and glycolaldehyde, and hydrolysis reaction to produce glucose. Isomerisation reactions dominate the primary reactions of cellobiose decomposition, contributing to 71−87% of cellobiose decomposition depending on reaction conditions. In contrast, cellobiose hydrolysis makes only limited contributions (10−20% depending on reaction conditions) to the primary decomposition of cellobiose. The contribution of retro-aldol condensation reaction is very small (<5%) at 225-275 °C. This indicates that hydroxyl ions have a more significant effect in

catalysing the isomerisation reactions to produce cellobiulose and glucosyl-mannose. The catalytic effect of hydrogen ions is weak probably because of the high affinity of hydrogen ions for water molecules, which reduces the availability of hydrogen ions for catalysing the hydrolysis reaction. At increased temperatures, the affinity of hydrogen ions for water molecules decreases because of the weakened hydrogen bonds in water, leading to an increase in the selectivity of the acid-catalysed hydrolysis reaction. The results indicate that the reaction solution becomes acidic at the early stage of cellobiose decomposition, most likely due to the formation of organic acids, resulting in the subsequent reactions exhibiting more characteristics of acid-catalysed reactions. The results further suggest that the formed acidic products have a little catalytic effect on the primary reactions of cellobiose decomposition, but are effective in catalysing secondary reactions of various reaction intermediates such as hydrolysis and dehydration reactions to form glucose and 5-HMF, respectively.

Secondly, this study further reports a systematic investigation on the primary decomposition mechanism and kinetics of cellobiose in HCW at 200−275 °C and a wide initial concentration range of 10−10,000 mg L^{-1}. Isomerisation reactions are always the dominant primary reactions of cellobiose decomposition in HCW at various initial cellobiose concentrations. However, the selectivities of isomerisation reactions decrease and the selectivity of hydrolysis reaction increases with an increase in initial cellobiose concentration. The enhancement of hydrolysis reaction at high initial cellobiose concentrations due to that there are insufficient amount of hydroxyl ions for all the cellobiose molecules. Therefore, the possibility of hydrogen ion to catalyse cellobiose decomposition is increased via hydrolysis reaction. The increase in the hydrolysis reaction at high initial cellobiose concentrations may also be related to the formation of acidic products at the early stage of cellobiose decomposition. The acidic conditions have little effect on the primary reactions of cellobiose decomposition at low concentrations (<1,000 mg L^{-1}). However, at high concentrations (i.e., 10,000 mg L^{-1}), those acidic products not only promote the decomposition of GF and GM, but also catalyse the primary reactions of cellobiose decomposition at the middle stage of cellobiose decomposition. As a result of the reduced molar ratio of ion product to cellobiose, the activation energies of both isomerisation and hydrolysis reactions

increase with increasing initial concentration, leading to a net increase in the apparent activation energy of cellobiose hydrothermal conversion.

Thirdly, this study investigates the difference in cellobiose decomposition mechanism under non-catalytic and weakly acidic conditions at 200 – 250°C and an initial pH range of 4−7. Similar to cellobiose decomposition under non-catalytic conditions, isomerisation and hydrolysis reactions are the main primary reactions of cellobiose decomposition under weakly acidic conditions. However, the selectivities of isomerisation reactions decrease while the selectivity of hydrolysis reaction increases under acidic conditions. The rate constants of isomerisation reactions under various pH conditions are found to be similar as those under non-catalytic conditions. In contrast, the rate constant of hydrolysis reaction increases significantly with reducing initial pH of cellobiose solution. Therefore, the acceleration of cellobiose decomposition under acidic conditions is mainly due to the increased contribution of hydrolysis reaction. The rate constant of hydrolysis reaction is found to be truly dependent on the hydrogen ion concentration at a reaction temperature. A kinetic model including the isomerisation and hydrolysis reactions, can well predict the cellobiose hydrothermal decomposition under various initial pH conditions at low temperatures (i.e., < 225 °C). However, such a model underestimates the rate constant of cellobiose hydrothermal decomposition at higher temperatures (i.e., 250 °C), probably due to the increased contribution of other reactions such as reversion reaction.

Fourthly, the catalytic effect of alkali and alkaline earth metal (AAEM) chlorides on cellobiose decomposition in hot-compressed water (HCW) was systematically investigated at 200 – 275 °C. The AAEM chlorides strongly catalyse the cellobiose decomposition in HCW, following an order of $MgCl_2$ > $CaCl_2$ > KCl > NaCl. The addition of AAEM chlorides not only enhance the reaction rate, but also change the selectivities of primary reactions of cellobiose decomposition. The isomerisation reactions to cellobiulose and glucosyl-mannose are strongly promoted by AAEM cations, due to their interactions with cellobiose as Lewis acids. The hydrolysis reaction to glucose is also promoted, probably because of the hydrolysis of hydrated

metal complexes to generate H_3O^+ as Brønsted acids. However, such catalytic effect on hydrolysis reaction is weak, resulting in a reduced selectivity of hydrolysis reaction. The AAEM chlorides also selectively catalyse the secondary decomposition of primary products, depending on the Lewis acidity and the Brønsted acidity of AAEM cations. As stronger Lewis acids, the alkaline earth metal cations greatly catalyse the isomerisation reactions of glucose to fructose and mannose, leading to the slower increase in glucose selectivity as cellobiose increases in the $MgCl_2$ and $CaCl_2$ solutions. The hydrolysis reactions of GF and GM are also promoted because of the stronger Brønsted acidity of hydrated metal complexes for Mg^{2+} and Ca^{2+}. Once fructose is formed, its dehydration to 5-HMF and the degradation of 5-HMF are further catalysed by H_3O^+, resulting in a decrease in the 5-HMF selectivity in the $MgCl_2$ and $CaCl_2$ solutions. In contrast, the 5-HMF selectivity is increased in the NaCl and KCl solutions, probably because the degradation of 5-HMF is suppressed due to the weak Brønsted acidity of hydrated metal complexes for Na^+ and K^+. Both the alkali and alkaline earth metal chlorides promote the retro-aldol condensation reaction to form glycolaldehyde.

Overall, the present study provides some new insights into the mechanism of cellobiose decomposition in HCW. This is the first time the formation of two cellobiose isomers (i.e. cellobiulose and glucosyl-mannose) as the primary products during cellobiose decomposition in HCW reported in this field, which clarify the reaction mechanism of cellobiose decomposition in HCW. Temperature, Initial cellobiose concentration, initial pH of solution and the alkali and alkaline earth metal species are found to be significantly influence the mechanism of cellobiose decomposition in HCW. The findings in this thesis have generated valuable knowledge on the fundamental chemistry of secondary reactions of primary products from cellulose and biomass decomposition in HCW.

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LIST OF PUBLICATIONS

Journal Papers

1. **Zainun Mohd Shafie**, Yun Yu, Hongwei Wu. Insights into the Primary Decomposition Mechanism of Cellobiose under Hydrothermal Conditions, Ind. Eng. Chem. Res., 2014, 53 (38), pp 14607–14616.

2. Yun Yu, **Zainun Mohd Shafie**, Hongwei Wu. Cellobiose Decomposition in Hot-Compressed Water: Importance of Isomerisation Reactions. Ind. Eng. Chem. Res., 2013, 52 (47), pp 17006–17014.

3. **Zainun Mohd Shafie**, Yun Yu, Hongwei Wu. Effect of Initial pH on Hydrothermal Decomposition of Cellobiose under weakly acidic conditions. Energy & Fuels, 2015, 158: 315-321.

4. Yun Yu, **Zainun Mohd Shafie**, Hongwei Wu. Effect of Alkali and Alkaline Earth Metal Chlorides on Cellobiose Decomposition in Hot-Compressed Water. Ind. Eng. Chem. Res., 2015, 54(20): 5450-5459.

Conference Paper

1. Yun Yu, **Zainun Mohd Shafie**, Hongwei Wu. Catalytic Effect of $MgCl_2$ on Cellobiose Decomposition in Hot-Compressed Water. APCChE 2015 Congress, 27 September – 1 october 2015, Melbourne, Australia.

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CHAPTER 1 INTRODUCTION

1.1 Background and motive

Since early 20th century, human relies primarily on fossil-based feedstock (i.e. petroleum, coal and natural gas) for supplying energy and synthesising chemicals.[1] Currently, 86% of energy and 96% of chemicals are produced from fossil-based resources worldwide.[2] The increasing global demand for fossil-based fuel causes the rise in the emission of carbon dioxide, i.e., from 20.9 gigatonnes (GT) in 1990 to 28.8GT in 2007, and the emission is predicted to reach 40.2 GT in 2030.[3] Carbon dioxide is one of the main gases contributing to the greenhouse effect, resulting global warming and subsequently climate change. In addition, another global concern is energy security related to the depletion of fossil fuels. Therefore, it is important to develop new technologies for the sustainable production of renewable energy and green chemicals.

Biomass is recognised as one of the most promising sources for producing renewable and environmentally friendly fuels and chemicals. There a few chemicals derived from biomass for example glycerol, sorbitol, 5-hydroxymethylfurfural, levulinic acid and lactic acid, have potential as a platform chemical for THE production of high value green chemicals.[4, 5] Another advantage of biomass is the recycle of carbon dioxide. The carbon dioxide produce during the conversion of biomass is used during photosynthesis process, hence the biomass utilisation contributes little to the increase in the greenhouse gas in the atmosphere.[6] As a result, governments around the world have set ambitious goals for biomass utilisation. For example, the United States intended to produce at least 25% of bio-based chemical and 10% of liquid fuels from biomass by 2020.[7] Australia government set a goal to produce 11,000 gigawatt hours per annum of electricity from biomass resources by 2020. This represents about 4% of the Australia forecast electricity demand.

Hydrothermal process using hot-compressed water (HCW) is recognised as one of the suitable methods for converting biomass into platform chemical and biofuel especially wet biomass such as algae.[8-10] Wet biomass does not need to undergo drying process before degrading in HCW as required by other biomass conversion methods.[8, 11, 12] Furthermore, water can react both as a solvent and reactant during biomass decomposition due to the low dielectric constant and high ion products of HCW.[13, 14] However, because of the complexity of lignocellulosic biomass structure, the production of target products with a high selectivity is yet to be achieved, which becomes a critical issue for HCW processing technology. A better understanding on fundamental of biomass decomposition in HCW is important before the technology can be adopted for the production of biofuels and biochemical.

As the main component of lignocellulosic biomass, cellulose is often used as a model compound in order to understand the principle of biomass decomposition mechanism reaction in HCW.[15-20] Previous studies revealed that cellulose decomposed into glucose and its oligomers as primary products, and subsequently further degraded into gases, oils and char.[15-17] Recently, Yu and Wu[21-24] studied the primary reaction of cellulose decomposition at the subcritical water. They had proven that cellulose produces various glucose oligomers as the primary reaction output. The glucose oligomers will undergo secondary reactions to produce other products. However, apart from glucose, the fundamental mechanisms of glucose oligomers decomposition in HCW are still not fully elucidated.

Cellobiose is the smallest glucose oligomers which contain two units of glucose. Limited studies have been conducted on cellobiose decomposition in HCW, mainly concentrating on high temperature conditions (>300 °C), which are targeted for the hydrothermal gasification process.[25-29] The mechanism of cellobiose decomposition at the temperature lower than 300 ^{o}C which is relevant to hydrothermal applications for biofuel production is still poorly understood. The cellobiose decomposition mechanism is strongly affected by temperature as the properties of HCW depend on temperature. Furthermore, the effects of various reaction conditions such as initial cellobiose concentration and initial pH on the mechanism of cellobiose decomposition in HCW are still unknown. Additionally, biomass contains alkali and alkaline earth

metallic (AAEM) species. The effect of AAEM species on the cellobiose decomposition mechanism and kinetics is largely unexplored. Therefore, a systematic study on cellobiose decomposition under hydrothermal conditions is required to gain further insight into the decomposition of sugar oligomers into monomer and other products in HCW. Such knowledge is of critical importance to the development of novel processes for producing biofuels and biochemicals from biomass.

1.2 Scope and Objectives

The main purpose of this study is to understand the principle of reaction mechanism and kinetics of cellobiose decomposition in HCW under different conditions. The detailed objectives of this thesis are listed below:

- To elucidate the cellobiose decomposition reaction mechanism in HCW at lower temperature (<300 °C);
- To investigate the effect of initial cellobiose concentrations on the decomposition of cellobiose in HCW.
- To compare the mechanism of cellobiose decomposition under weakly acidic condition with non-catalytic condition;
- To study the effect of alkali and alkaline earth metal (AAEM) species on the reaction mechanism and kinetics of cellobiose decomposition in HCW.

1.3 Thesis Outline

This thesis consists of eight chapters including this chapter. The outline of each chapter is listed below, and the thesis structure is schematically shown in the thesis map (Figure 1-1):

Chapter 1 introduces the background and the purposes of present study;

Chapter 2 reviews the existing literature on the fundamental chemistry of biomass, cellulose, glucose and cellobiose decomposition reaction pathways and kinetics. The research gaps are identified and the objectives of this thesis are then outlined;

Chapter 3 provides a description of experimental methods used to achieve the research objectives including the analytical instrumentations for products identification and quantification; also the data acquisition and processing;

Chapter 4 reveals new reaction pathways of cellobiose decomposition in HCW and discover the effect of temperature on the mechanism of cellobiose decomposition;

Chapter 5 examines the effect of initial cellobiose concentration on primary decomposition mechanism of cellobiose in HCW;

Chapter 6 studies the effect of initial pH on cellobiose decomposition under weakly acidic conditions;

Chapter 7 explores the effect of AAEM chlorides on cellobiose decomposition in HCW;

Chapter 8 presents the conclusions obtained from current study and outlines recommendations for future research.

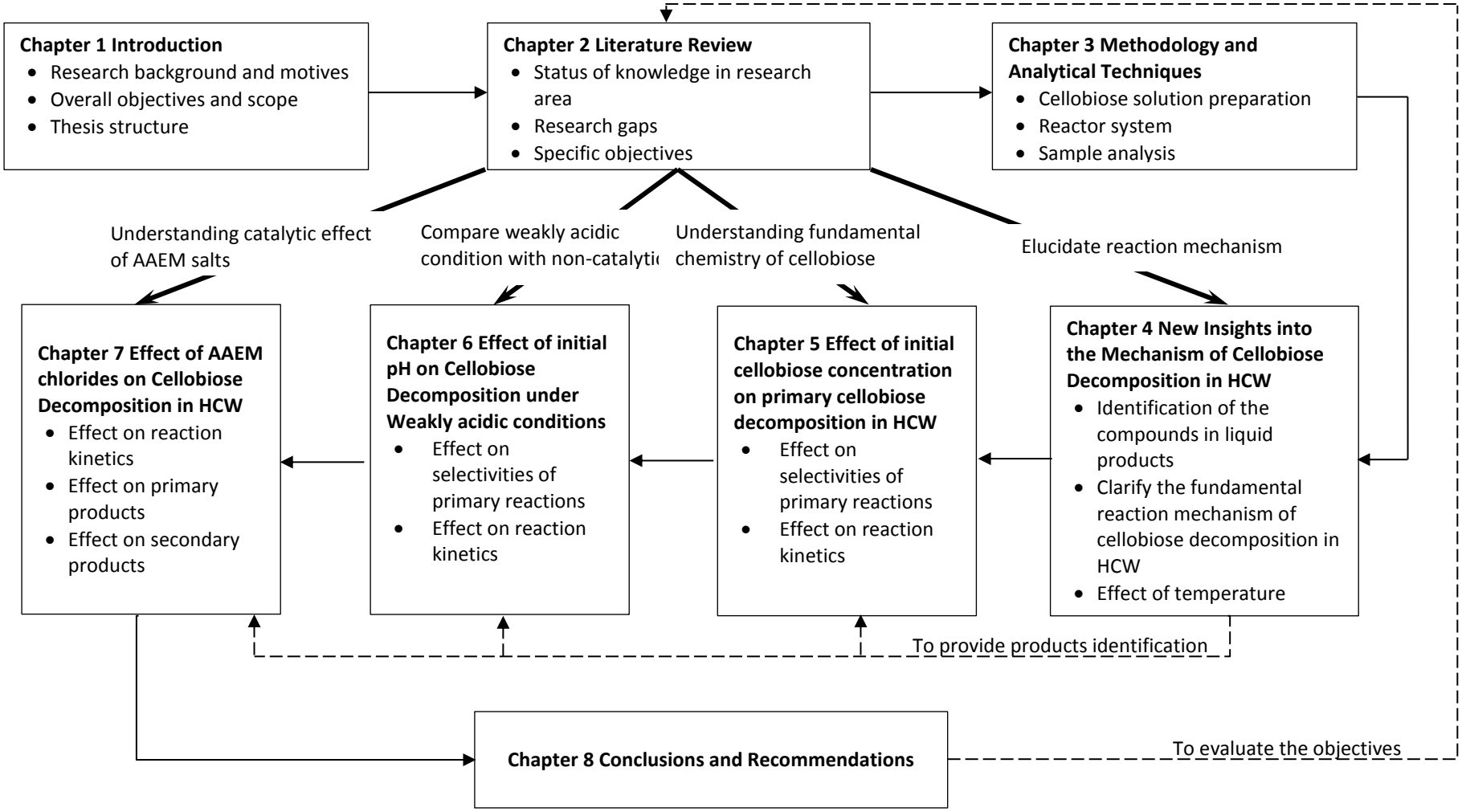

Figure 1- 1: Thesis map

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

Recently, there are growing interest in converting biomass for different application such as energy, chemical, pharmaceutical, and construction materials via biorefinery.[30] Basically, biorefinery concept is similar with the petroleum-based refinery, where feedstock (i.e. crude oil) is converted into fuels and chemical products.[31] Lignocellulosic biomass feedstock biorefinery is recognised as one of the most potential large-scale industries biorefinery. Each component in lignocellulosic biomass can be transformed into valuable products. For example, sugars from cellulose and hemicellulose can be transformed into ethanol via the fermentation process.[32] 5-hydroxymethylfurfural (5-HMF) is one of the direct products of cellulose decomposition is consider a promising platform chemical for various products such as furan dicarboxylic acid (for polyesters production).[33] Furfural is one of hemicellulose products can be utilised as a starting material for nylon 6 and nylon 6,6.[31]

Converting biomass into multiple high value products will offset the high cost production of biofuel, thus improving the economic performance of lignocellulosic biorefinery.[34, 35] However, there are several challenges which have to be overcome before lignocellulosic biomass biorefinery concept can be successful. One of the key challenges is that the composition of lignocellulosic biomass varies even among the same plant species. Furthermore, raw biomass usually contains a lot of waters. Hence, it is very difficult to integrate biomass directly into existing chemical process.[36] Therefore, the development of low-cost, efficient, high capacity and environmentally friendly technologies for the conversion of biomass is essential to ensure the success of biorefinery concept.[34]

Biomass hydrothermal conversion in hot-compressed water (HCW) is recognised as one of the promising technologies for the synthesis of green energy and chemical in the biorefinery.[8, 37] HCW is an ideal medium for biomass conversion as react both as solvent and reactant due to low dielectric constant and high ionic product.[13, 14] Biomass hydrolysis in HCW is very complex, often in multistep and parallel reactions, resulting in the formation of multiple valuable products. Significant studies have been performed using lignocellulosic biomass and model compounds (e.g. cellulose, hemicellulose, glucose, and cellobiose) to gain further insight into the mechanism of biomass conversion in HCW.

This chapter reviews the research progress on conversion of biomass and its model compounds in HCW. A brief introduction of biomass and its components, and properties of HCW is presented, followed by a detailed overview of biomass conversion in HCW, comprising the decomposition of biomass main components (cellulose, hemicellulose and lignin). This chapter then reviews the mechanism and kinetic of glucose and cellobiose decomposition in HCW, including factors influencing the reaction mechanism. Finally, key research gaps are identified and the thesis objectives are proposed.

2.2 Lignocellulosic Biomass Components

There are large amount of lignocellulosic biomass including wood grass, agriculture waste, municipal waste, dedicated energy crops and forest residue.[38-41] The polymeric carbohydrates [$CH_{1.4}O_{0.6}$] in biomass, mainly cellulose and hemicellulose are formed during photosynthesis process.[38] Lignocellulosic biomass mostly consists of cellulose, hemicellulose, lignin and small amount of other substances for instance extractives and inorganic species.[42-44]

2.2.1 Cellulose

The cellulose structure is comprised of glucose units connected by β-1,4-glycosidic bonds to form a lengthy and straight chain (Figure 2-1).[45] The degree of polymerisation (DP) which indicates the number of glucose molecules in the cellulose chain. The

value of DP for cellulose range between 7000 and 15 000 with the molecular weight of 300 000 to 500 000.[43, 46]

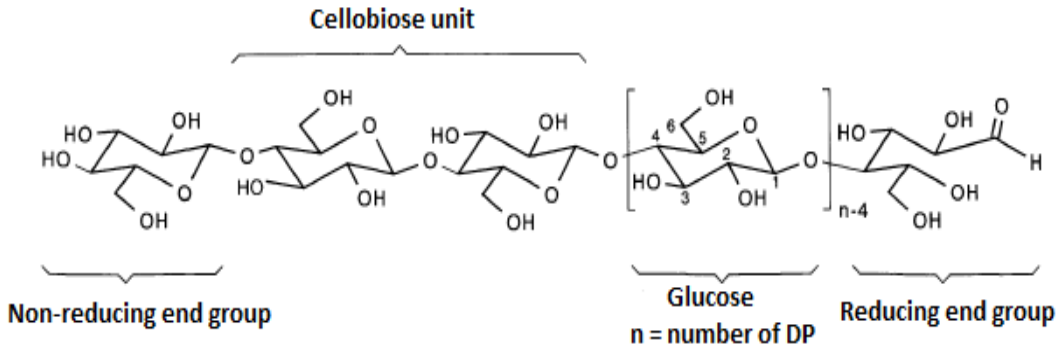

Figure 2- 1: Cellulose Structure[47]

The two ends of cellulose chain have different hydroxyl behaviour where hydroxyl group at one end which attached to C-1 has reducing properties; meanwhile, the hydroxyl group attached at C-4 at the other end has non-reducing properties.[47] The hydrogen bonds forming between hydroxyl groups and oxygen on the same or on adjacent chains result in microfibrils structure which provides the rigidity of the plant cell wall.[44] Cellulose microfibrils consist of crystalline and amorphous regions. In crystalline regions, the cellulose chains are arranged in parallel to forms a crystalline structure. The regions that are less ordered non-crystalline structure known as amorphous.[48] Due to its structure, crystalline cellulose is water insoluble and highly resistance to chemical and biological hydrolysis.[49] However, amorphous regions are easily degraded compare to crystalline regions.[50]

2.2.2 Hemicellulose

Hemicellulose has heterogeneous structure which mainly consists of xylose, arabinose rhamnose, glucose, mannose, galactose, 4-*o*-methylglucuronic, D-glucuronic, D-galactouronic acids and other carbohydrates.[12, 51] Hemicellulose has short chain backbone and branches with one monosaccharide and/or small oligosaccharides.[52] The backbone of hemicellulose is connected by β-(1,4)-glycosidic bond or β-(1,3)-glycosidic bond.[50] There are different types of hemicellulose depending on their

primary monomer on the backbone such as xylans, xyloglucans, mannans, glucomannans, arabinoxylans, glucoronoarabinoxylans and galactoglucomannan. Figure 2-2 shows the example of hemicellulose types. The DP value of hemicellulose is 100 to 200 units, which considerably lower than cellulose. Due to its structure, hemicellulose relatively easy to hydrolyse compare to cellulose.[53]

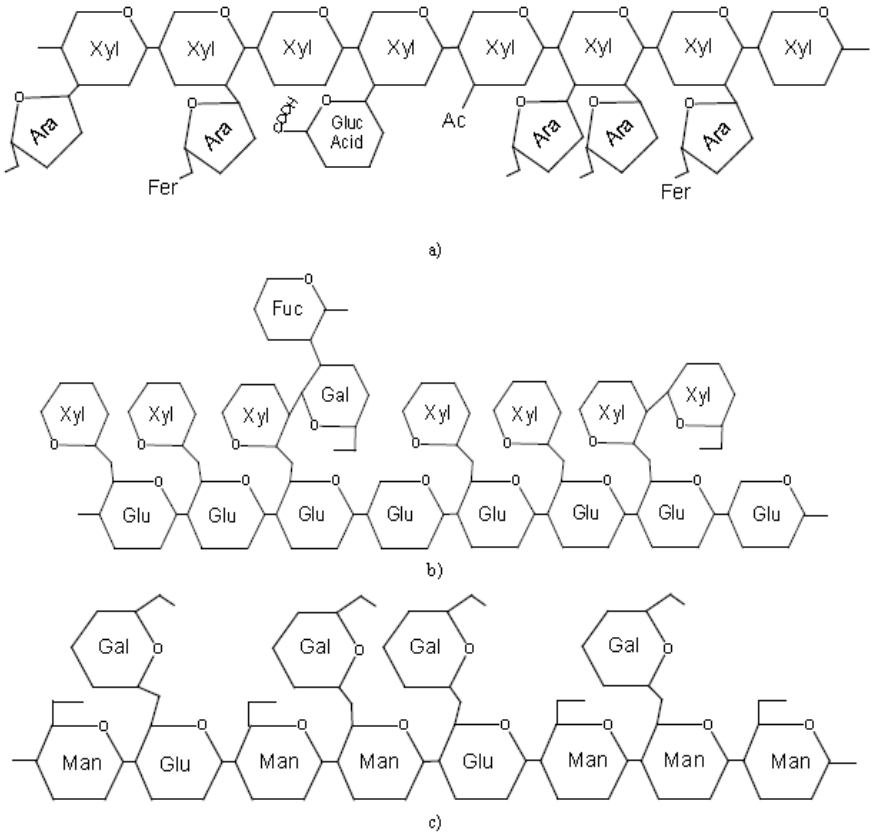

Figure 2-2: Schematic diagram illustrating typical hemicellulose: (a) glucoronoarabinoxylans, (b) Xyloglucans and (c) galactoglucomannan[38]

2.2.3 Lignin

Lignin exists in cellular wall of lignocellulosic biomass to provide support for plant structure and also protection against microbial and oxidative stress.[54] Lignin is highly branched aromatic polymer containing phenylpropane-based units join together by different type of linkages.[50, 53] Figure 2-3 illustrates the basic form of lignin which consists of trans-p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.[55] Lignin

is insoluble in water and usually interferes the hydrolysis of carbohydrate (i.e. cellulose and hemicellulose) in biomass.[34]

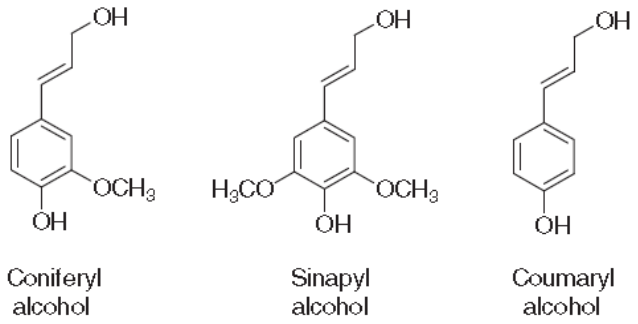

Figure 2- 3 : Structure of monomeric lignin building units[55]

2.2.4 Other Components

Lignocellulosic biomass contains some extractive materials from 0.4 to 8.3% on a dry weight basis.[56] Extractive materials include fats, waxes, essential oils, alkaloids, phenolics, resins, fatty acids, gums and pectin.[43] Other than that, lignocellulosic biomass also comprises a little amount of inorganic species for example alkali and alkaline earth species (Na, K, Mg, Ca, etc.), silica, carbonates and chlorides.[50, 57]

2.3 Properties of Hot-Compressed Water

HCW can be considered as an ideal and environmentally friendly reaction medium for various biomass conversions processes such as hydrothermal degradation, gasification and liquefaction because of it non-toxicity and non-flammability behaviour.[43, 58] HCW also has the ability to process wet biomass without preliminary drying process. Furthermore, biomass conversion in HCW is relatively high. Almost 100% conversion can be obtained in a short time.[59] Unlike acid and alkaline hydrolysis, hydrolysis in HCW has fewer problems due to corrosion, waste management and recycling process.[38] All these benefits make HCW economically competitive compare to other biochemical and thermochemical processes.[59]

HCW refers to water at the temperature above 150 ºC and various pressures.[43] Figure 2-4 clearly demonstrates that water properties strongly depend on temperature. In contrast, pressure has a low impact on water properties at temperatures below 350 ºC,

but at the temperature above 350 °C, pressure greatly influences HCW properties. Water properties can be manipulated to increase the selectivity of desired products, reaction kinetics, and also increase the solubility of organic and inorganic matters by changing temperature and pressure.[59, 60]

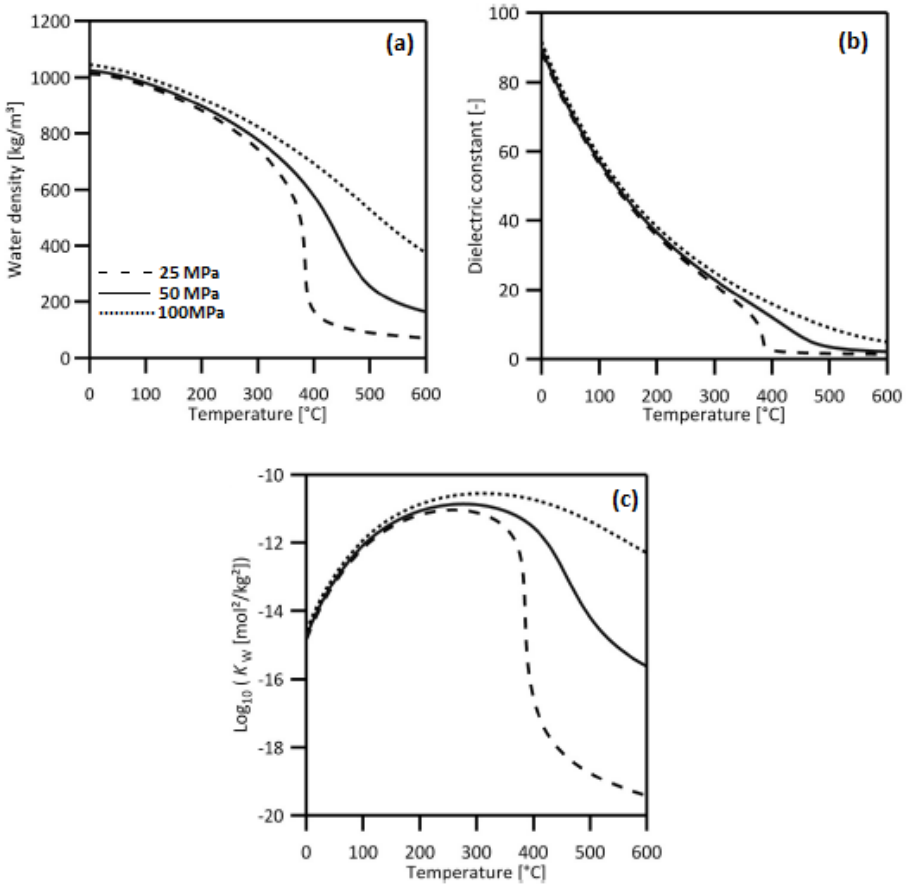

Figure 2- 4: Properties of water versus temperatures at various pressures. (a) Water density; (b) dielectric constant; and (c) ionic products[60]

HCW can be divided into the subcritical and supercritical water. Subcritical water is defined as water at above 100 ºC under atmosphere pressure and below critical point (T_c = 374 ºC, P_c = 22.1 MPa, ρ_c = 320 kg m^{-3}).[36] At this state, water maintains in a liquid state under pressurised conditions.[61] Water with pressure and temperature above critical point is known as supercritical water.[60] The properties of supercritical water are between gas-like and liquid-like depend on temperature and pressure.[62]

Table 2- 1: Water properties at subcritical and supercritical water compare with normal water [63, 64]

Properties	Normal water	Subcritical water	Supercritical water	
Temperature T (ºC)	25	250	400	400
Pressure P (MPa)	0.1	5	25	50
Density ρ (g cm^{-3})	0.997	0.80	0.17	0.58
Dielectric constant ε	78.5	27.1	5.9	10.5
pK_w	14.0	11.2	19.4	11.9
Heat capacity C_p (kJ kg^{-1} K^{-1})	4.22	4.86	13.0	6.8
Dynamic viscosity η (mPas)	0.89	0.11	0.03	0.07
Heat conductivity λ ($mWm^{-1}K^{-1}$)	608	620	160	438

In subcritical water, the dielectric constant declines with an increase in temperature from 78.5 (normal water) to 27.1 at 250 °C, which is almost comparable to some organic solvent for instance acetone and ethanol at ambient temperature.[63, 65] Due to low dielectric constant, the solubility of organic compound increases, making it suitable for extraction of hydrophobic compounds from plants.[36, 65] Moreover, ionic reactions increase when dielectric constant is decreased. Therefore, subcritical water is an excellent medium for a variety of synthesis and degradation reactions.[66] The ionic products of subcritical water rise with temperature and reached its maximum at around 300 ºC. At this condition, the ionic products are up to 3 order of magnitude higher than at ambient temperature.[13, 67] This indicates that hydrogen and hydroxyl ions concentration are high in subcritical water due to the enhancement of self-dissociation of water molecules, thus promotes the acid/base catalysed reactions without adding acid and bases catalyst.[14, 66]

In supercritical water, the dielectric constant further reduces to 5.9 (at 400 ºC and 25 MPa). Thus, make water exhibit non-polar solvent behaviour, promoting free radical reactions such as breaking of C-C bond during gasification process.[59] It is well known that non-polar organic compounds and gases such as nitrogen, oxygen and carbon dioxide are immiscible with water. However, these substances are miscible in supercritical water. Thus, supercritical water is a suitable medium for reactions

involved organic compounds that have gases for example hydrothermal oxidation process.[68] Even though supercritical water behaves like non-polar solvent, it still can react with ions as the single water molecule still behaves as a polar molecule.[14] The ionic products value reduces in supercritical water as temperature increase at low pressure (at 25MPa). The ionic products at 400 ºC and 25 MPa are 19.4, which is lower than those at the ambient water.[64] However, at high pressure (at 100 MPa), the ionic products value is almost similar with subcritical water. Therefore, by altering the temperature and pressure in supercritical water, reaction mechanism could be shifted from free radical reactions to ionic reactions.[43]

2.4 Biomass Conversion in HCW

Biomass conversion in HCW has received significant interests in recent times. A number of investigations have been conducted utilising the main components of biomass (cellulose, hemicellulose, and lignin) and various biomass materials in order to further understand on how biomass decomposed in HCW. The following sections will provide an overview of biomass components and lignocellulosic biomass decomposition in HCW.

2.4.1 Cellulose Decomposition in HCW

Cellulose is the main component of biomass with the percentage of 40–50 %. Therefore it always used as a model compound in order to have further insight into the biomass decomposition mechanism in HCW.[15, 16, 18, 21-24, 69-81] Mechanism of cellulose hydrolysis in HCW has been comprehensively investigated by Sasaki et al.[17, 82, 83] at a temperature of 290–400 ºC and a pressure of 25 MPa. The studies showed that the hydrolysis of cellulose mostly formed glucose, fructose, erythrose, glycolaldehyde, dihydroxyacetone, glyceraldehyde, pyruvaldehyde, levoglucosan and glucose oligomers (cellobiose, cellotriose, cellotetraose, cellopentaose and cellohexaose). Based on previous studies on cellulose model compound (e.g. glucose and cellobiose), glucose oligomers are further degraded into glucose. After that, Glucose is rearranged into fructose, and then fructose and glucose are further decomposed into 5-HMF, erythrose, glycolaldehyde, glyceraldehyde, dihydroxyacetone, pyruvaldehyde and 1,6-

anhydroglucose (also known as levoglucosan).[25, 84, 85] The proposed reaction pathway for hydrolysis of cellulose is illustrated in Figure 2-5.

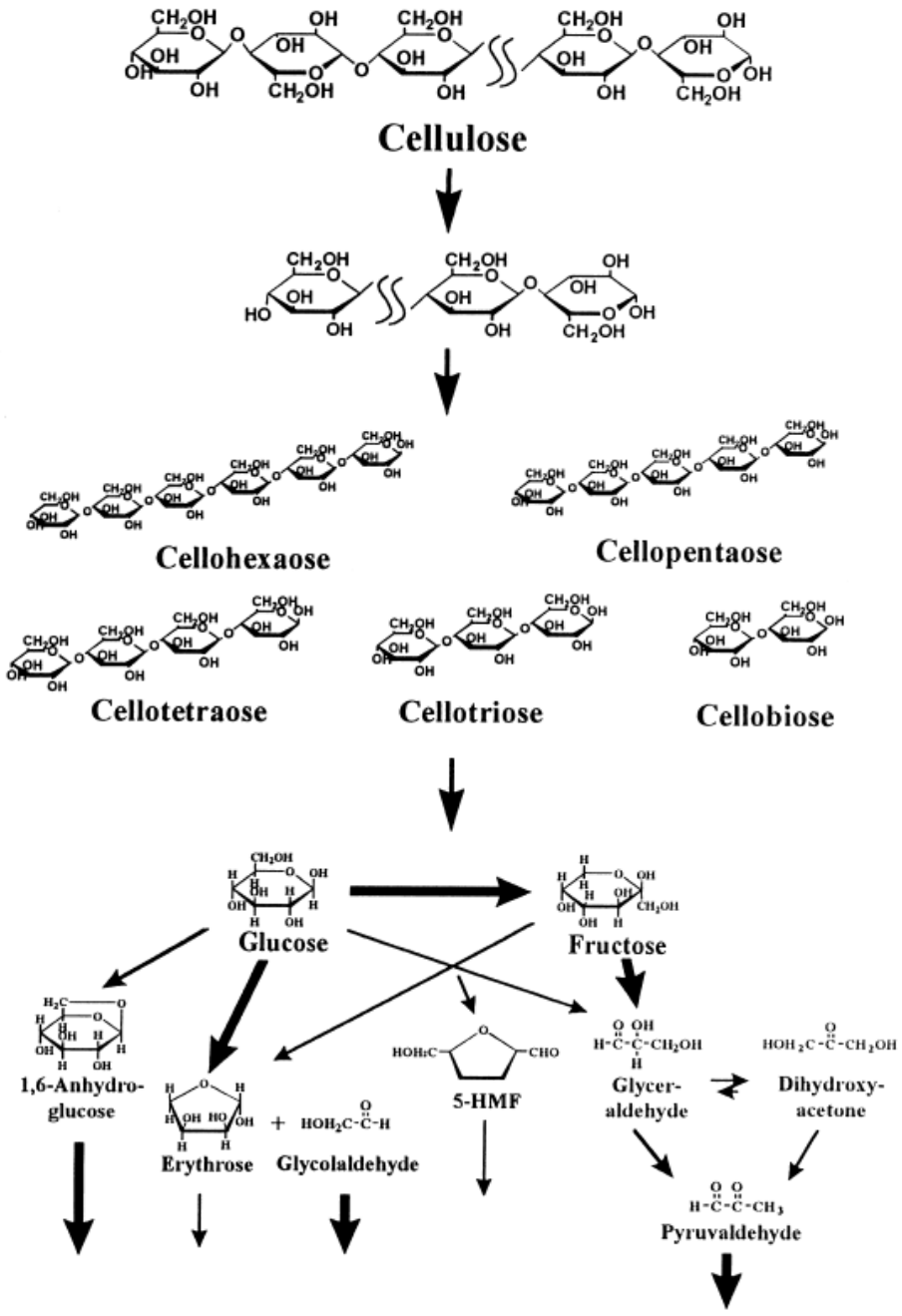

Figure 2- 5: Reaction pathway of cellulose hydrolysis[17]

Table 2-2 summarises the results of experimental studies on cellulose decomposition in HCW. It clearly shows that the difference of cellulose decomposition behaviour in subcritical and supercritical water. The yields of sugars (glucose and fructose and

glucose oligomers) are lower in subcritical water than supercritical water. Meanwhile, the yields of degradation products (e.g. 5-HMF, furfural, glycolaldehyde, erythrose, levoglucosan) are higher in subcritical water than supercritical water.[17, 72, 86, 87] In subcritical water, sugars decomposition rate are greater than cellulose hydrolysis rate, resulting in lower yields of sugar products.[86] However, in near- and supercritical water, cellulose hydrolysis rate was found to increase more than ten times and more quickly than decomposition rate of sugars, thus a higher sugar recovery can be obtained.[17] Sasaki et al.[86] suggested that these phenomena happen due to the change of the reaction mechanism at higher temperatures. In subcritical water, the hydrolysis of cellulose happens at the surface of the crystalline structure without swelling or dissolving, resulting in a slow conversion rate of cellulose hydrolysis in HCW.[82] In near- and supercritical water, cellulose was swelling and dissolving around the surface forming cellulose molecules with an amorphous structure. These molecules easily hydrolyse into sugars with smaller DP, thus increasing the cellulose hydrolysis rate of in supercritical water.[82]

Supercritical water clearly is a more excellent ambience for hydrolysis of cellulose for production of fermentable sugars (i.e. ethanol production). However, the glucose oligomers produce in subcritical water has low DP than those in the supercritical water. These high DP glucose oligomers will precipitate when settling at room temperature.[72] Furthermore, sugars produced from cellulose hydrolysis rapidly decomposed into degradation products, hence reduce the amount of fermentable sugars. In contrast, the decomposition rate of sugars is lower in subcritical compared to supercritical water. However, cellulose is difficult to hydrolyse in subcritical water.[78] Therefore, a combined treatment of supercritical and subcritical water has been proposed by Ehara and Saka[72] to overcome these problems. In combined treatment, cellulose was decomposed in supercritical water for 0.1 s, followed by treatment in subcritical water for 15 to 45 s. The combined treatments produced high yields of sugars (66.8% at 30.1 s). Similar results were reported by Zhao et al.[78, 88] Therefore, combined treatment is a good way to manipulate the reaction condition produce high sugars yield.[72]

Table 2- 2: Summarise of cellulose decomposition in HCW obtained from literatures

Reactor type	Temperature (°C)	Pressure (MPa)	Residence time	Maximum products yield	Reference
Continuous	320 – 400	25	0.05 – 10 s	Monomers 25.3% (350 °C, 3.5 s) 42.6% (400 °C, 0.15 s) Oligomers 50.6% (350 °C, 1.5 s) 72.2% (400 °C, 0.01 s) Decomposition products 95% (350 °C, 8.8 s) 43.7% (400 °C, 0.15 s)	Sasaki et al.[17]
Continuous	290 - 400	25	0.02 – 13.1 s	Monomers and Oligomers 40% (320 °C, 1.8 s) 30% (400 °C, 0.02 s)	Sasaki et al.[82]
Continuous	250 - 380	25	0.25 – 0.75 s	Monomers 22% (360 °C, 0.5 s) 17% (380 °C, 0.5 s) Degradation products 5-HMF – 5%(360 °C, 0.75 s) Furfural – 2% (360 °C, 0.75 s)	Tolonen et al.[87]
Continuous	Subcritical 280 Supercritical 400 Combined treatment 1st – 400 2nd – 280	40	0.1 – 240 s	Monomers 17.1% (280 °C, 240 s) 14.5% (400 °C, 0.3 s) 35.6% (combine treatment, 45. 1s) Oligomers 8.8% (280 °C, 120 s) 32.2% (400 °C, 0.3 s) 55.4% (combine treatment, 30.1 s) Degradation products 60% (280 °C, 240 s) 47.2% (400 °C, 0.3 s) 47.9% (combine treatment, 45.1 s)	Ehara and Saka[72]
Batch	Combined treatment 1st – 380 2nd – 280 – 360		1st – 16 s 2nd – 15-50 s	Monomers 26.3% (380 °C, 16 s) 39.5%(combine treatment, 28 0°C, 44 s) Oligomers 28.1% (380 °C, 16 s)	Zhao et al.[78]
Continuous	380	25 - 40	2 – 8 s	Monomers 18.9% (380 °C, 0.48 s, 40 MPa) Oligomers 41.1% (380 °C, 0.12 s, 40 MPa) Degradation products 73.6% (380 °C, 0.48 s, 40 MPa)	Ehara and Saka[71]
Batch	380	100	0.12 – 0.48 s	Monomers 29.7% (380 °C, 5 s) Oligomers 1.6% (380 °C, 2 s) Degradation products 87.2% (380 °C, 8 s)	Ehara and Saka[71]
Batch	225 - 375	3 - 20	1 hr	Monomers 0.015% (225 °C, 1 hr) Degradation products 5-HMF – 18.34% (225 °C, 1 hr) Formic acid – 5.06% (375 °C, 1 hr) Acetaldehyde – 3.6% (375 °C, 1 hr)	Sinag et al.[89]
Semi-continuous	230 - 280	10M	1 – 4 s	Monomers ~15%[a] (230 °C, ~2 s) Oligomers ~75%[a] (250 °C, 1 s) Oligomers with DP up to 28 (270 °C)	Yu and Wu[22]

Monomer: glucose and fructose; Oligomers: glucose oligomers; Degradation products (include furfurals, aldehydes, etc.)

Reactor types also play significant roles on cellulose decomposition in HCW. Ehara and Saka[71] studied the difference between batch and continuous flow type reactor systems. Compared to the batch type reactor system, the time for heating, treating and cooling in continuous flow reactor system is shorter. Thus, reduce the secondary reactions of sugars into degradation products. As a result, higher yields of sugars can be achieved by using continuous flow type reactor system.

Recently, a series of systematic works have been conducted by Yu and Wu [21-24] to understand the primary decomposition reactions of cellulose in HCW. A semi-continuous reactor was used to minimise secondary reactions during the decomposition of cellulose in HCW. The studies were conducted at 10M Pa and temperature ranging from 180 to 280 ºC. The results reveal that cellulose primarily decomposed into glucose oligomers with DP more than 25 as shown in Figure 2-6.[22] The studies indicate that the primary reactions occur on the surface of the cellulose by breakage the glycosidic bond that reachable with randomly manner. This finding clearly suggests that HCW is a promising pretreatment method for microcrystalline cellulose for recovery of sugars which can be fermented bioethanol.[22]

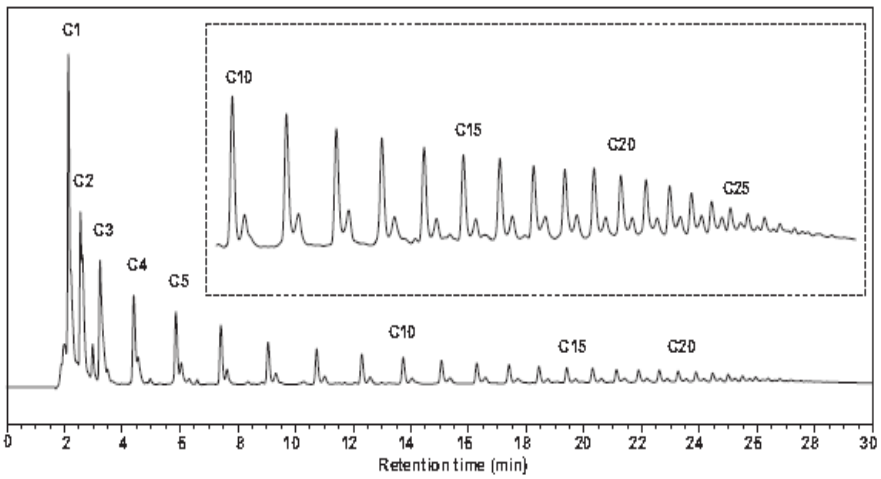

Figure 2- 6: Typical IC chromatogram of the sample from hydrolysis of cellulose in HCW.[21] C1 to C25 represent glucose oligomers according to their DP values. For example, C1 is glucose, C2 is cellobiose, and C3 is cellotriose.

2.4.2 Hemicellulose Decomposition in HCW

Compare to cellulose, hemicellulose decomposes at a relatively low temperature in HCW.[67] The decomposition of hemicellulose in HCW produces various structures and composition of sugar oligomers, furfural and organic acids.[38] Pińkowska et al.[90] used beech wood xylan as a model compound to investigate the decomposition of hemicellulose in HCW at temperatures between 180 and 300 °C. The liquid products contain xylose, xylose oligomers, arabinose, carboxylic acid (acetic, formic, lactic and oxalic), furfurals (furfural and 5-HMF), aldehydes (glyceraldehyde, glycolaldehyde and pyruvaldehyde) and dihydroxyacetone. Yang and Wyman[91] studied the decomposition of xylan (oat spent xylan) in HCW at 200 to 240 °C. They reported that xylan depolymerised into xylose and xylose oligomers with DP up to 30. Xylose oligomers then further decomposed into xylose.[90, 91] Xylose and arabinose dehydrated into furfural and 5-HMF, which further degraded into formic acid. Glycolaldehyde and glyceraldehyde are produced via retro-aldol condensation of xylose and arabinose. Glyceraldehyde then converted into dihydroxyacetone and pyruvaldehyde. Pyruvaldehyde will transform into acid lactic.[90] Therefore, the yield of xylose oligomers decreases while the yield of the monosaccharide, acetic acid and sugars decomposition products such as furfural increases with increasing reaction time.[92] Figure 2-7 illustrated the proposed reaction pathways for hemicellulose decomposition in HCW.

The previous study on hydrolysis of various hemicelluloses materials (i.e. corn cob, almond shell, olive stone, rice husk, wheat straw and barley straw) at 179 °C showed that the yield and composition of xylose oligomers produce depends on the amount of xylan and its accessibility. Moreover, the yield of xylose oligomers was proportional to the content of acetyl group in the hemicellulose.[93] Corn cob produced the higher yield of xylose oligomers (60% initial xylan) due to its higher content of acetyl group. Acetyl group in hemicellulose plays an important role during hydrolysis in HCW as the cleavage of this group produce acetic acid which can further catalyse the primary hydrolysis of xylan into xylose oligomers and the subsequent secondary reactions of xylose oligomers (decomposition of xylose oligomers into other products).[93]

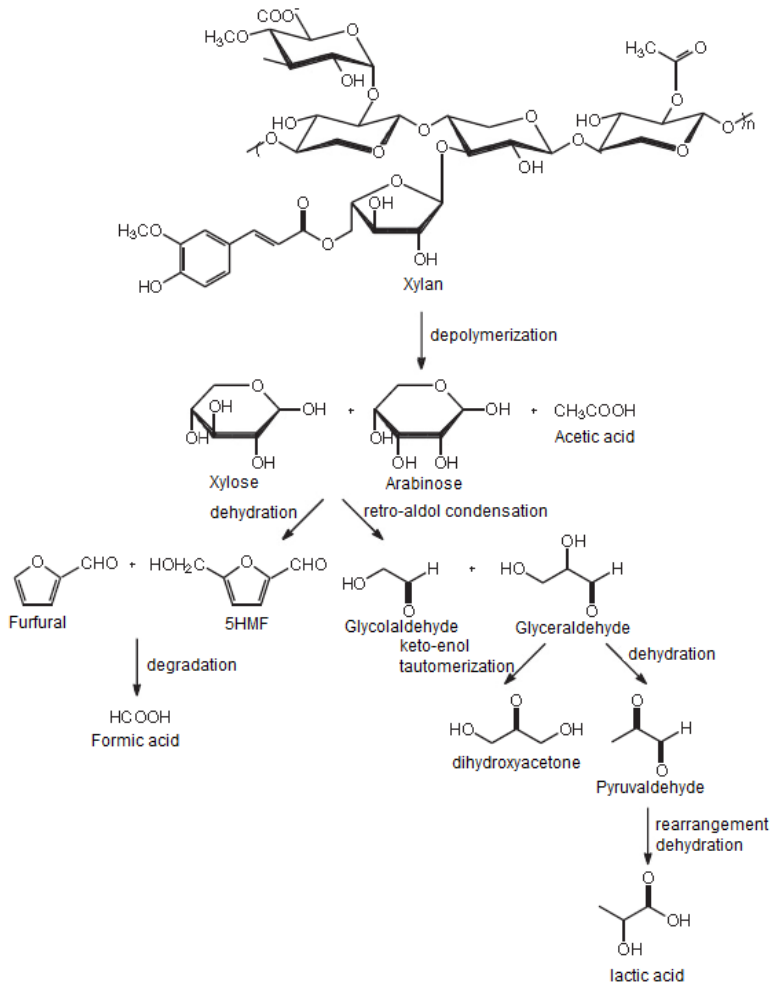

Figure 2- 7 : Reaction pathways of xylan decomposition in HCW[90]

The study on xylose decomposition in HCW at the temperature from 360 to 420 °C and pressures of 25 to 40M Pa by Sasaki et al.[94] indicated that retro-aldol condensation reaction was significantly higher at the temperature near critical and supercritical water. Meanwhile, at a lower temperature, dehydration process to form furfural and formic acid was promoted. This finding is similar to the case of glucose decomposition in HCW.

2.4.3 Lignin Decomposition in HCW

Lignin decomposes into various phenols and methoxy phenols in HCW via the cleavage of ether-bond.[95] Wahyudiono et al.[96] used guaiacol as a model compound for

to study the decomposition of lignin at the temperature range of 380 to 400 °C and various pressures. The results show that guaiacol decomposed into catechol, phenol, and o-cresol. The formation of these products increases with temperature and pressure. As reaction time increases, the amount of guaiacol oligomers and compounds with the low-molecular-weight increase. The formation of char was found to occur during guaiacol decomposition in HCW.[96] The proposed reaction pathways for the decomposition of guaiacol are shown in Figure 2-8.

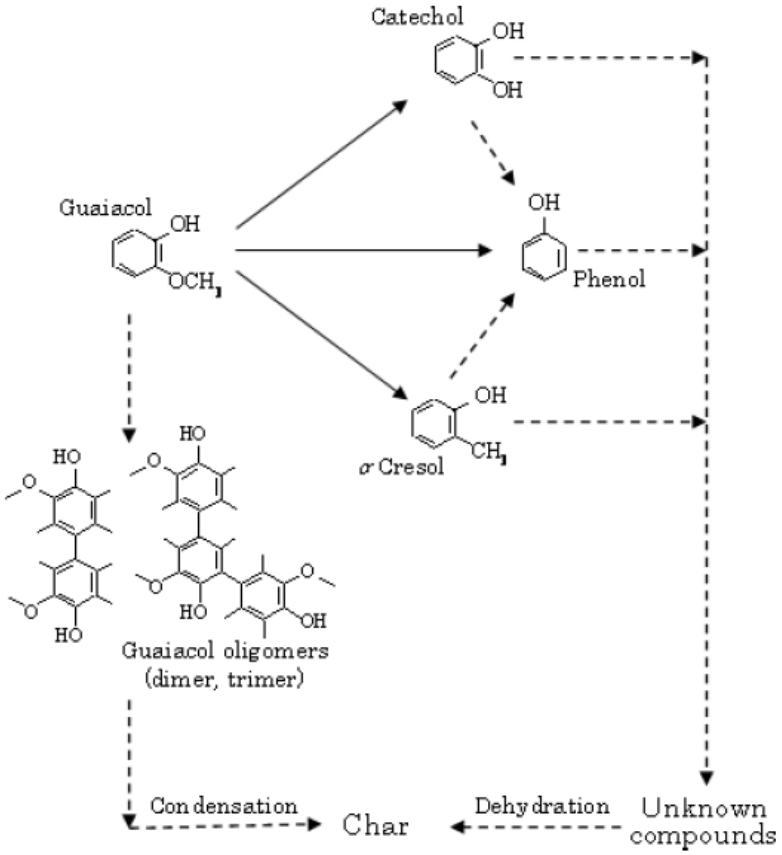

Figure 2- 8: Reaction pathways for guaiacol decomposition in near critical and supercritical water[96]

Zhang et al.[97] studied the hydrothermal treatment for five type of lignin and biomass residues at 300 to 374 °C. Guaiacol and phenolic compounds are found in the liquid products. They reported that about 33-79 wt% of liquids and 12–49 wt% of solids were formed during hydrothermal treatment. This results clearly indicated that products yield depends on the raw materials composition and structure.[97]

2.4.4 Lignocellulosic Biomass Decomposition in HCW

Substantial studies have been conducted on lignocellulosic biomass decomposition in HCW.[67, 72, 98-102] Biomass decomposed in HCW into sugar monomers (e.g. glucose, xylose, and arabinose), oligomers (mainly glucose oligomers and xylose oligomers), decomposition products (e.g. 5-HMF, glycolaldehyde and furfural), aromatic compounds (e.g. phenol and cresols) and organic acids (e.g. acetic acid, levulinic acid and formic acid).[98, 103] Small components (e.g. 5-HMF and furfural) from biomass decomposed will further transform into bio-oil, water soluble substance, char, and gases such as H_2, CO, CO_2 and CH_4.[59, 95]

One of the key drawbacks of lignocellulosic biomass decomposes in HCW is the relatively low yields of target products.[79] Moreover, it is very difficult to optimise the hydrothermal process of biomass especially if the target product is fermentable sugars due to the difference in biomass components (cellulose, hemicellulose and lignin). Cellulose with the crystalline structure is more difficult to decompose compared to hemicellulose. Ando et al.[67] reported that cellulose starts to decompose at the temperature above 230 ºC, whereas hemicellulose begin decomposes at 180 ºC. Furthermore, cellulose only partially decomposes in relatively low temperature, but at high temperature, sugars from cellulose and hemicellulose hydrolysis can easily decompose into un-fermentable products.[103] The extraction of lignin usually happen at a moderately low temperature and flow out with hemicellulose decomposed products. However, there are a certain amount of lignin leave behind in the reactor after the cellulose has been removed especially for biomass that contains high percentage of lignin for example Japan cedar.[67] In addition, Hashaikeh et al.[101] examined the willow dissolution in HCW and found that the decomposition and dissolution of hemicellulose and lignin were achieved at low temperature (i.e. 200 ºC), while cellulose liquefied in the temperature range of 280–320 ºC. However, the dissolution rate of hemicellulose and lignin reduce at the temperature above 230 ºC due to recondensation reactions to form solid precipitates. These solid precipitates blocked the cellulose material, render it inaccessible by water. This cause cellulose to dehydrate and form char-like precipitates.[101]

As cellulose, hemicellulose and lignin hydrolysis cannot be optimised at the same reaction condition, there is a need to develop an efficient process to separate the components in biomass. A two-step hydrolysis process in HCW has gained attention as it has the potential to address this issue and improves biomass conversion and sugar recovery.[101, 104-107] The studies on two-step process using semi-continuous reactor showed that the amorphous phase in biomass (i.e. hemicellulose, amorphous cellulose and lignin) decomposed in the first stage process (at 230 ºC), while crystalline cellulose decomposed during the second stage process(at 270 ºC).[105, 106] It was reported that around 88–96% of biomass was dissolved in HCW by this treatment. The water-insoluble residue (4-12%) mainly consists of lignin.[101, 105, 106] According to the liquid analysed by Lu et al. [106], the liquid products from first stage process contain xylose, xylose oligomers, glucuronic acid and acetic acid from hemicellulose, and lignin products such as guaiacyl and syringyl. Meanwhile, in second stage process, liquid products mainly consist of glucose and glucose oligomers from cellulose.

Zhao et al.[88, 108] used combined supercritical and subcritical water technology to pre-treat and decompose lignocellulosic biomass with the aim to increase the yield of fermentable hexoses (i.e. glucose and fructose). First, lignocellulosic biomass is treated with supercritical water for lignin removal and cellulose decomposition into oligomers, follow by the second treatment in subcritical water to transform the oligomers into fermentable hexoses.[103, 108] The results show that almost 30% (relative to the raw material) of hexoses was formed from corn stalks (43.2% cellulose and soluble sugar in total) by using this method.[88] This is considerably higher compared to other methods. For example, only 20% of glucose was recover from willow (50% cellulose) with two-step dissolution process.[88, 101] However, when glucose yield from cellulose decomposed reached the maximum, all xylose from hemicellulose decomposition are degraded into smaller products, result in further loss of fermentable sugars for bioethanol production.[108]

In summary, a two-step process is suitable for sugar recovery from cellulose and hemicellulose since this method can avoid further degradation of sugars. Furthermore, by using this method, separate dissolution of biomass component can be achieved, which is important for the production of fermentable sugars. Combined supercritical

and subcritical water method may not be appropriate for fermentable sugars production from lignocellulosic biomass, since all xylose were degraded when glucose yield is maximum. However, this technology looks promising for the production of valuable chemicals such as furfural and 5-HMF. Since, Ehara and Saka[72] reported that the yield of dehydrated products of cellulose (i.e. levoglucosan, 5-HMF and furfural) increase when residence time of second treatment at the subcritical water was increased.

2.4.5 Reaction Kinetics of Biomass and its main components

A lot of studies have been carried out to obtain kinetic data on the decomposition of biomass and its main components. Table 2-3 summaries the kinetic parameters available in the literatures. Sasaki et al.[82] examined the kinetic of cellulose decomposition in subcritical and supercritical water (290–400 °C, 25 MPa). It revealed that the rate of cellulose decomposition in supercritical water is higher than that in subcritical water due to at supercritical water, the cellulose was swelling.[82] Therefore, the higher yield of sugars is obtained with supercritical water. However, these sugars are rapidly decomposed in supercritical conditions. Furthermore, both cellulose and the sugars decomposed in short reaction time. Therefore, it is very difficult to control the reactions.

A number of investigations have been executed to study the kinetic of hemicellulose decomposition in HCW. Basically, the reaction rate of hemicellulose decomposition is faster than cellulose decomposition. The global activation energy of hemicellulose and cellulose decomposition reactions are 59–161 and 149–230 kJ mol^{-1} respectively.[58, 82, 90, 104, 109, 110] The wide range of activation energies values presented in previous literatures probably due to variation in raw materials origin and reaction conditions used in their investigations.

Table 2- 3: Kinetic parameters of biomass and its main components

Feedstock	Reaction	Reactor type	Temperature (°C)	Pressure (MPa)	Residence time	Activation energy (kJ mol^{-1})	Frequency factor	Reference
Microcrystalline cellulose	Cellulose decomposition	Continuous	290 - 400	25	0.02 – 13.1 s	Subcritical water 149 supercritical water 547.9	Subcritical water $10^{11.9}$ supercritical water $10^{44.6}$	Sasaki et al.[82]
Pure cellulose	Cellulose decomposition	Continuous	240 - 310	20 - 25	Up to 200 s	163.9	7.7×10^{13}	Rogalinski et al.[58]
Pure cellulose	Cellulose decomposition	Batch	250 - 300	10		230	1.6×10^{19}	Mochidzuki et al.[104]
Rice husk	Cellulose decomposition	Batch	250 - 300	10		180	5.9×10^{14}	
	Hemicellulose decomposition	Batch	250 - 300	10		100	7.4×10^{6}	
Birch wood	Cellulose decomposition	Batch	180 - 240		2 – 200 min	153.77	4.79×10^{13}	Borrega et al.[110]
	Hemicellulose decomposition	Batch	180 - 240		2 – 200 min	161.04	3.12×10^{17}	
Beech wood xylan	Hemicellulose decomposition	Batch	160 - 220	4	5 – 60 min	65.58	2.46×10^{6}	Zhuang et al.[109]
Beech wood xylan	Hemicellulose decomposition	Batch	180 - 300		2 – 30 min	58.89	2.22×10^{3}	Pińkowska et al.[90]
Spent malt	Hemicellulose decomposition	Batch	250 - 300	10		96	4.4×10^{8}	Mochidzuki et al.7
Rice straw	Biomass decomposition	Batch	160 - 220	4	5 – 60 min	68.76	6.89×10^{6}	Zhuang et al.[109]
Palm shell	Biomass decomposition	Batch	160 - 220	4	5 – 60 min	95.19	3.13×10^{8}	Zhuang et al.[109]
Kraft pine lignin	Lignin decomposition	Batch	300 – 374	10 - 22	Up to 30 min	37	70.2	Zhang et al.[97]

Only a few papers have been published on the kinetic parameters for lignocellulosic biomass decomposition in HCW. Zhuang et al.[109] studied the kinetic of rice straw and palm shell decomposition in HCW at the temperature range of 160 – 220 °C and a pressure of 4 MPa. Rice straw and palm shell have the activation energy of 68.76 and 95.15 kJ mol^{-1} respectively. The difference in the activation energy values indicates that biomass composition and structure can affect the rate of the biomass decomposition in HCW.

The kinetic parameters for others lignocellulosic biomass decomposition in HCW are still largely unknown. Therefore, systematic studies on different types of lignocellulosic biomass decomposition in HCW are required. Furthermore, the research on kinetic of lignin decomposition in HCW is scarce. These data are important for efficient reactor design and optimise operating condition for biomass conversion in HCW.

2.5 Decomposition of Glucose and Its Oligomers in HCW

As mention in section 2.4.2, primary reactions of cellulose produce glucose and its oligomers with various DP. These primary products will be further decomposed into other products.[22] Glucose decomposition in HCW is widely studied under subcritical and supercritical conditions.[16, 29, 85, 111-124] However, only a few studies have been conducted on glucose oligomers decomposition mostly used cellobiose as a model compound.[25-28, 125-129] The studies on glucose and cellobiose focus on hydrolysis performance, and reaction mechanisms and kinetics, with and without catalysts. Detail overviews of research progress on glucose and cellobiose decomposition in HCW are given in the following sections.

2.5.1 Mechanism of Glucose Decomposition in HCW

Glucose is one of the important product from hydrolysis of cellulose/biomass in HCW. Glucose can be converted into transport fuel such as bioethanol via the fermentation process. Other than that, glucose also can be converted into platform chemical for green biochemicals such as 5-HMF,[130-132] levulinic acid[133-135] and lactic acid.[136, 137]

Therefore, it is very important to understand the chemistry of glucose decomposition reaction mechanism in HCW in order to improve the production of desired products.

According to previous research on the mechanism of glucose decomposition in HCW, glucose decomposition in HCW mainly produced fructose, erythrose, glycolaldehyde, dihydroxyacetone, glyceraldehyde, levoglucosan, 5-HMF, pyruvaldehyde, Levulinic and formic acid.[112, 116] Figure 2-9 illustrated the main reaction pathways of glucose decomposition in HCW. Based on previous studies, glucose decomposition reaction was found to be as follows:

(1) Glucose is isomerised into fructose by Lobry-de Bruyn-van Ekenstein transformation.[116, 132] Kabyemela et al.[85] studied the glucose isomerisation and decomposition in subcritical and supercritical water (300–400 °C, 25–40 MPa). It was demonstrated that the rate of isomerisation process of fructose into glucose is slower than the rate of isomerisation process of glucose to fructose. Yu and Wu[138] revealed that the selectivity of fructose is very high (> 90%) at the early stage of glucose decomposition at the temperature between 175 and 275 ºC and pressure of 10 MPa. These results suggested that isomerisation of glucose to fructose is one of the primary reaction of glucose decomposition in HCW.

(2) Glucose is dehydrated into levoglucosan by losing a molecule of water without changing the ring structure.[85] The study on fructose decomposition in HCW (300–400 °C, 25–40 MPa) by Kabyemela et al.[116] shown that no levoglucosan was found in the liquid products. Therefore, the results implied that levoglucosan is a direct product of glucose decomposition

(3) Glucose decomposes via retro-aldol condensation into aldehyde and ketone.[139] After the opening of glucose ring, it will be transformed into glycolaldehyde and erythrose or glyceraldehyde and dihydroxyacetone via retro-aldol condensation. Erythrose will be further decomposed via retro-aldol condensation to form glycolaldehyde.[117] Glyceraldehyde is isomerised into dihydroxyacetone, and then both are dehydrated into pyruvaldehyde.[140]

(4) Fructose transformed into 5-HMF by discarded three molecules of water during the dehydration process. HMF then will be further decomposed via rehydration

into levulinic acid and formic acid.[141] 5-HMF also can be polymerised into char and/or decomposed into desirable gaseous products such as H_2 and CH_4.[142]

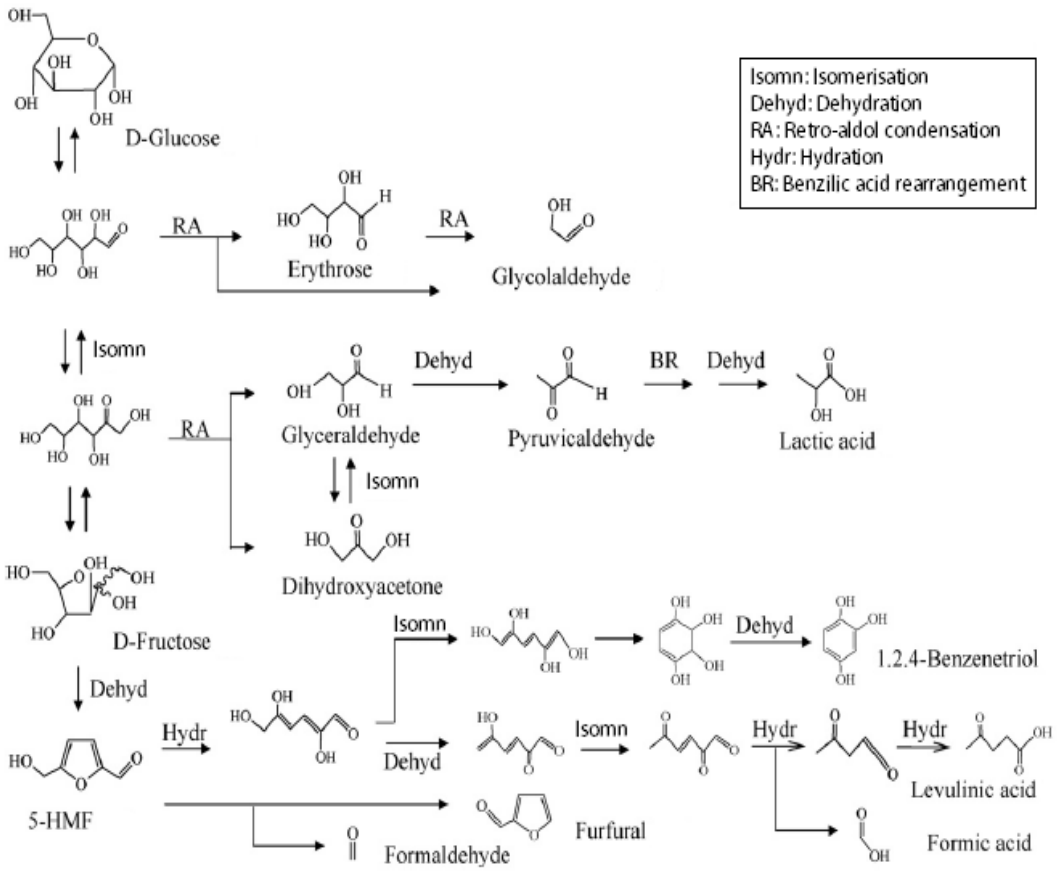

Figure 2- 9: Glucose decomposition in HCW reaction pathways[112]

Sinag et al. [143, 144] investigated decomposition of glucose in supercritical water (400-500 °C) and they come out with a simplified reaction pathway for decomposition of glucose as illustrated in Figure 2-10. The proposed reaction pathways clearly illustrates that there are two main reactions during decomposition of glucose in supercritical water as follows: (1) dehydration which involved the breakage of C-O, and (2) The cleavage of C-C bond for example retro-aldol condensation.[121, 144] Glucose is converted into furfural via dehydration reaction and then further dehydrates into phenols. Meanwhile, acids and aldehydes are produced from glucose, furfurals and phenols through C-C bond breaking reactions. Acids and aldehydes are further transformed via bond breaking into gaseous such as H_2, CO_2, CO and CH_4.[139, 144]

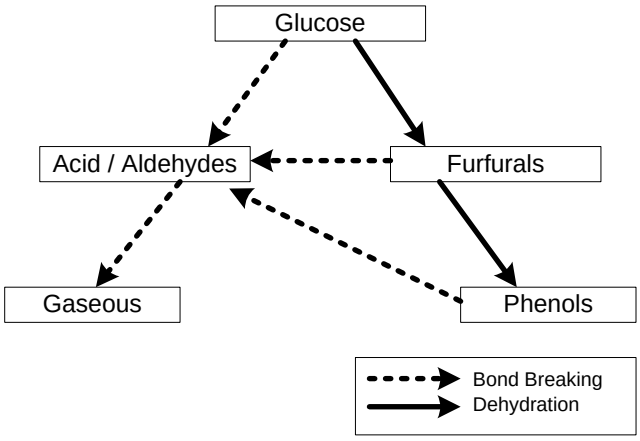

Figure 2- 10: Simplified reaction pathways for glucose decomposition reaction in HCW[139]

Significant studies have been conducted on glucose decomposition under the acidic condition in HCW.[118, 121, 145-147] Watanabe et al.[121] and Srokol et al.[148] reported that in the presence of acid, the formation of 5-HMF and levoglucosan are promoted, while the formation of fructose via isomerisation is suppressed. In addition, the acid also catalysed 5-HMF degradation reaction into smaller products for example levulinic acid and formic acid.[148, 149] The addition of acid also increases the rate of glucose decomposition in HCW.[118, 121, 149, 150] McKibbins et al.[149] studied the acid catalysed decomposition of glucose at 140 to 250 °C with sulphuric acid concentrations of 0.025 to 0.8 N. The rate of glucose decomposition was found to be proportional to acid concentration. An increase in acid concentration also increase the yields of 5-HMF and levulinic acid.[149] Xiang et al.[145] studied glucose decomposition at 200 to 230 °C and low sulphuric acid concentration of 0.05 to 0.3 wt%, covering pH values of 1.5 to 2.2. Kupiainen et al.[118] used sulphuric and formic acid as the catalyst for glucose decomposition at 180 to 220 °C with pH values below 2.2. A similar result is reported from both studies. Based on the ab ignitio molecular dynamic simulation studied, glucose decomposes in acidic conditions proceed via the addition of proton from water to the hydroxyl group on the glucose ring.[151] These finding clearly suggested that hydrogen ion concentration (related to acid concentration) play an important role during decomposition of glucose since the protonation is the initiator of glucose decomposition reaction.

In contrast to the acidic condition, the presence of alkaline promotes the isomerisation of glucose into fructose and retro-aldol condensation to produce glycolaldehyde, erythrose and glyceraldehyde. The yield of pyruvaldehyde, lactic acid and acetic acid also increases under alkaline conditions. However, the formation of 5-HMF and levoglucosan is inhibited by the alkaline catalyst.[36, 121, 148] Maclaurin and Green[152] investigated the glucose decomposition under the alkaline system at 22 °C and 1 M NaOH. They reported that glucose transformed into fructose and mannose. Based on their studied on fructose and mannose, this reaction is reversible. De Bruijn et al.[153-155] studied the influence of reaction variables on the degradation of sugar monomers (i.e. glucose, fructose, mannose and psicose) in alkaline conditions. They suggested that enediol anion species were formed during glucose decomposition in alkaline solution as an intermediate. These species are involved in both isomerisation and degradation reactions of glucose. Higher hydroxyl ion concentration promotes the enolisation rate, thus increase the rate of isomerisation and degradation of glucose, and subsequently increase the rate of overall glucose decomposition. Furthermore, they also suggested that the formation of lactic acid is the secondary product of retro-aldol condensation of ketose (fructose). Higher concentration of hydroxyl ion promotes the isomerisation of aldose to ketose and also the retro-aldol condensation of ketose leading to enhancement of lactic acid formation.[153]

2.5.2 Mechanism of Cellobiose Decomposition in HCW

Cellobiose has two unit of glucose that linked by a glycosidic bond. It is the glucose oligomers with the simplest structure. Pioneer study of cellobiose decomposition in HCW was conducted by Bobleter and Bonn in 1980s[28] using batch reactor (autoclave) at the temperature of 180–249 °C showed that decomposition of cellobiose in HCW produced glucose with yield up till ~60%. Kabyemela et al.[25] and Sasaki et al.[26] performed systematic studies to elucidate the reaction pathways and evaluation the reactions kinetics at higher temperatures(300−420 °C) using a continuous reactor. They proposed that cellobiose is decomposed by hydrolysis and retro-aldol condensation reactions. During hydrolysis reaction, the glycosidic bond was breaking to produce two molecules of glucose. Whereas, retro-aldol condensation happen at reducing end of glucose to form glucosyl-erythrose (GE) and glycolaldehyde as shown

in Figure 2-11. GE subsequently decomposes into glucose and erythrose by hydrolysis and/or transformed into glucosyl-glycolaldehyde (GG) via the retro-aldol condensation. Meanwhile, GG is transformed into glucose and glycolaldehyde via the hydrolysis reaction. Glucose that produced from cellobiose, GE and GG hydrolysis will be decomposed into fructose, 5-HMF, glycolaldehyde, and other products.[26]

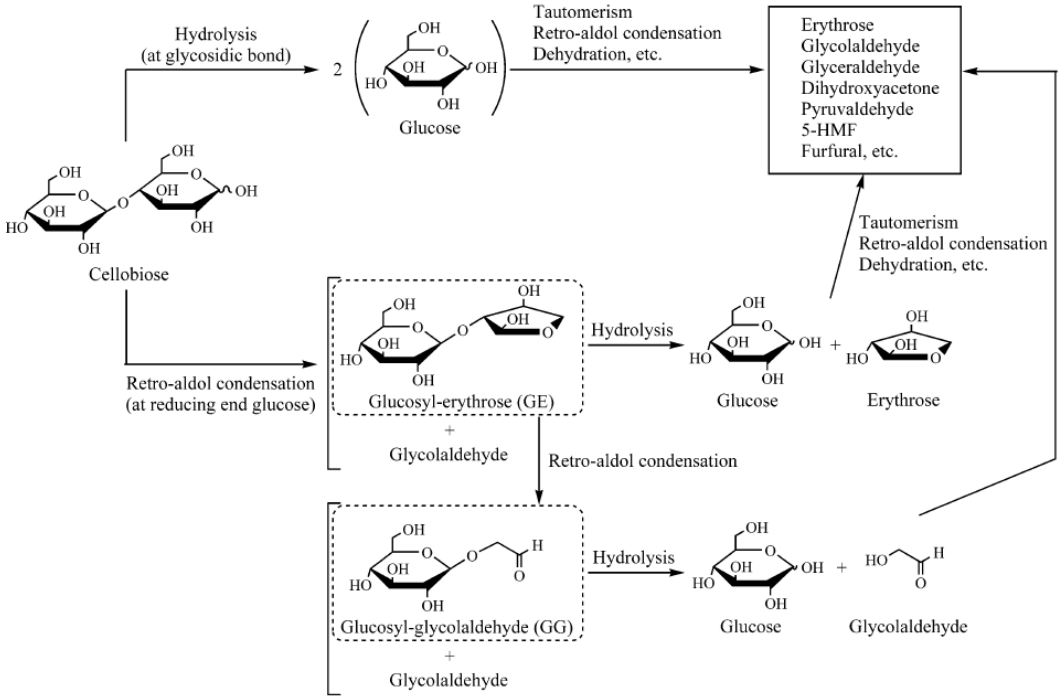

Figure 2- 11: Main reaction pathways of cellobiose decomposition in HCW[26]

Recently, Kimura et al.[29] conducted a study on glucose oligomers decomposition at low temperature (100−140 °C). They reported that glucose oligomers decomposition proceeds through isomerisation of glucose unit at reducing end into fructose follow by the cleavage of the glycosidic bond to remove the fructose (Figure 2-12). Such mechanism was confirmed to be valid for glucose oligomers with DPs until 4.[29] This study clearly indicates that isomerisation is an important primary reaction of cellobiose decomposition in HCW, which is not reported in previous studies on cellobiose.[25-28] Therefore, there are contradictions among the existing literatures regarding the data and proposed reaction pathways. The actual reaction pathway of cellobiose decomposition in HCW is still unclear.

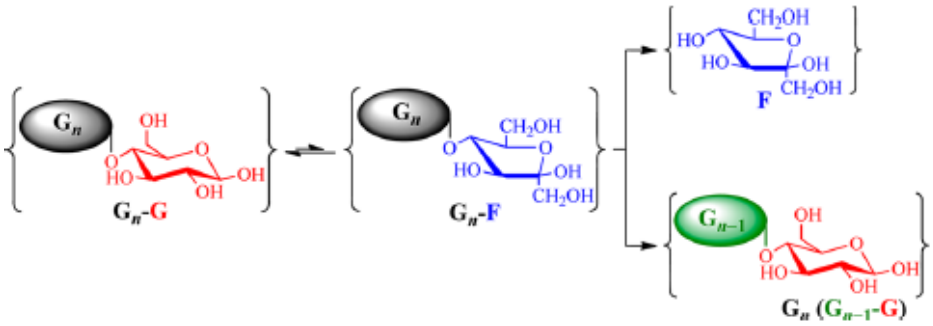

Figure 2- 12: Reaction pathways of glucose oligomers decomposition under non-catalytic condition[29]

Similar to glucose, the addition of acid also increase cellobiose decomposition rate.[126, 156, 157] Moreover, the rate of cellobiose decomposition also depend on the acid concentration.[126] Furthermore, acid catalysts increase the production of glucose by hydrolysis reaction of cellobiose at the glycosidic bond.[156] Recent simulation study on cellobiose hydrolysis suggested that the mechanism of cellobiose hydrolysis in acidic conditions proceed in two steps.[128] Step 1: the protonation of glycosidic oxygen from the acid proton (H_3O^+) and the breakage of glycosidic bond to produce glucose and oxacarbeniun ion species ($C_6H_{11}O_5^+$). Step 2: the hydration of oxacarbeniun ion to form another glucose molecule and produce back H_3O^+ ion:

$$C_{12H22}O_{11} + H_3O^+ \rightarrow C_6H_{12}O_6 + C_6H_{11}O_5^+ + H_2O \quad \text{(Step 1)}$$

$$C_6H_{11}O_5^+ + 2H_2O \rightarrow C_6H_{12}O_6 + H_3O^+ \quad \text{(Step 2)}$$

Therefore, the availability of hydrogen ion to catalyse the hydrolysis of cellobiose into glucose enhanced with the increase of the concentration of acid.

The studied on cellobiose decomposition under alkaline conditions (22 °C, 1 M NaOH) showed that cellobiose isomerises into cellobiulose (glucosyl-fructose, GF) and glucosyl-mannose (GM).[158] These results clearly indicated that isomerisation is the important primary reaction of sugars in alkaline conditions. The also suggested that isomerisation products are formed initially, and then hydrolysis via glycosidic bond

breakage to form monosaccharides (glucose, fructose and mannose). Bonn et al. reported that the rate of cellobiose disappearance increase with the increasing of NaOH concentration.[125] This result clearly suggested that the cellobiose decomposition rate under alkaline conditions depend on hydroxyl ion concentration.

2.5.3 Factors Influencing Glucose and Cellobiose Decomposition in HCW

Glucose and cellobiose decompose in HCW via isomerisation, dehydration and retro-aldol condensation. Previous studies showed that reaction conditions can influence the reaction rate and product distributions of glucose and cellobiose in HCW.[25-27, 85, 112, 119, 121, 138, 142, 159-161] The Following section will discuss the effect of temperature, pressure, initial concentration of reactant and catalysts on glucose and cellobiose decomposition in HCW.

2.5.3.1 Temperature

The reaction rate of glucose and cellobiose decomposition in HCW really dependent on temperature. For example, almost 100% of glucose is decomposed in 60 s at 300 °C, but it took only 0.5 s at 460 °C. A similar observation has been reported for cellobiose. Kabyemela et al.[25] reported that the cellobiose conversion reached 80% in 1.4 s at 300 °C. However, 80% of cellobiose was converted in 0.15 s at 400°C.

Products distribution of glucose decomposition in HCW also greatly depends on temperature. Promdej and Matsumara[142] examined the influence of temperature on glucose decomposition in subcritical and supercritical water. Their study showed that isomerisation of glucose to fructose and dehydration of glucose to 5-HMF and furfural are not promoted in supercritical water. However, these processes (i.e isomerisation and dehydration) were suggested to be dominant in subcritical water.[121, 160] However, retro-aldol condensation (involve C-C bond breaking) of glucose into glycolaldehyde and erythrose is reported to be promoted in supercritical water.[160] The isomerisation and dehydration process are known to be an ionic reaction. The value of ionic products is higher in subcritical water compared to supercritical water. Therefore, it can be summarised that ionic reactions are promoted at the subcritical water, while radical reactions (C-C bond breaking) are promoted at the supercritical water.[121]

Studies on cellobiose decomposition in HCW do not provide clear information on the effect of temperature on cellobiose reaction pathway. Therefore, there is a need to studies the influence of temperature on cellobiose decomposition in HCW product distribution.

2.5.3.2 Pressure

In subcritical water, the influence of pressure on the reaction of glucose and cellobiose decomposition in HCW is insignificant compared to that in supercritical water.[25, 26, 85, 112, 160] Sasaki et al.[160] investigated glucose decomposition at the supercritical water. They revealed that an increase in pressure of supercritical water promotes isomerisation and dehydration reactions, while a decrease in pressure, promote retro-aldol condensation reaction to form erythrose and glycolaldehyde.[160] On the other hand, the increase in the pressure increases the production of 5-HMF through the dehydration process.[112] The change in pressure of supercritical water clearly shifts the reaction pathways from radical reactions at low pressure to ionic reactions at high pressure.

Similar results on cellobiose decomposition also reported by Kabyemela et al.[25] and Sasaki et al.[26] In supercritical water, retro-aldol condensation reaction to form GE and GG is promoted at low pressure and suppressed at high pressure. Meanwhile, hydrolysis reaction to form glucose is promoted at high pressure in supercritical water.[25, 26]

2.5.3.3 Initial Concentration of Reactant

Previous studies on glucose decomposition in HCW showed that the reaction rate of glucose decomposition decrease when initial glucose concentrations increase.[119, 138, 159] Furthermore, initial glucose concentration can influence the products distribution.[138] It was found that at low initial glucose concentration enhance the isomerisation reactions to produce fructose and retro-aldol condensation reactions to produce glycolaldehyde and erythrose. However, higher initial glucose concentrations promote the dehydration reactions to produced 5-HMF and levoglucosan.[138]

Moreover, higher initial glucose concentrations produce more water-solvent insoluble products such as char than at lower initial glucose concentrations.[159] These results obviously show that initial concentration of reactant can affect the reaction mechanism of sugars decomposition in HCW.

2.5.3.4 Catalysts

Catalysts were used to promote the selectivity of desired products and enhance the reaction rate of biomass or model compounds conversion in HCW.[36] In general, there are two types of catalysts, homogeneous such as mineral acid[118, 126, 145, 150, 162-164], organic acid[118, 157, 165] and bases (e.g. sodium hydroxide)[121, 125] and heterogeneous such as metal oxide (e.g. ZrO_2 and TiO_2),[121, 161, 166] zeolite,[167-169] and zirconium phosphate.[170] Solid acid/based catalysts are the most common heterogeneous catalysts used for cellulose/biomass conversion and sugars (e.g. glucose) decomposition in HCW. Solid catalyst can be considered to be environmentally friendly as it can be reusable, and separable from solvent and reactant.[60] Moreover, using acid/based solid catalysts does not lead to corrosion issues usually observed with the utilisation of homogenous acid/based catalysts.[60, 161]

Watanabe et al. studied the influence of metal oxides on glucose decomposition in HCW at 200 °C. [121, 161] They found that ZrO_2 act as a base catalyst where its presence enhances the isomerisation of glucose and fructose. Meanwhile, anatase TiO_2 promotes both isomerisation and dehydration into 5-HMF, thus indicates that anatase TiO_2 has both acid and base properties. Watanabe et al. [121, 161] suggested that the high yield of 5-HMF from glucose due to their dual character of acidity and basicity. The studies on the effect of zeolite catalysts on glucose decomposition shown that high yield of levulinic acid is achieved with the addition of these catalysts.[169, 171] Onda et al.[172] examined the effect of activated hydrotalcites as solid base catalysts on glucose decomposition in water at 50 °C. It was demonstrated that the yield of lactic acid increase with the presence of activated hydrotalcites.[172] The results of the study on heterogeneous solid catalysts indicate that this type of catalyst has the potential for efficient production of high value and green chemical products such as 5-HMF, levulinic acid and lactic acid.

2.5.3.5 Alkali and Alkaline Earth Metallic (AAEM) Species

It is notable that biomass contains abundant AAEM species such as Na, K, Mg and Ca. These AAEM species usually bound with inorganic anions such as chloride, sulphate and phosphate to form an inorganic salt in biomass.[173] A number of researchers reported that AAEM salts affect the conversion of biomass and sugar in HCW.[173-177] The presence of inorganic salt during pretreatment of biomass demonstrated that alkaline earth metal salts ($MgCl_2$ and $CaCl_2$) increased hemicellulose removal from biomass and accelerated xylose degradation reactions, result in lower sugar recovery. On the other hand, alkali metal salts (NaCl and KCl) reduce hemicellulose removal, thus produce a low yield of xylose and xylose oligomers.[174, 176] However, the studies on xylose and xylotriose revealed that all AAEM salts increase xylose and xylotriose decomposition in HCW.[173]

Little has been reported on the effect of AAEM salts on glucose and cellobiose decomposition in HCW. Wu et al.[177] reported that the presence of potassium salts increased glucose and fructose decomposition rate and selectivity of 5-HMF. Therefore, AAEM salts have an impact on the decomposition rate of sugars monomers and oligomers in HCW. However, the effect of AAEM salts on degradation mechanism of sugars monomers and oligomers are still unclear.

2.5.4 Reaction Kinetics of Glucose and Its Oligomers

Several studies have been carried out to gain the kinetics data of glucose and cellobiose decomposition in HCW. All previous studies reported that both glucose and cellobiose decomposition follow the law of first order kinetic. [25-28, 85, 116, 119, 138, 142, 159, 178] Furthermore, the reaction rate of glucose and cellobiose decomposition in HCW without catalyst can be controlled by manipulating the reaction parameters for example temperature, pressure and initial concentration of reactant. Kinetic parameters of glucose and cellobiose decomposition in HCW are summarised in Table 2-4.

Table 2- 4: Summary of kinetic parameters of glucose and cellobiose decomposition in HCW

Feedstock	Reactor type	Initial concentration	Temperature (°C)	Pressure (MPa)	Residence time	Activation energy (kJ/mol)	Frequency factor (s^{-1})	Reference
Glucose	Continuous Flow type	0.12 wt% (1.2 g/L)	300 – 400	25 - 40	0.02 – 2s	96		Kabyemela et al.[85]
Glucose	Continuous Flow type	0.02 – 0.12M (3.6 – 21.6 g/L)	175 - 400	25	Up to 350s (at 175°C)	121	1.33×10^{10}	Matsumara et al.[119]
Glucose	Continuous Flow type	1.5 wt% (15 g/L)	300 - 460	25	Up to 60s	95.5	6.9×10^{7}	Promdej and Matsumara[142]
Glucose	Batch	0.06 M (10.8 g/L)	180 – 220	10	Up to 180 min	118.8	1.4×10^{11}	Jing and Lu[178]
Glucose	Batch	0.73 – 162 g/L	250 - 350		10s to 10 days	114	7.7×10^{8}	Knezevic et al.[159]
Cellobiose	Batch	10 g/L	180 - 249		Up to 14 min	136		Bobleter and Bonn[28]
Cellobiose	Continuous Flow type	0.00241M (0.824 g/L)	300 - 400	25	0.04 – 2s	96.4		Kabyemela et al.[25]
Cellobiose	Continuous Flow type	1 wt% (10 g/L)	320 - 420	25 - 40	Up to 3s	51		Park and Park[27]
Cellobiose	Continuous Flow type	0.0286 – 0.0714M (9.8 – 24.4 g/L)	325 - 400	25 - 40	0.01 – 0.54s	111.2	$1 \times 10^{9.4}$	Sasaki et al.[26]

Table 2-4 clearly indicates that the apparent activation energy of glucose and cellobiose are not consistent. This probably because of the difference reaction conditions and reactor types were used by the researchers. As aforementioned, reaction parameters such as temperature, pressure and initial reactant concentration can shift the reaction pathways of glucose and cellobiose decomposition in HCW. Every reaction pathways have different activation energy as shown in Table 2-5 and Table 2-6 for glucose and cellobiose respectively. Therefore, the apparent activation energy of glucose and cellobiose decomposition will also change when the reaction pathways are shifted.

Table 2- 5: Kinetic parameters of different reaction pathways of glucose decomposition in HCW[179]

Products	**Reaction**	**Activation energy (kJ/mol)**	**Frequency factor (s^{-1})**
Fructose	Isomerisation	78.6	5.71×10^{4}
Erythrose	Retro-aldol condensation	96.2	2.7×10^{6}
Glyceraldehyde	Retro-aldol condensation	95.6	6.59×10^{6}
5-HMF	Dehydration	125.9	8.19×10^{8}
Levoglucosan	Dehydration	193.2	1.21×10^{17}

Extensive studies have been conducted to gain kinetic parameters for glucose decomposition reaction at various reaction conditions. In contrast, most of the available kinetic parameters for cellobiose decomposition were conducted at high temperatures (> 300 °C). Therefore systematic studies on cellobiose decomposition in HCW at the lower temperature (< 300 °C) are essential as lower temperature condition is relevant for liquefaction of biomass for biofuel production. Furthermore, there is no kinetic data available for other glucose oligomers. This data is very important to optimise the yield of desired products and efficient reactor design.

Table 2- 6: Kinetic parameters of different reaction pathways of cellobiose decomposition in HCW

Products	Reaction	Temperature (°C)	Activation energy (kJ/mol)	Frequency factor (s^{-1})	Reference
Glucose	Isomerisation	325 - 400	104.5	$10^{7.1}$	Sasaki et al.[26]
		300 - 400	108.6		Kabyemela et al.[25]
GE	Retro-aldol condensation	325 - 400	122.6	$10^{10.1}$	Sasaki et al.[26]
		300 - 400	30.4		Kabyemela et al.[25]
GG	Retro-aldol condensation	300 - 400	69.3		Kabyemela et al.[25]

2.6 Conclusions and Research Gaps

Hot-compressed water (HCW) is a potential medium for synthesis of renewable energy and green chemical from biomass. However, the detail reaction mechanism and kinetics of all the components during biomass conversion in HCW have not been fully elucidated. Significant studies have been conducted to investigate the reaction mechanism and kinetics of biomass conversion in HCW, mainly using cellulose as a model compound. It is well published that glucose and glucose oligomers are the primary products of cellulose decomposition in HCW. However, there are limited studies conducted on the mechanism of glucose oligomers decomposition in HCW. Therefore, further R&D is required to enhance the fundamental understanding of glucose oligomers decomposition reactions in HCW, including:

- Elucidation of cellobiose decomposition mechanism in HCW. There are contradictions on the cellobiose decomposition reaction mechanism reported by previous literatures.

- Cellobiose decomposition reaction mechanism in HCW at the lower temperature (<300 °C) still unclear. Previous studies on cellobiose decomposition mostly conducted at the higher temperature (> 300 °C). The information is important since lower temperature conditions are relevant to the most hydrothermal applications such as hydrothermal liquefaction of biomass.

- The reaction mechanism and kinetic of glucose oligomers decomposition at various reaction conditions. These reactions are important to understand the mechanism of primary products from cellulose and biomass decomposed in HCW. These secondary reactions lead to low sugar yield from the decomposition process.

- Influence of initial reactant concentration. The previous study on glucose shown that initial concentration affected the reaction rate and mechanism of glucose decomposition in HCW. However, such effect on glycosidic bond breakage (hydrolysis reaction) in glucose oligomers and cellulose/biomass is not fully understood.

- Effect of weakly acidic condition on the decomposition of glucose oligomers and cellulose/biomass in HCW. Cellulose/biomass conversion in HCW produces some organic acids. Therefore the reaction conditions during cellulose/biomass conversion changes from non-catalytic to weakly acidic conditions as the conversion proceed.

- The role of AAEM species on glucose oligomers decomposition mechanism in HCW. The presence of AAEM species has an impact on biomass and sugar decomposition in HCW. However, the role of AAEM species on the reaction mechanism of sugars decomposition is not clearly understood.

2.7 Research Objectives of Present Study

Several research gaps have been identified from the literature review above. However, it is impossible to conduct research to address every research gaps identified. Therefore, this thesis focuses on cellobiose decomposition in HCW under various conditions. Cellobiose was used as the model compound in this thesis to understand the mechanism of glucose oligomers decomposition in HCW. This will provide further understanding on cellulose and biomass decomposition in HCW. The main objectives of this thesis are:

1. To clarify the mechanism of cellobiose decomposition in HCW at lower temperature conditions (< 300 °C). A new reaction pathway for cellobiose

decomposition in HCW will be proposed. The effect of temperature on the mechanism of cellobiose decomposition will be discovered.

2. To investigate the effect of initial cellobiose concentration on the mechanism of cellobiose decomposition in HCW.

3. To understand the difference in cellobiose decomposition mechanism between non-catalytic and weakly acidic conditions.

4. To examine the influence of AAEM species cellobiose decomposition mechanism in HCW.

CHAPTER 3: METHODOLOGY AND EXPERIMENTAL TECHNIQUES

3.1 Introduction

In this chapter, the general research methodologies used to achieve all objectives mentioned in Section 2.7 are discussed. Furthermore, the experimental and analytical techniques are also described in details.

3.2 Methodology

To gain a better understanding of the fundamental mechanism and kinetics of cellobiose decomposition in hot-compressed water (HCW). A continuous reactor system is used for the experiments at various temperature and pressure of 10 MPa. Moreover, systematic studies were conducted to investigate the effects of temperatures, initial cellobiose concentration, weakly acidic conditions, and alkali and alkaline metal (AAEM) chlorides on mechanism and kinetics of cellobiose decomposition in HCW. The liquids samples collected were analysed by high-performance anion exchange chromatography with pulsed amperometric detection and mass spectrometry (HPAEC-PAD/MS). Total organic carbon was also determined by total organic carbon (TOC) analyser. The total carbon in the liquid samples was found to be ~100%. Thus, the formation of gases from cellobiose decomposition is this study is insignificant. To demonstrate that the organic acids were forming during cellobiose decomposition in HCW, the pH value of the solutions were measured before and after the experiments. To ensure the results were reproducible, the experiments and analysis were replicated. Figure 3-1 shows the overall methodology applied to achieve the objectives in this thesis and the detail explanations were provided in following sections.

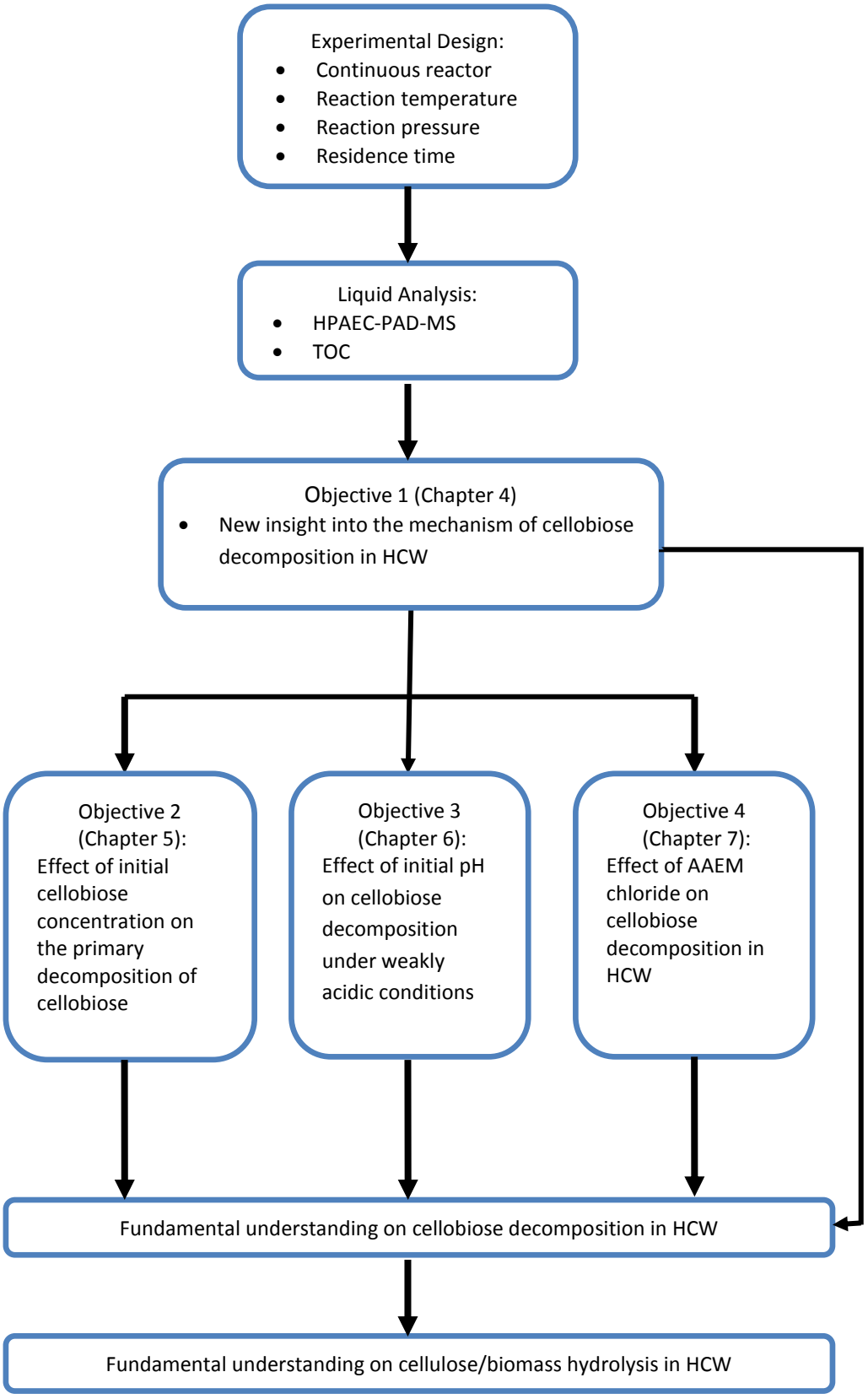

Figure 3- 1: Research methodology

3.2.1 New Insight into the Mechanism of Cellobiose Decomposition in HCW

As mention in Chapter 2, there are discrepancies in the proposed reaction mechanism of cellobiose decomposition in HCW by previous literatures. Therefore, experiments were conducted to elucidate the reaction mechanism of cellobiose decomposition in HCW. The experiments were performed at temperatures range of 225 to 275 ^{o}C and various residence times with initial cellobiose concentration of 1000 mg L^{-1}. The liquid products were analysed by HPAEC-PAD/MS for products identification and the products with available standards were further quantified. With HPAEC-PAD/MS unique capabilities, this study provides new knowledge on cellobiose decomposition mechanism in HCW. In addition, the total carbon in the liquid sample was quantified by TOC analyser to determine the closure of mass balance and formation of gaseous products during experiments.

3.2.2 Effect of Initial Cellobiose Concentration on the Primary Decomposition Mechanism of Cellobiose in HCW

The effect of initial cellobiose concentration on the primary reactions of cellobiose decomposition in HCW was investigated. The experiments were conducted at various temperatures (200–275 ^{o}C) and initial cellobiose concentrations (10–10,000 mg L^{-1}). The liquid samples collected were analysed by HPAEC-PAD/MS and TOC analyser. Kinetic analysis on cellobiose decomposition in HCW was conducted based on cellobiose concentrations quantified. Furthermore, the kinetics of isomerisation and hydrolysis reactions during cellobiose decomposition were calculated by using delplot method.

3.2.3 Effect of Initial pH on Cellobiose Decomposition under Weakly Acidic Conditions

A series of experiments were performed to examined the effect of weakly acidic condition to cellobiose decomposition reaction and compare it with the non-catalytic condition. The study was conducted at various initial pH (4 -7) and temperatures (200 – 250 ^{o}C). The initial pH of cellobiose solution was adjusted to the desired pH by using sulphuric acid. The liquid sample collected from the reactor were analysed with HPAEC-PAD/MS and TOC analyser.

3.2.4 Effect of Alkali and Alkaline Metal Salts on Cellobiose Decomposition in HCW

A systematic study was performed to examine the effect of AAEM chlorides (e.g. NaCl, KCl, $MgCl_2$ and $CaCl_2$) on the cellobiose decomposition mechanism and reaction pathways in HCW. Cellobiose solution was mixed with AAEM chlorides at desired concentration. The liquid samples collected from the experiments were analysed with HPAEC-PAD/MS and TOC analyser.

3.3 Experimental

3.3.1 Cellobiose Solution Preparation

Cellobiose (product number: 22150) with 99% purity purchased from Sigma-Aldrich was used in this study. Cellobiose solution was prepared by dissolving cellobiose in deionised water at the concentration three times higher than desired concentration as the ratio of preheated water and cellobiose solution flow rates were set as 2:1.

In Chapter 6, the pH of the cellobiose solution was adjusted to the desired pH (4 – 6) with the addition of 72% sulphuric acid. Meanwhile in Chapter 7, AAEM chloride (NaCl, KCl, $MgCl_2$ or $CaCl_2$) was added to cellobiose solution. The appropriate amount of AAEM chloride salt was mixed with the cellobiose solution to achieve a salt concentration of ~29 mM corresponding to the molar ratio of salt and cellobiose at 10:1.

3.3.2 Reactor System

A schematic representation of continuous flow reactor employed in this thesis is shown in Figure 3-2. This reactor system contains one container filled with deionised water, one container filled with cellobiose solution, two HPLC pumps for delivering water and cellobiose solution, fluidized sand bath for heating of the water preheating tube and reactor, thermocouple to monitor the reaction temperature, cooling unit to quench the liquid products quickly and one back pressure regulator to control the reaction pressure.

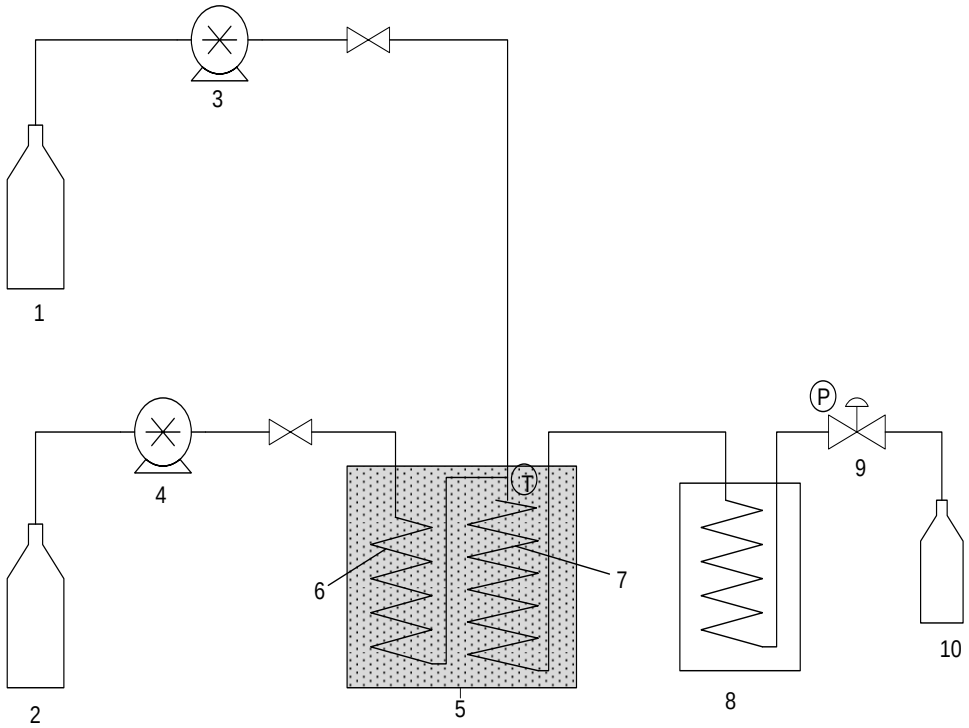

Figure 3- 2: Schematic representation of the continuous flow type reactor system for cellobiose decomposition in HCW: (1) Cellobiose solution container ; (2) deionised water container ; (3) and (4) HPLC pump; (5) fluidized sand bath; (6) preheating tube; (7) continuous reactor; (8) cooling bath; (9) back-pressure regulator; (10) sample collector[138]

The cellobiose solution was delivered to the system by an Altech 626 HPLC pump at the flow rate of 2-10 mL min^{-1}. Deionised water was delivered by an Altech 627 HPLC pump at the flow rate twice of the cellobiose solution. The deionised water was preheated in a preheating tube submerged in a fluidised sand bath (Techne, model SBL-2D) before it was mixed with the cellobiose solution to rapidly increase the temperature of the feed solution to the desired reaction temperature. The reaction temperature was measured by a thermocouple at a position of 2 cm below the mixing point. Various residence times were achieved by changing the continuous reactor length and flow rates. Water mixed with ice were used as the cooling fluid in the cooling bath so that the effluent from the reactor can be cooled immediately. A back-pressure regulator was used to maintain the reaction pressure at 10 MPa.

Stainless steel (SUS 316) tube from Swagelok with the outer and inner diameter of 25.4 and 4.572 mm respectively was used to make the reactors with the length of 0.25 to 2 m. However, a smaller tube with the outer and inner diameter of 1.6 and 0.508 mm respectively, was used for short residence times.

Calibration of the temperature inside the tube reactor at various flow rates, particularly the temperature of the position where the water and cellobiose solution mix together was carried out to find out the suitable ratio of water and cellobiose solution flow rates to achieve a fast heating of cellobiose solution. The ratio of 2:1 between water and cellobiose solution flow rates was found to be sufficient enough to allow rapid heating of cellobiose solution to the reaction temperature. During the experiments, the temperature at the inlet of the reactor was similar to the sand bath temperature where the temperature difference usually less than 3 ^{o}C.

Reynold number (*Re*) and Grashof number (*Gr*) were calculated in order to analyse the flow characteristics under various conditions. The Re and Gr were calculated using the following equations:

$$Re = \frac{DV\rho}{\mu} \qquad \text{(Equation 3.1)}$$

$$Gr = \frac{g\beta\Delta T D^3 \rho^2}{\mu^2} \qquad \text{(Equation 3.2)}$$

The *Re* and *Gr* for the various condition are presented in Table 3.1. Based on the *Re* calculation, the flow in the short residence time reactor is turbulence but for other reactors are laminar. However, the mixed of two liquids at different temperature can cause natural convection. Previous studies[180, 181] have shown that the natural convection can cause significant turbulence in the reactor. Based on the calculation of Grashof number, all the selecting flow velocities of cellobiose and water for this study fall down under turbulent regimes.

Table 3- 1: Total flow rate of water and cellobiose solution and corresponding Reynolds number (Re) and Grashof number (Gr) at different reaction time and temperature

Reaction Time	Total flow rate (ml min^{-1})				Reynolds number				Grashof number (10^9)			
	Temperature (°C)				Temperature(°C)				Temperature(°C)			
	200	225	250	275	200	225	250	275	200	225	250	275
5.1	30	30	30	30	8026	8735	9369	9910	2.3	3.4	4.9	6.9
10.4	30	30	30	30	893	972	1043	1103	2.3	3.4	4.9	6.9
17.6	30	30	30	30	893	972	1043	1103	2.3	3.4	4.9	6.9
31.9	30	30	30	30	893	972	1043	1103	2.3	3.4	4.9	6.9
46.1	30	30	30	30	893	972	1043	1103	2.3	3.4	4.9	6.9
60.5	30	30	30	30	893	972	1043	1103	2.3	3.4	4.9	6.9
92.3	15	15	15	15	446	486	521	551	2.3	3.4	4.9	6.9
120.9	15	15	15	15	446	486	521	551	2.3	3.4	4.9	6.9

3.4 Sample Analysis

The collected liquid products (i.e. before and after reaction) were analysed using HPAEC-PAD/MS for products identification and quantification, and TOC analyser to determine total carbon in liquid samples.

The chemicals used for cellobiose calibration are as follows: Cellobiose (99%), glucose monohydrate (99%), fructose (99%), mannose (99%), glycolaldehyde dimer (98%), erythrose (75%), 5-HMF (99%) and 1,6-anhydro-β-D-Glucose (99%) purchased from Sigma Aldrich, and 1,6-anhydro-β-D-Cellobiose (98%), cellobiulose (glucosyl-fructose, GF; 95%), glucosyl-mannose (GM; 95%) and Glucosyl-glycolaldehyde (GG; 95%) obtained from LG Scientific Inc.

3.4.1 Dilution

For the quantification of compounds in a liquid sample, the sample was diluted to a few dilution factors to ensure the concentrations of compounds in analytes fall down under the detection limit of HPAEC-PAD. Hamilton Microlab 500 series diluter was used for accurate and precise dilution.

3.4.2 High-Performance Anion Exchange Chromatography with Pulsed Amperometric Detection and Mass Spectrometry (HPAEC-PAD/MS)

High-Performance Anion exchange Chromatography with Pulsed Amperometric Detection and Mass Spectrometry (HPAEC-PAD/MS) permits more reliable, faster and direct analysis of underivatised carbohydrate at low-picomole levels.[182] Furthermore, MS detector can be used to identify unknown peaks on the chromatogram based on their molecular weight. There are two detectors used for this system, which are pulsed amperometric Detector (PAD) and mass spectrometry detector (MS). Basically, the chromatography system consists of the autosampler, guard and analytical column, splitter, desalter, electrochemical detector (i.e. PAD) and MS detector as demonstrated in Figure 3-3.

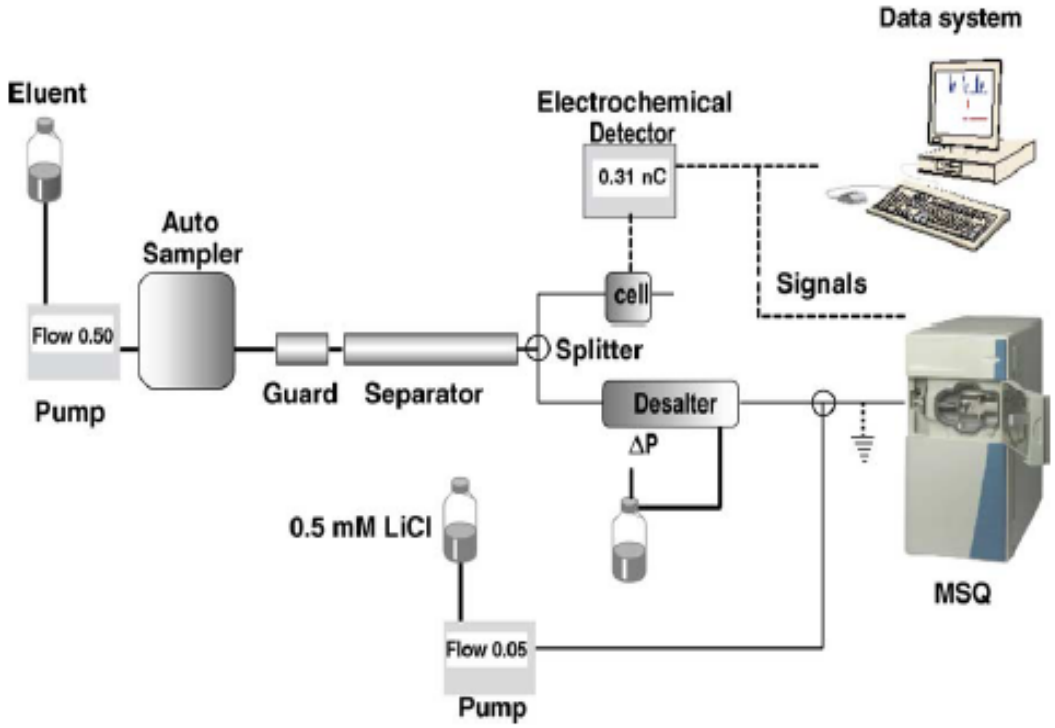

Figure 3- 3: Schematic diagram of HPAEC-PAD/MS system[182]

The carbohydrate in the sample are oxidised at the gold electrode surface and generated the electrical current. The resulting current will be detected by the PAD. Electrical current produced is proportional to carbohydrates concentration.[183, 184] The electrode surface need to be cleaned after every measurement as the products from the

oxidation reaction can poison it, causing loss of analyte signal.[184] It can be achieved by applied repeating sequence of potential after the detection potential as illustrated in Figure 3-4. First potential (E_1) is the current measured from the oxidation of carbohydrate. The electrode potential is increased to E_2, where the gold surface can be oxidised and removed the products from carbohydrate oxidation. After that, the potential will decrease to E_3 to reduce the electrode surface from gold oxide into gold, therefore allowing detection in the next cycle.[183] To ensure the only current from carbohydrate oxidation is determined during the detection period, the current is measured after a delay to permit the changing current (produced by changing potential) to decay.[183]

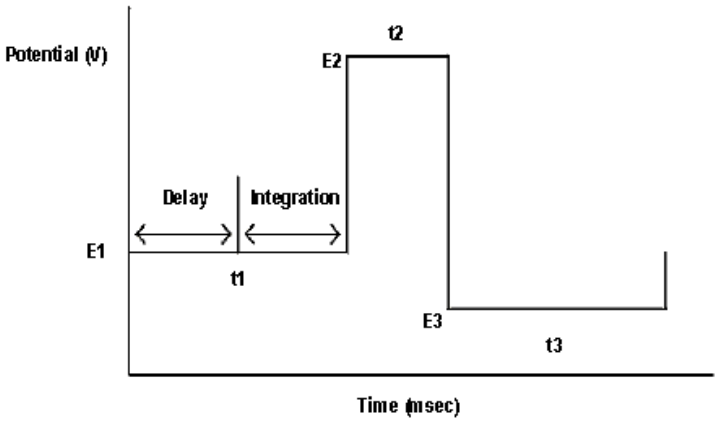

Figure 3- 4: Schematic of potential sequence for carbohydrate detection with PAD[183]

The MS detector can be used to identify an unknown compound, and also to determine the chemical structure. Figure 3-5 demonstrates the schematic diagram of MSQ detector system. In general, the sample from the column needs to be ionised before it can be detected by Mass detector. The electrospray (ESI) will change the ions in the liquid droplets into the gas stage. This process is also known as Ion Evaporation.[185] The sample passes through stainless steel insert capillary at the high potential of 3 to 5 kV. The high potential combine with atomised nitrogen gas flow created a strong electric field. Highly charged droplets are formed at the tip of the probe due to the electric field. The charge density on the surface increase as the solvent is removed via evaporation supported by the heated nitrogen gas.[186] When the charge density reaches

Rayleigh limit, the droplets will shatter into smaller droplets via columbic explosion. This process is repeated until at the end only charged ions remain. The high electric field and the gas flow forced the ions into the focusing region through the entrance cone. The ions then pass through RF lens where its help focus the ions before they are filtered based on their mass to change ratio in the mass analyser.[185, 186] The quadrupole mass analyser can control which ions (specific mass to charge ratio) can go through at any one time to the detector by adjusting the voltage of the four rods in the quadrupole. The ions from analyser hit a conversion dynode and produce electrons. The electrons then move toward the channeltron electron multiplier result in an electron cascade. The current generated then transformed into the voltage signal for further analysed by data acquisition system.

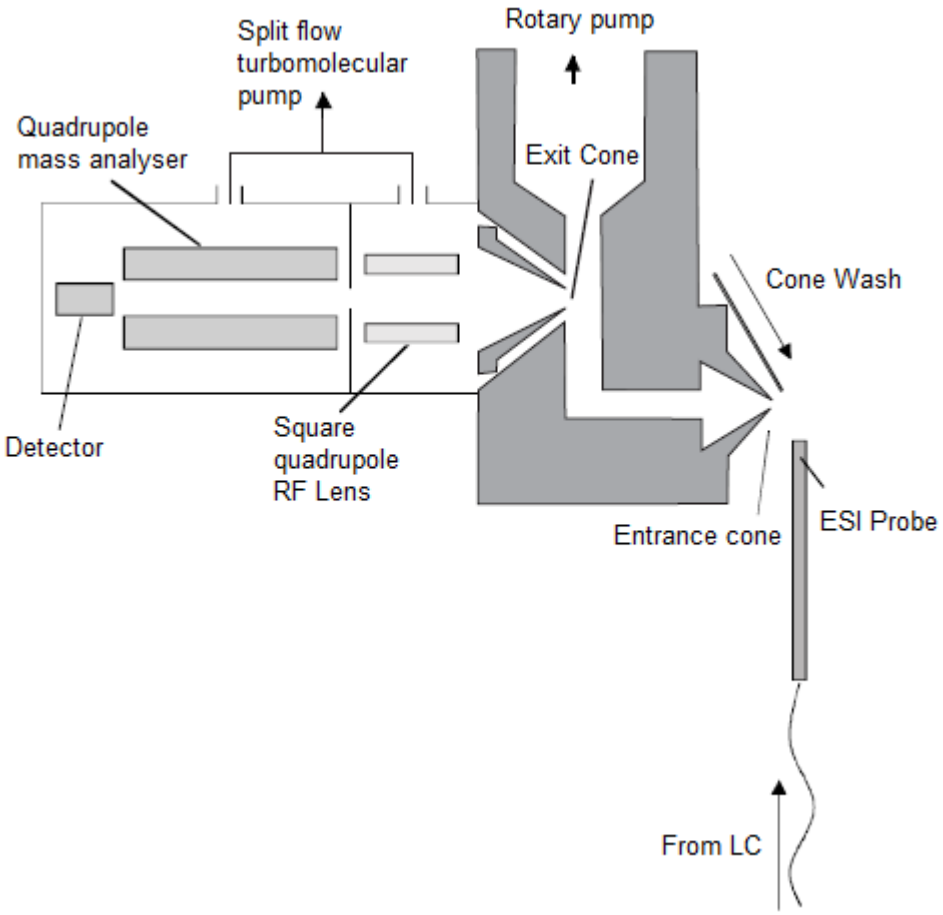

Figure 3- 5: Schematic diagram of MSQ detector system[185]

A Dionex ICS-5000 ion chromatography (IC) system coupled with MSQ plus mass spectrometer was used for products identification and quantification. The carbohydrates in the sample were separated by CarboPac PA20 analytic column (3 × 150 mm) and a guard column (3 × 30 mm) using NaOH solution the eluent. Both gradient and isocratic methods were employed to achieve sufficient separation of the analytes. A gradient method was developed to completely separate the glucose and cellobiose isomers. For the gradient method, the eluent is run for 10 minutes with NaOH concentration of 5 mM at a flow rate of 0.5ml min^{-1}. After that, the NaOH concentration is raised to 50 mM within 30 minutes. Glucosyl-glycolaldehyde (GG) cannot be detected by PAD when using the gradient method developed due to insufficient detector respond from GG. An isocratic method with 50 mM NaOH as eluent at the flow rate of 0.5 ml min^{-1} is used for quantification of GG.

A PEEK splitter was used to split the flow from analytical column into two flows for PAD and MS detectors. The split ratio was kept at 1:1. A Dionex AERS 500 (2 mm) suppressor was used as an in-line desalter for removal of NaOH from the eluent before entering the MS detector. The eluent from desalter was mixed with 0.5 mM LiCl at 0.05 mL min^{-1} for effective ionisation. Then, the mixed liquids flowed through ESI interface for MS analysis. The single quadrupole MS was used in this chromatography system. The carbohydrates detected as in positive mode as Li-adducts $[M + Li]^+$ at $[M + 7]^+$ or negative mode as chloride adducts $[M + Cl]^-$.[182]

The calibration curves for all compounds with available standards were built up based on their peak area as shown in Figure 3-6. The detection limit for standards was less than 5ppm. To ensure that all the compounds in the samples fall at detection limit, several dilution factors were used for every sample. For example, for the sample with initial cellobiose concentration of 1000 mg L^{-1}, dilution factors of 500, 200, 100, 50 and 10 times dilution were analysed.

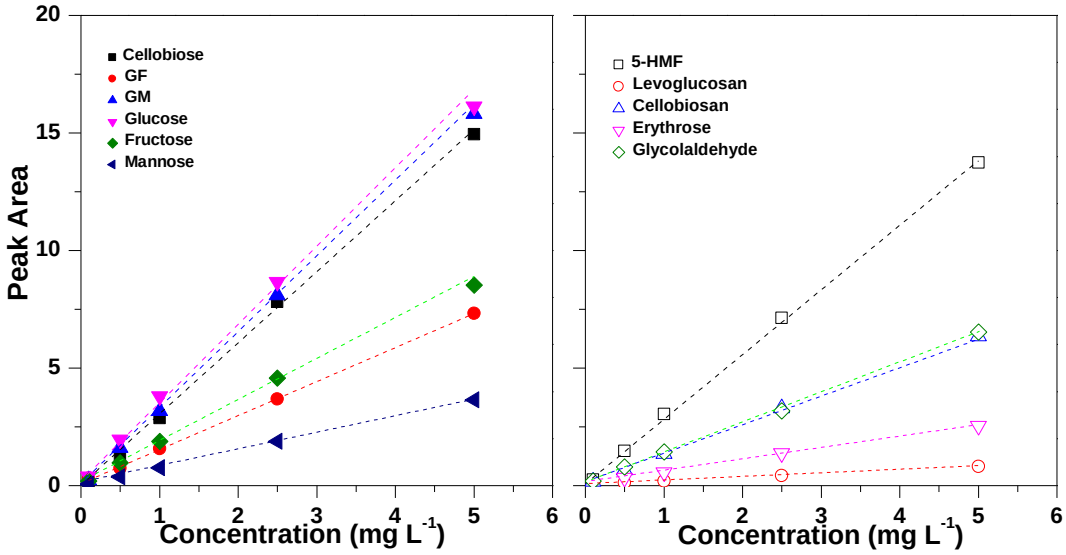

Figure 3- 6: Calibration curve for all compounds with available standard by HPAEC-PAD/MS using gradient method

3.4.3 Total Organic Carbon

The total organic carbon (TOC) in liquid samples was measured by using a Shimadzu TOC-V_{CPH} Analyser. Basically, the liquid samples were injected into combustion tube filled with a catalyst at 680 ^{o}C. The carbon in the sample was converted into carbon dioxide detectable by a Non-dispersive infrared detector (NDIR).[187] The carbon concentration in the liquid sample was calculated based on calibration curve between carbon concentrations versus peak area. The analysis was carried in at least two replicates with the average result reported.

3.5 Data Acquisition and Processing

3.5.1 Conversion, Yields and Selectivity

The following equations were used to calculate the cellobiose conversion (X), the yield (Y_i) and the selectivity (S_i) of a compound i at a reaction time of t. All calculation were based on the carbon basis.

$$X = \frac{C(0)-C(t)}{C(0)} \quad \text{(Equation 3.3)}$$

$$Y_i = \frac{C_i \times a_i}{C(0) \times a} \quad \text{(Equation 3.4)}$$

$$S_i = \frac{Y_i}{X} = \frac{C_i \times a_i}{[C(0)-C(t)] \times a} \quad \text{(Equation 3.5)}$$

Where C_i represent the compound *i* concentration (mg L^{-1}); *C(0)* is the initial cellobiose concentration (mg L^{-1}) before the reaction; *C(t*), is the cellobiose concentration (mg L^{-1}) after the reaction; *a* and a_i are corresponding to the carbon contents based on weight percent of cellobiose and compound *i*, respectively.

For those compounds without standards, the relative selectivity was calculated based on the peak area as the following equation:

$$S_j = \frac{A_j \, X \, a_j}{(C_{20} - C_2) \, X \, a_2} \qquad \text{(Equation 3.6)}$$

Where A_j represent the peak area of an unquantified compound *j* sample after reaction; and a_j correspond to the percent of carbon content of unquantified compound *j* based on the carbon basis.

All the samples collected during the experiments were diluted to ensure that the concentration of the compound in the samples is fallen down under the linear response range of the detector and the relative selectivity of the unquantified compound is commensurable between various samples. The suitable dilution factor for determination of relative selectivity was selected as following method: The sample with the largest peak area was selected and then diluted by two times. If the ratio between the peak area of raw and diluted sample equal to two, then two times dilution factor will be applied for all the samples. However, if the ratio of the peak area is lower than two, it's mean that the concentration of the compound in the diluted sample is higher than the linear response range of the detector. Therefore, the sample will be further diluted until the appropriate dilution factor is discovered.

3.5.2 Kinetic Calculation

The cellobiose decomposition reaction rate, k (s^{-1}) was calculated using Equation 3.7 by assuming the reaction follows first-order kinetic.

$$-ln\frac{C(t)}{C(0)} = k\tau \quad \text{(Equation 3.7)}$$

Equation 3.8 was used to determine the residence time, τ (s).

$$\tau = \frac{V\rho}{F} \quad \text{(Equation 3.8)}$$

where V (m^3) correspond to the reactor volume; ρ (kg m^{-3}) correspond to the water density under reaction condition and F (kg s^{-1}) represent the total mass flow rate of water and cellobiose solution.

By using Equation 3.3, cellobiose conversion was calculated for various temperatures and residence times. Then by plotting *-ln[C(t)/C(0)]* versus residence times, the reaction rate constant k (s^{-1}) was obtained from the slope of the curve for all reaction temperatures.

The activation energy and pre-exponential factor were determined based integral form of Arrhenius equation[188]:

$$ln\ k = ln\ A - \frac{Ea}{RT} \quad \text{(Equation 3.9)}$$

where *Ea* and A are activation energy (kJ mol^{-1}) and pre-exponential factor (s^{-1}), respectively. R is gas constant (i.e. 8.314 J mol^{-1} K^{-1}) and T represents temperature (K) of the reaction. The Arrhenius graph can be plotted with *ln k* against *1/T*. The activation energy and pre-exponential factor can be estimated from the slope and the intercept of Arrhenius graph.

3.5.3 Delplot method

Delplot method[189-191] can be used to determine the products rank (i.e. primary, secondary, tertiary, etc.) which is very useful in developing reaction pathway. The first-rank delplot analysis was carried out to sort out the primary and non-primary products from cellobiose decomposition in HCW for this thesis. The first-rank delplot analysis was conducted by plotting product selectivity versus conversion for each product *i*. If the intercept of product selectivity at X → 0 (i.e. $\lim_{x\to 0}$ (Y_i/X)) is non-zero, then the product is primary. However if the extrapolation of the data at X → 0 have zero intercept, the product is not a primary product (i.e. secondary, tertiary, etc.).

Based on Chapter 4, there are three major primary products from cellobiose degradation in HCW which are cellobiulose and glucosyl-mannose from isomerisation process; and glucose from hydrolysis process. The isomerisation (k_{GF} and k_{GM}) and hydrolysis (k_G) reaction rates can be estimated by using delplot method as shown in Equation 3.10 – 3.12.

$$\frac{k_{GF}}{k} = \lim_{X\to 0} S_{GF} = \lim_{X\to 0} \frac{Y_{GF}}{X} \qquad \text{(Equation 3.10)}$$

$$\frac{k_{GM}}{k} = \lim_{X\to 0} S_{GM} = \lim_{X\to 0} \frac{Y_{GM}}{X} \qquad \text{(Equation 3.11)}$$

$$\frac{k_{G}}{k} = \lim_{X\to 0} S_{G} = \lim_{X\to 0} \frac{Y_{G}}{X} \qquad \text{(Equation 3.12)}$$

Based on the equations above, the product selectivity intercept at cellobiose conversion X →0 represents the ratio of the primary reaction rate constant to cellobiose conversion rate constant.

3.5.4 Hydrogen Ion Concentration

In Chapter 6, the dissociation of sulphuric acid and water were considered during the estimation of the concentration of hydrogen ion at the reaction temperature. It is known that water has higher concentration of H^+ and OH^- ion at elevated temperature compare

with water at room temperature. Equation 3.13 was used to estimate the concentration of H^+ ion at temperature T.

$$[H^+]_{W,T} = \sqrt{K_{W,T}} \quad \text{(Equation 3.13)}$$

where, $K_{W,T}$ represent the ionisation constant of water at temperature T (K). The value of $K_{W,T}$ at 200 – 250°C is between 11.31 and 11.20.[192]

For sulphuric acid, its dissociation process is proceed in two step as illustrate below:

$H_2SO_4 \leftrightarrow H^+ + HSO_4^-$ (First Dissociation)

$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$ (Second Dissociation)

According to Oscarson et al.[193], the first dissociation reaction was assumed a complete dissociation as it has dissociation constant of 5.8 and 2.6 at the temperature of 200 – 250 ^oC.

The second dissociation constant was determined as per Equation 3.14[194]:

$$Log\ K_{2,T} = 56.889 - 19.8858\ log\ T - 2307.9/T - 0.006473T \quad \text{(Equation 3.14)}$$

where T correspond to the reaction temperature (K). This equation is suitable for the temperature range of 25 – 350 ^oC.

The concentration of hydrogen ion for sulphuric acid at a temperature T was calculated as per Equation 3.15[118]:

$$[H^+]_{SA,T} = C_{SA,0} + 0.5(-C_{SA,0} - K_{2,T} + \sqrt{(C_{SA,0} + K_{2,T})^2 + 4C_{SA,0}K_{2,T}}) \quad \text{(Equation 3.15)}$$

where $C_{SA,0}$ is the initial sulphuric acid concentration (mol L^{-1}).

Therefore, the concentration of hydrogen ion (mol L^{-1}) at Temperature T was estimated as:

$$[H^+]_T = [H^+]_{W,T} + [H^+]_{SA,T} \quad \text{(Equation 3.16)}$$

3.6 Summary

Cellobiose was used in this study as a model compound to understand the mechanism of glucose oligomers decomposition in HCW. Cellobiose solution was prepared by dissolving the cellobiose into the deionised water. Sulphuric acid was added to cellobiose solution to understand the effect of initial pH on cellobiose decomposition in HCW. Various AAEM salt was added to the cellobiose solution to study their catalytic effect on the decomposition reaction.

The experiments of cellobiose decomposition were conducted using continuous flow reactor system at various temperatures and residence times. The liquid samples collected from the experiments were analysed using TOC analyser for determination of total carbon organic and HPAEC-PAD/MS for identification and quantification of the compounds in the liquid products.

CHAPTER 4 NEW INSIGHTS INTO THE MECHANISM OF CELLOBIOSE DECOMPOSITION IN HCW

4.1 Introduction

Cellulose as a main component in lignocellulosic biomass has been widely used as a model compound to understand the mechanism of biomass decomposition in HCW.[17-19] Recent studies [20-24] have reported that the primary decomposition of cellulose in HCW produces glucose and its oligomers with a wide range of degrees of depolymerisation (DPs). The decomposition of glucose in HCW is well documented, but the decomposition of sugar oligomers in HCW is scarcely reported. Cellobiose is the most widely studied of glucose oligomers probably because it's relatively simple structure. At 300−420 °C, it was proposed that hydrolysis reaction to produce glucose and retro-aldol reaction to produce glucosyl-erythrose (GE) are the main primary reactions of cellobiose decomposition in HCW[25-27]. Recently, Kimura et al.[29] suggested that the decomposition of glucose oligomers (with DPs up to 4) in HCW at 100−140 °C proceeds by transforming the terminal glucose into fructose, followed by the cleavage of the glycosidic bond to release fructose. Under alkaline conditions (1M NaOH), isomerisation of cellobiose was reported to take place even at room temperature (22 °C). As a reaction medium, HCW has a high ion product and promotes both acidic and alkaline catalysed reactions. Under such unique conditions, isomerisation may also take place. Unfortunately, there only a few reports on the isomerisation reactions particularly under practical conditions (at temperatures above 225 °C) which relevant to most HCW applications.

Consequently, this chapter aims to clarify the fundamental reaction mechanism of cellobiose decomposition in HCW. A series of systematic experiments were performed using a continuous reactor under non-catalytic conditions at 225–275 °C and cellobiose concentration of 1000mg L^{-1}. A state-of-the-art high performance anion exchange chromatography equipped with pulsed amperometric detection and mass

spectrometry (HPAEC-PAD-MS) was used for the analysis of liquid products. The unique capabilities of the HPAEC-PAD-MS enable this study to provide some new insights into the fundamental mechanism of cellobiose decomposition in HCW under prevailing experimental conditions. The total carbon in a liquid sample was also determined by a Total organic carbon (TOC) analyser (Shimadzu TOC-VCPH). Carbon balance was found to be ~100% under all conditions, indicating the gas produced from cellobiose decomposition is negligible under the reaction conditions in this study.

4.2 Identification of the Compounds in the Liquid Products from Cellobiose Decomposition in HCW

A typical IC chromatogram of liquid sample from cellulose decomposition at 275 °C is shown in Figure 4-1. With the available standards, a series of compounds has been identified in the liquid sample, including sugar products (i.e., glucose, fructose and mannose), dehydration products (i.e., cellobiosan, levoglucosan, and 5-HMF), and fragmentation products (i.e., glycolaldehyde, erythrose, and GG). Most of these compounds have been reported in previous literature[25, 26]. However, there are still several main peaks which can be detected by PAD but cannot be identified due to unavailability of the standards, including peak 10 – 12 as shown in Figure 4-1.

Based on the simultaneous analysis of the same sample by MS, the selected ion monitoring (SIM) scan at m/z 349 (corresponding to a molecular weight of 342, i.e., that of cellobiose and its isomers) shows three individual peaks that match exactly the peaks 9−11 detected by PAD. Peak 9 is confirmed to be cellobiose by the standard. For peaks 10 and 11, the detailed mass spectra are then presented in Figure 4-2a and b, each of which clearly shows a single major peak at m/z 349. Therefore, peaks 10 and 11 must be two different isomers of cellobiose. Such identifications are significant to the understanding on the fundamental reaction mechanism of cellobiose decomposition in HCW. This is the first time the formation of two cellobiose isomers from cellobiose decomposition in HCW has been reported. Although the formation of cellobiulose (glucosyl-fructose, an isomer of cellobiose) from cellobiose decomposition has been recently reported by Kimura et al.[29] at the low temperature of 100–140 °C, the presence of two cellobiose isomers was not reported previously. In

fact, the formation of cellobiose isomers have never been identified by other works on cellobiose decomposition at higher temperatures, possibly due to the instrument used for sample analysis. Kimura et al. employed ^{13}C NMR spectroscopy which is able to detect cellobiulose (glucosyl-fructose, GF). However, other studies[25-27] relied on HPLC systems which are difficult to separate the cellobiose and its isomers. Therefore, the results presented in this study demonstrate that the HPAEC-PAD system is powerful to separate and detect the isomers of cellobiose.

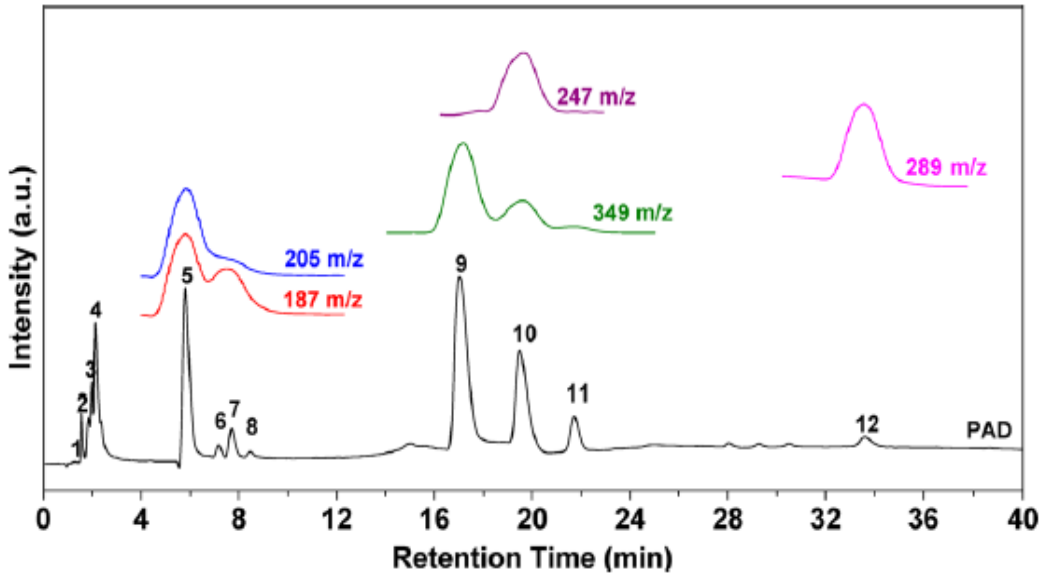

Figure 4- 1 The IC chromatogram and different SIM scans of a liquid sample from cellobiose decomposition in HCW at 275 °C. Peaks: 1, levoglucosan; 2, cellobiosan; 3, glycolaldehyde; 4, 5-HMF; 5, glucose; 6, mannose; 7, fructose; 8, erythrose; 9, cellobiose; 10, isomer of cellobiose (i.e., cellobiulose); 11,isomer of cellobiose (i.e., glucosyl-mannose); 12, GE

Although it was indicated that one of cellobiose isomer could be GF according to a recent work by Kimura et al.[29], the other cellobiose isomer is still unknown. Detailed analysis of monomer sugars in the liquid sample indicates that mannose is also present in the liquid sample, but was never reported before in any open literature on cellobiose decomposition in HCW. This may indicate that the other isomer of cellobiose could be glucosyl-mannose (GM). A thorough review of the literature also suggested that

cellobiose decomposition leads to the formation of GF and GM under alkaline conditions.[158] Therefore, it is very likely that the two cellobiose isomers identified in this study are GF and GM. Fortunately, we manage to obtain the standard for GF and GM from LC Scientific recently. Based on the standards, peak 10 was identified as GF and peak 11 as GM.

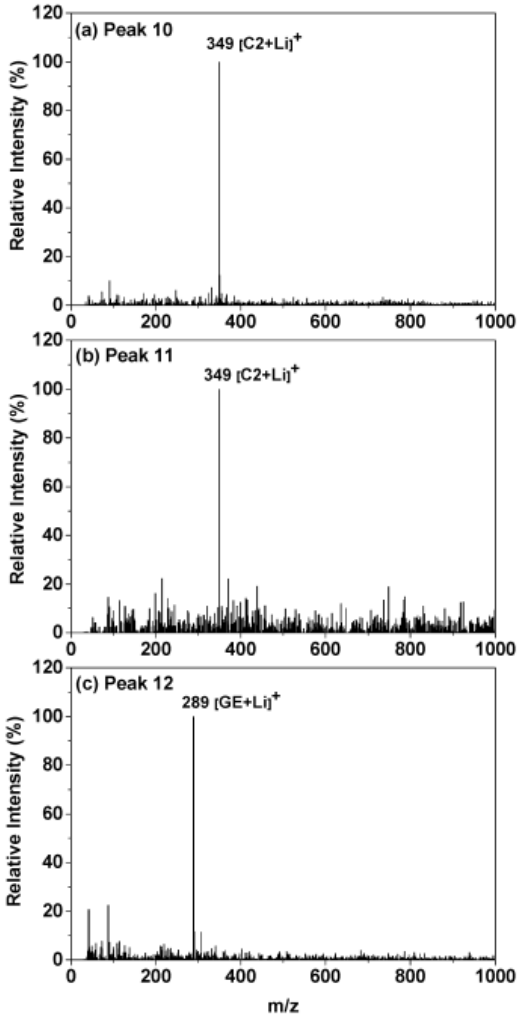

Figure 4- 2 Mass spectra of main unidentified peaks. (a) Peak 10; (b) Peak 11; and (c) Peak 12

For the other unknown peak 12, the mass spectrum (see Figure 4-2c) via the SIM scan of MS at m/z 289 match the position of the peak well. Therefore, the peak corresponds to glucosyl-erythrose (GE), which has been widely reported as a main primary product of cellobiose decomposition in HCW.[25, 26] A careful comparison of the compounds

published in other works[25, 26] indicates that glucosyl-glycolaldehyde (GG) was not identified by PAD in Figure 4-1. To confirm the presence of GG in the liquid sample, the SIM scan at m/z 247 was performed. Indeed, a large peak appeared at a position close to peak 10. While separation of cellobiose and its isomers can be effectively achieved, the data suggest that PAD analysis using the designed gradient method has a very low response to GG. This is confirmed by the tiny peak of the PAD analysis for standard GG solutions. Therefore, this study has developed an isocratic method which can effectively identify and quantify GG in the liquid samples.

4.3 Yields and Selectivities of Products during Cellobiose Decomposition in HCW.

It has been clearly demonstrated in the above sections that HPAEC-PAD/MS is powerful to identify the compounds in the liquid products from cellobiose decomposition in HCW. The compounds were further quantified with available standards. The yields of various products are then calculated on a carbon basis, and the results are shown in Figure 4-3. It can be found that cellobiose can be easily decomposed in HCW, i.e., with a conversion of over 90% for ~30 s at 275 °C. Longer reaction time is needed for cellobiose decomposition at low reaction temperatures.

It can also be seen that various products including isomerisation, hydrolysis, dehydration and fragmentation products, have been identified in the liquid products from cellobiose decomposition in HCW. For isomerisation products, GF has a higher yield than GM for all reaction conditions. The yield of GF and GM initially increases until reached a maximum, and then decreases as the residence time increases. The results suggest that isomerisation products are prone to decompose for producing other secondary products at increased residence time. The maximal yield of GF is 23% at 250 °C (at the residence time of 30 s), whereas the maximal yield of GM is 2.3% at similar reaction condition. Another interesting observation from Figure 4-3 is the yield of GF is generally higher than other products, especially at the early stage of cellobiose decomposition. Clearly, at the early reaction stage, isomerisation reaction for GF production is more favoured than the other products

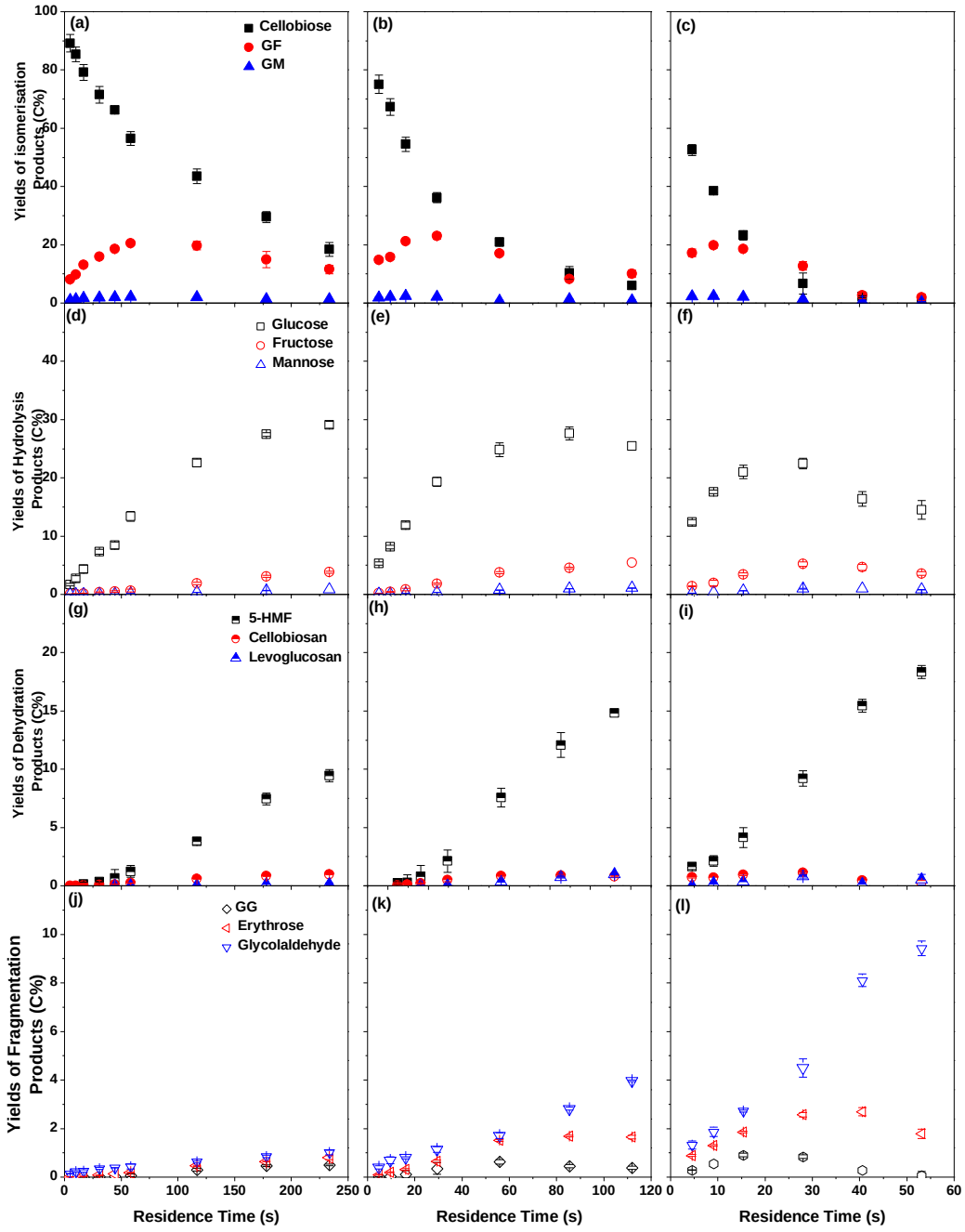

Figure 4- 3: Yields of various products as a function of residence time at 225−275 °C. (a) Yields of isomerisation products at 225 °C; (b) Yields of isomerisation products at 250 °C; (c) Yields of isomerisation products at 275 °C; (d) yields of hydrolysis products at 225 °C; (e) yields of hydrolysis products at 250 °C; (f) yields of hydrolysis products at 275 °C; (g) yields of dehydrated products at 225 °C; (h) yields of dehydrated products at 250 °C (i) yields of dehydrated products at 275 °C; (j) yields of fragmented products at 225 °C; (k) yields of fragmented products at 250 °C; and (l) yields of fragmented products at 275 °C

For hydrolysis products, glucose has the highest yield, compare to other hydrolysis products including fructose and mannose. At 225 °C, the glucose yield continuously increases as cellobiose decomposition proceeds. Under the range of residence time studied, the highest glucose yield at 225 °C reached 31% based on total carbon in cellobiose after a residence time of ~233 s (corresponding to a cellobiose conversion of ~79%). At higher temperature (e.g. 275 °C) the glucose yield initial increases, achieved a maximum and then decreases as decomposition proceed. It can be seen that highest glucose yield achieved under the experimental conditions in this study is reduced at higher temperature from ~31% at 225 °C (at residence time of ~233 s, corresponding to a cellobiose conversion of ~79%) to ~28% at 250 °C (at a residence time of 85 s, corresponding to cellobiose conversion of ~90%) and then to ~23% at 275 °C (at residence time of ~28 s, corresponding to a cellobiose conversion of ~93%). This indicates that glucose decomposition is more pronounced at higher temperatures so that high temperature conditions are not favoured for the production of glucose from cellobiose.

For the dehydration products, 5-HMF has the highest yield, and its formation continuously increases as cellobiose decomposition proceeds. The maximal yield of 5-HMF achieved in this study is ~18% at 275 °C so that 5-HMF is one of the main compounds from cellobiose decomposition in HCW. This is consistence with the previous reports on 5-HMF being the products of fructose dehydration. For the fragmentation products, glycolaldehyde has the highest yields compare to GG and erythrose. The yield of glycolaldehyde also continuously increases as the residence time increases, indicating that it is also the main product from cellobiose decomposition. Under the experimental conditions in this study, the maximal yield of glycolaldehyde is ~9% at 275 °C, lower than of 5-HMF. For GG and erythrose, its yields are even lower, with a maximal yield of ~0.9% and ~2.7% respectively at 275 °C.

Based on the product yields at various temperatures, the selectivities of different products were further estimated (on a carbon basis) and plotted as a function of cellobiose conversion in Figure 4-4 to 4-7. It should be noted that at a high cellobiose conversion (e.g., >95% at 275 °C, corresponding to a residence time longer than 50 s, see Figure 4-3), the reactions are dominant by secondary reactions of primary products produced from cellobiose decomposition because the primary reactions of cellobiose have nearly completed. Yet, the data in Figure 4-3 clearly suggest that such secondary reactions lead to significant changes in the product selectivities.

Figure 4-4 presents the results on the selectivities (on a carbon basis) of GF and GM. The selectivities of both GF and GM decrease with increasing cellobiose conversion. For example, at a low conversion (i.e., ~11%), the selectivity of GF is as high as ~69% at 225 °C, compared to only ~9% for the selectivities of GM under the same condition. GF and GM are is indeed a primary products from cellobiose decomposition according to the delplot method,[189, 191] because the intercept of GF and GM selectivity at $X \rightarrow 0$ (i.e., $\lim_{X \rightarrow 0} \frac{Y_{GF}}{X}$) is non-zero when the GF and GM selectivity is extrapolated to $X \rightarrow 0$ (see extrapolated lines in Figure 4-4). It is important to note that the two isomerisation reactions account for ~71-87% of cellobiose decomposition reaction depending on temperature. The results clearly demonstrated that isomerisation reactions are indeed responsible for the majority of cellobiose decomposition in HCW, particularly the isomerisation of cellobiose to produce GF. An increases in reaction temperature, reduces the intercept of GF and GM selectivity at $X \rightarrow 0$, that is from ~76 to ~63% and ~11 to ~8% for GF and GM respectively. The data clearly suggest that high temperature suppresses the isomerisation reactions.

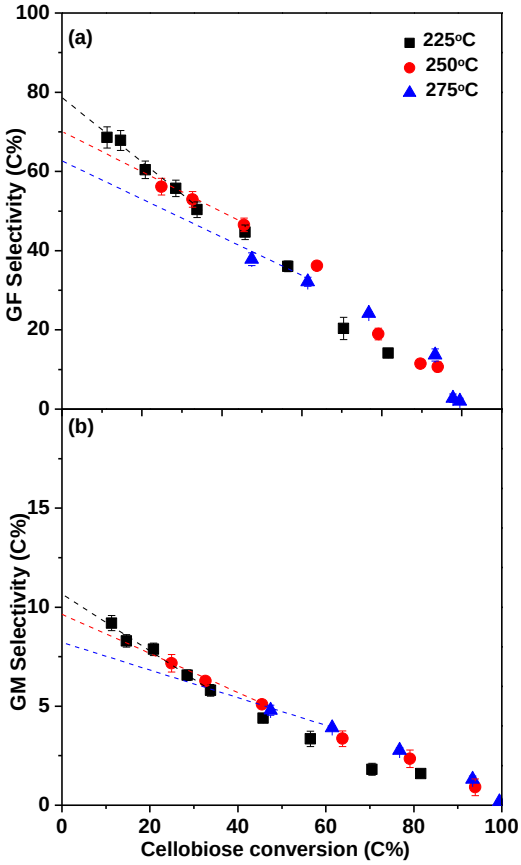

Figure 4- 4: Selectivities of isomerisation products as a function of cellobiose conversion at 225 – 275 °C. (a) GF and (b) GM

Figure 4-5 shows that the selectivity of glucose initially increases with cellobiose conversion, achieves a maximum, and then decreases as the conversion further increases. The maximal selectivity of glucose is ~40%, which is achieved at 225 °C and a cellobiose conversion of ~70%. An increase in reaction temperature leads to a reduction in the maximal selectivity of glucose, from ~40% at 225 °C, to ~32% at 250 °C and then to ~29% at 275 °C. It should be noted that the condition where the maximal glucose selectivity is achieved is not same as the condition where the maximal glucose yield is achieved. For example, at low temperatures (i.e., 225 °C), although the glucose selectivity starts to decrease at conversions >70%, the glucose yield still increases as cellobiose conversion increases (see Figure 4-3), because of more glucose formation than glucose decomposition. Glucose also a primary product from cellobiose decomposition as the intercept of glucose selectivity at $X \rightarrow 0$ is nonzero. The intercept of glucose selectivity at $X \rightarrow 0$ is only ~10% so that at the

initial stage only ~10% of cellobiose is converted into glucose via the hydrolysis reaction. Such observation suggested that glucose is not a main primary product from cellobiose decomposition. An increase in the reaction temperature increases the intercept of glucose selectivity at $X \rightarrow 0$, indicating that high temperatures enhance the selectivity of hydrolysis reaction during cellobiose decomposition (i.e., from ~10% at 225 °C to ~20% at 275 °C). The data in Figure 4-5 also show that the evolution of glucose selectivity largely depends on the reaction temperature. Although the initial glucose selectivity is low at a low temperature, it increases rapidly as cellobiose conversion increases. At cellobiose conversions >25%, the glucose selectivity at 225 °C is actually higher than that at 275 °C. Such an increase in glucose selectivity could be due to two possible reasons. One is that glucose can be produced from some intermediates from cellobiose decomposition, and such reactions are promoted at low temperatures. The other is that some products from cellobiose decomposition may catalyse the hydrolysis reaction to produce glucose from cellobiose.

As shown in Figure 4-5b and c, the selectivities of fructose and mannose increase with cellobiose conversion up to a high conversion (i.e., ~90%), but are much lower than that of glucose. The highest selectivities are ~5.8% for fructose and ~1.2% for mannose at 250 °C, respectively. An increase in reaction temperature has slight inhibition effect on the formation of fructose and mannose. It is also clear that fructose and mannose are not the primary products from cellobiose decomposition as the two compounds are found at cellobiose conversions >10%.

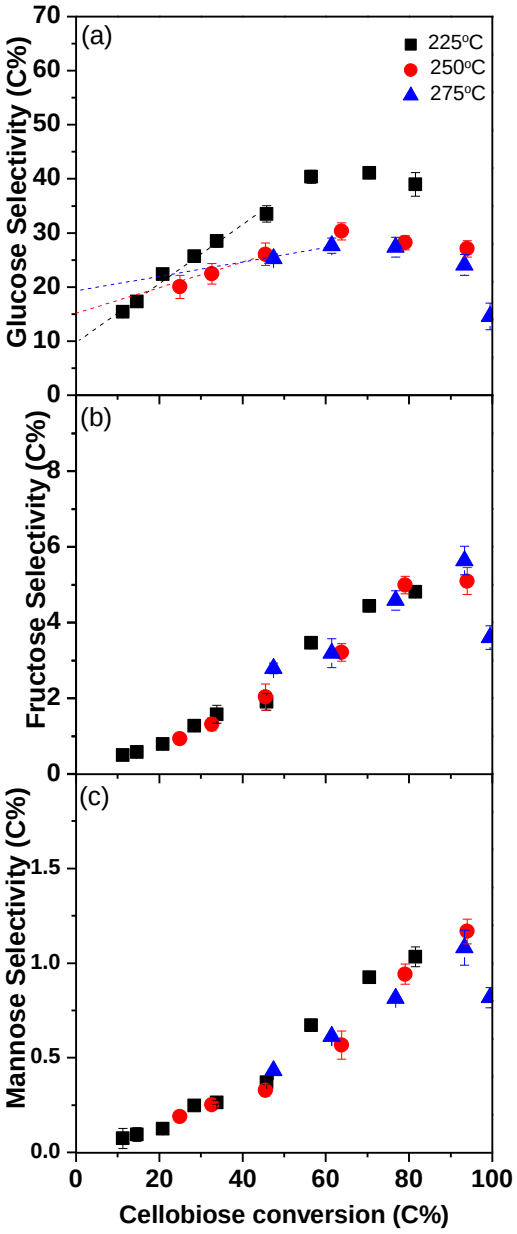

Figure 4- 5: Selectivities of hydrolysis products as a function of cellobiose conversion at 225 – 275 °C. (a) Glucose; (b) fructose; and (c) mannose

The selectivity of 5-HMF, which is a main product from cellobiose decomposition, increases as cellobiose conversion increases (see Figure 4-6a). A decrease in reaction temperature promotes the formation of 5-HMF, as the selectivity of 5-HMF is always higher at lower temperatures at the same cellobiose conversion level. It is also clear that 5-HMF is also not a primary product from cellobiose decomposition as it is found at cellobiose conversions >20%. Compared to 5-HMF, other dehydration products

such as cellobiosan and levoglucosan have very low selectivities (i.e., <1.5%) and an increase in reaction temperature slightly promotes the formation of these products (see Figure 4-6b and c). The data suggest that the formation mechanism of cellobiosan and levoglucosan may be different from that of 5-HMF, because the selectivity of 5-HMF increases with decreasing reaction temperature while those of cellobiosan and levoglucosan follow the opposite trend.

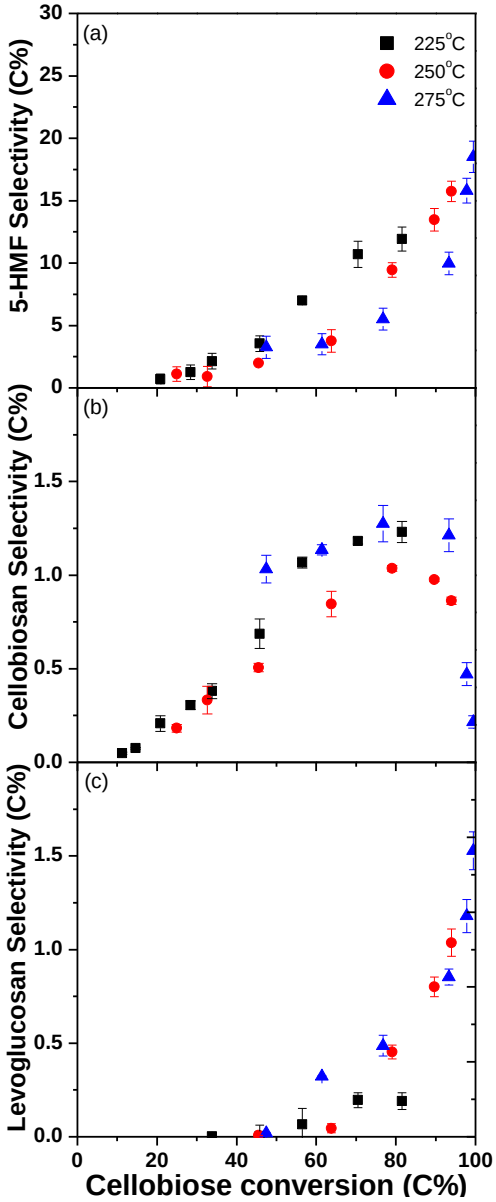

Figure 4- 6: Selectivities of dehydration products as a function of cellobiose conversion at 225 – 275 °C. (a) 5-HMF; (b) cellobiosan; and (c) levoglucosan

As for the fragmentation products, glycolaldehyde and erythrose are the two main products from cellobiose decomposition, with the maximal selectivities of ~10% and ~3% at 275 °C, respectively (see Figure 4-7a and b). The selectivities of these products increase as cellobiose conversion increases and also increase as reaction temperature increases. Glycolaldehyde appears to be a primary product from cellobiose decomposition although the intercept of glycolaldehyde at X → 0 is very small. Erythrose is obviously not a primary product as it can only be found at conversions >10%. Compared to glycolaldehyde and erythrose, the selectivity of GG is even lower, and it increases with cellobiose conversion and starts to decrease at conversions >70% (see Figure 4-7c). Similarly, GG is also not a primary product as it can only be found at conversions >25%.

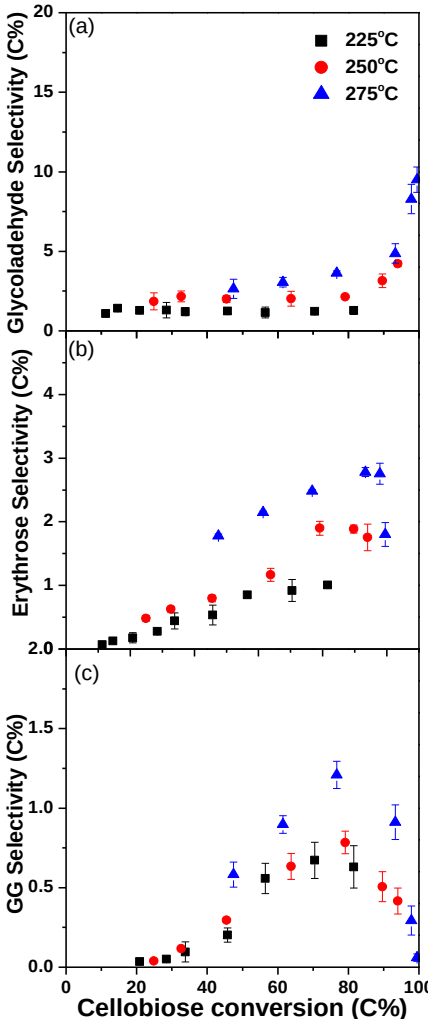

Figure 4- 7: Selectivities of fragmentation products as a function of cellobiose conversion at 225 – 275 °C. (a) Glycolaldehyde; (b) erythrose; and (c) GG

Previous studies indicated that GE is a primary product of cellobiose decomposition in HCW. However, GE cannot be quantified due to unavailability of the standard. A relative selectivity method (as explained in section 3.4.1) was used to evaluate GE based on its peak area. The relative selectivity of GE (peak 12) in Figure 4-8 shows a decreasing trend as cellobiose conversion increases. This clearly shows that GE is also the primary products from cellobiose decomposition. The formation of GE as a primary product from cellobiose decomposition is in consistence with the conclusions drawn in previous studies.[25, 26] Figure 4-8 also illustrated that the extrapolation of the relative selectivities of GE is significantly increased with an increase in reaction temperature. This indicates that high temperature promotes the decomposition of cellobiose via retro-aldol condensation reactions to produce GE.

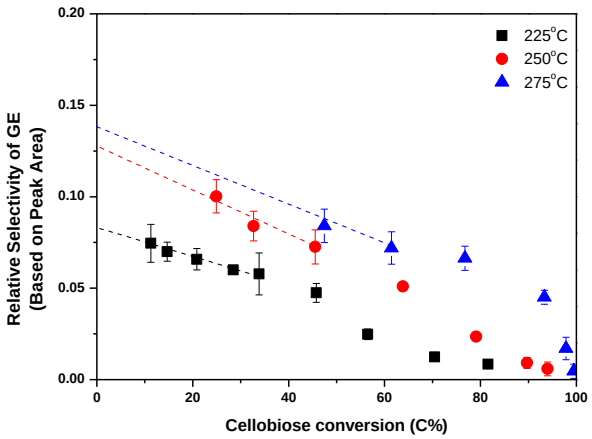

Figure 4- 8: Relative selectivity of GE as a function of cellobiose conversion at 225 – 275 °C

Further analysis of carbon balances indicates that the total quantifies products at low cellobiose conversions are above 95% and decrease as the cellobiose conversion increase. At high conversion, the secondary reactions of the primary products become very important. It is known that pyruvaldehyde, furfural, dihydroxyacetone and organic acids can be produced as a result of the secondary reaction of glucose. However, these compounds cannot be quantified by ion chromatography. Therefore, these organic compounds may account for a large amount of carbon at high conversion.

4.4 Reaction Pathways and Mechanism of Cellobiose Decomposition in HCW

The results presented in this chapter so far provide some new insights into the reaction pathways of cellobiose decomposition in HCW. Figure 4-9 summarised the state-of-the-art understanding of the reaction pathways of cellobiose decomposition in HCW under the reaction conditions, considering the reports in previous publications [25, 26, 29] and this study. The data in this study has clarified at least four important points related to the primary products of cellobiose decomposition in HCW. First, Isomerisation to produce GF is a major primary reaction of cellobiose decomposition at 225−275 °C, contributing to 64 - 76% of cellobiose decomposition depending on temperature. Isomerisation reaction to produce GM and hydrolysis reaction to produce glucose are only minor primary reactions, contributing to 8−11% and 10−20% of cellobiose decomposition, respectively. Although the retro-aldol reaction to produce GE is also a primary reaction, it contribution is very low (<5%) under current reaction conditions. However, it is expected that such a retro-aldol reaction could play an important role at high temperatures (i.e., >350 °C), as reported in the previous studies.[25, 26]

Second, this study confirms that GG is not a primary product of cellobiose decomposition. This clarifies the discrepancies in the literature. For example, in the study by Kabyemela et al.,[25] GG was considered as a primary product of cellobiose decomposition in HCW via retro-aldol condensation reactions. However, in another study by Sasaki et al.,[26] GG is not considered as a primary product of cellobiose decomposition, rather, GG is considered as a secondary product of GE via retro-aldol condensation reactions. The experimental data in this study clearly show that GG is not a primary product because GG can only be found at cellobiose conversions higher than 25% (see Figure 4-7c), supporting the proposed production pathway proposed by Sasaki et al.[26]

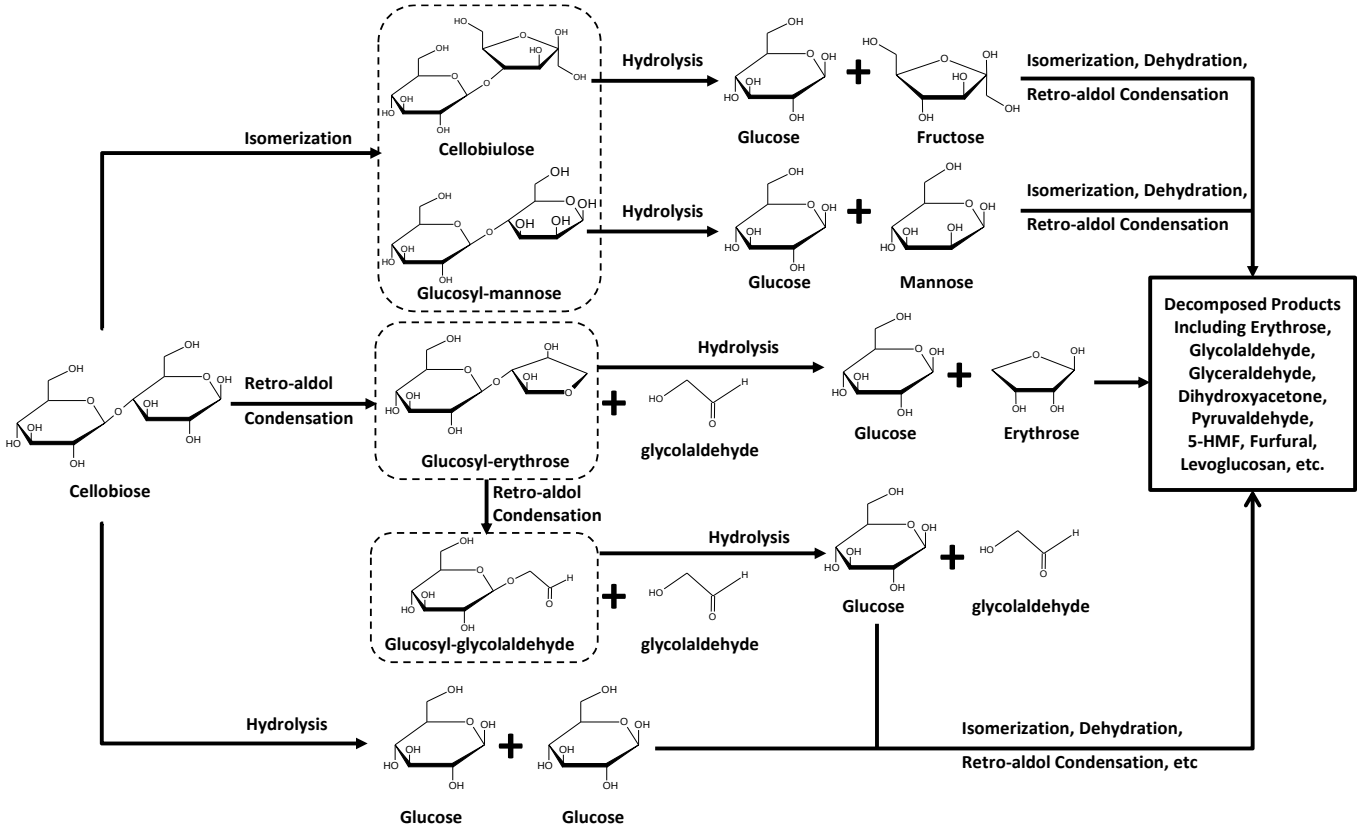

Figure 4- 9: Main reaction pathways during cellobiose decomposition in HCW

Third, the high selectivity of isomerisation reaction to produce GF is consistent with a previous study of cellobiose decomposition at the low temperature range of 100−140 °C.[29] A previous study proposed that the decomposition of cello-oligosaccharides proceeds with the terminal glucose transformed to fructose, followed by the release of fructose by the cleavage of the glycosidic bond.[29] However, that ignores the presence of a high ion product in HCW, which promotes both acidic and alkaline catalysed reactions. It is known that cellobiose can be isomerised into GF and GM under alkaline conditions (1 M NaOH) even at room temperature (22 °C).[158] However, under HCW conditions, water contains the same amount of hydrogen ion (H^+) and hydroxyl ion (OH^-). Therefore, the results suggest that hydroxyl ions have a more significant effect than hydrogen ions in catalysing the decomposition reactions of cellobiose in HCW, consistence with the previous finding on glucose decomposition in HCW.[138] The lower contribution of acid-catalysed hydrolysis reaction to cellobiose decomposition may be due to the higher affinity of hydrogen ions for water molecules,[123] which limits the transfer of hydrogen ions from the bulk water to catalyse the hydrolysis reaction. The acid-catalysed hydrolysis of cellobiose was postulated to proceed in two steps.[128, 195] Step 1 involves the initialisation of hydrolysis reaction by the transfer of the proton (i.e. hydrogen ion) from solvent to the glycosidic oxygen and the dissociation of the glycosidic bond to form glucose and one oxacarbeniun ion species ($C_6H_{11}O_5^+$). Step 2 involves the hydration of oxacarbeniun ion to produce a second glucose and regenerate the proton. In contrast, isomerisation reactions are known to proceed via the removal of the proton from α-carbonyl to form enediol species[153-155] These species will undergo rearrangements to form GF and GM. It easier to transfer the proton to water than remove the proton from water as the proton has a higher affinity for water molecules. Thus, the lower contribution of the hydrolysis reaction compare to the isomerisation reactions.

Fourth, the promotion of hydrolysis reaction at high temperatures cannot be explained by the increased amount of hydrogen ions, since the amount of hydroxyl ions also increases with temperature to the same level as that of hydrogen ions. The enhancement of hydrolysis reactions during cellobiose primary decomposition seems to be consistent with the important role of hydrogen-bonding interactions between water and hydrogen ion in sugar decomposition under acidic conditions as reported in

a recent simulation study.[123] At higher temperatures, water has much weaker hydrogen bonds, thereby reducing the affinity of the proton for water molecules. This leads to more protons to be involved to catalyse the hydrolysis of cellobiose, thereby promoting the hydrolysis reactions at high temperatures.

Depending on the residence time, these primary products may further decompose to other secondary products via complicated reaction pathways. Some typical secondary reactions of primary products were also summarised in Figure 4-9, according to current data and previous literature.[25, 26] For example, this study indicates that the hydrolysis reactions of GF and GM lead to the formation of glucose and fructose, and glucose and mannose, respectively. Similarly, the hydrolysis reaction of glucosyl-erythrose produces glucose and erythrose, as reported elsewhere.[25, 26] Glucose, fructose, mannose, glycolaldehyde and erythrose produced from hydrolysis of cellobiose, GF, GM and GE will further decomposed into other decomposition products depending on reaction conditions such as residence time.[85, 111, 116, 117, 160]

It is noteworthy that significant interactions among different intermediate products may also take place, some of which may be catalysed by the products from cellobiose decomposition. As aforementioned, glucose is only a minor primary product from cellobiose decomposition in HCW and only accounts for ~10−20% of the total primary products of cellobiose decomposition reactions at the early stage. However, it is important to note that the selectivity of glucose continuously increases to ~30− 40% depending on reaction temperature, up to a cellobiose conversion of ~70% (see Figure 4-5a). Obviously, further secondary hydrolysis reactions of at least some of the reaction intermediates also contribute to glucose production. Such hydrolysis reactions require the participation of hydrogen and hydroxyl ions. It was reported that some organic acids could be produced during cellulose and glucose decomposition under neutral and alkaline hydrothermal conditions.[196, 197] Therefore, this study further analysed the pH values of liquid samples under all conditions, with the results plotted in Figure 4-10 as a function of cellobiose conversion at different reaction temperatures. It can be seen that the pH value of the liquid samples reduces continuously with increasing cellobiose conversion under all conditions, from ~7 to a value as low as 3.

The data in Figure 4-10 also show that a significant decrease in the pH value takes place at the early stage (i.e., at a conversion of ~20%) at 225 °C, implying that organic acids have already been produced at the early stage, resulting in an acidic medium for subsequent cellobiose decomposition reactions.

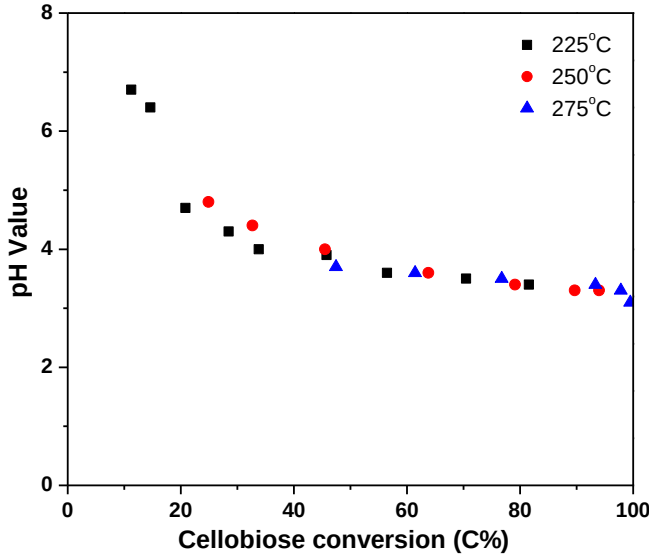

Figure 4- 10: pH value of reaction solution as a function of cellobiose conversion at 225−275 °C

The data also suggest that a decrease in reaction temperature enhances the formation of an acidic condition because the pH value becomes lower at a lower temperature. Certainly, such an acidic condition facilitates the hydrolysis reactions to produce glucose, leading to an increase in glucose selectivity as cellobiose decomposition proceeds. However, it has the insignificant effect on the primary reactions of cellobiose decomposition because the change in the reaction rate during cellobiose decomposition is negligible. Rather, the resulted acidic condition has significant effect on the secondary decomposition reactions of some primary products. As shown in Figure 4-4a and b, the decomposition of cellobiose isomers is enhanced with decreasing reaction temperature. Given the more acidic medium at lower temperatures, it is reasonable that the hydrolysis of the primary products such as cellobiose isomers is enhanced. Such acidic conditions also catalyse the dehydration reactions,

contributing to the formation of 5-HMF with an increased selectivity (see Figure 4-6a).

4.5 Conclusion

This study investigates cellobiose decomposition in HCW using a continuous reactor at 225−275 °C. The liquid products were characterised by HPAEC-PAD-MS, which enables this study to identify the formation of two cellobiose isomers (i.e., cellobiulose and glucosyl-mannose) as the primary products from cellobiose decomposition in HCW, as the first in the field. Under the current reaction conditions, cellobiose is dominantly isomerised into GF and GM, with a small portion of cellobiose being hydrolysed to glucose. Retro-aldol condensation reaction is also confirmed to be a primary reaction to produce the glucosyl-erythrose (GE) and glycolaldehyde as, but its contribution is even smaller than hydrolysis reaction to produce glucose. Due to the high affinity of hydrogen ions to water molecules, hydroxyl ions have a higher priority to catalyse the isomerisation reactions to produce GF and GM, leading to a high selectivity of isomerisation reactions, especially at low temperatures (i.e., 200 °C). As reaction temperature increases, the affinity of hydrogen ions to water molecules is reduced because of the weakened hydrogen bonds in water, thereby promoting the acid-catalysed hydrolysis reaction at increased temperatures. The results also suggest that organic acids are likely to be produced at the early stage of cellobiose decomposition, resulting in an acidic reaction condition. Such an acidic condition leads to the exhibition of more characteristics of acid-catalysed reactions at the middle and later stages of cellobiose decomposition. The acidic condition appears to be effective in catalysing the secondary hydrolysis reactions of the primary products from cellobiose such as, cellobiose isomers, but its effect on the primary reactions of cellobiose decomposition is negligible.

CHAPTER 5 EFFECT OF INITIAL CELLOBIOSE CONCENTRATION ON PRIMARY CELLOBIOSE DECOMPOSITION IN HCW

5.1 Introduction

The study in Chapter 4 provides new insight into the reaction mechanism of cellobiose decomposition in HCW at the temperature of 225 to 275 °C. Cellobiose mainly decomposed into cellobiulose (glucosyl-fructose, GF) and glucosyl-mannose (GM) via isomerisation reactions and only a small portion of cellobiose is hydrolysed into glucose. Compared to the isomerisation and hydrolysis reactions, the retro-aldol reaction to produce GE is negligible.

Yu and Wu[138] investigated the effect of initial glucose concentration on the mechanism of glucose decomposition in HCW at 175–275 °C and a wide range of initial glucose concentrations. It was revealed that there is a shift in the reaction pathways of glucose decomposition as the initial glucose concentration increase. Isomerisation reaction to fructose and retro-aldol condensation reaction to glycolaldehyde, glyceraldehyde and erythrose are the dominant reactions during glucose decomposition in HCW, especially at low initial concentration. On the other hand, at high glucose concentration, dehydration reaction to produce 5-HMF is promoted. However, the effect of initial reactant concentration on hydrolysis reaction (glycosidic bond breakage) of cellulose and glucose oligomers is still unknown. Therefore, the purpose of this study is to investigate the effect of initial cellobiose concentration on the mechanism and kinetic of primary decomposition of cellobiose in HCW. The study was conducted at the initial concentration of 10−10,000 mg L^{-1} and temperature range of 200−275 °C. The results of this study will provide new knowledge on the fundamental chemistry in the primary decomposition of sugar oligomers into monomer and other decomposed products.

5.2 Yields and Selectivities of Primary Products from Cellobiose Decomposition at Various Initial Cellobiose Concentrations

Figure 5-1 presents the yields (on a carbon basis) of cellobiose and its main primary products as a function of residence time at various initial concentrations and temperatures. The initial concentration can significantly influence cellobiose decomposition in HCW. Such observations are similar to those for glucose decomposition in HCW, as reported previously.[138] Cellobiose decomposes more rapidly at a lower initial concentration. For example, at an initial concentration of 10 mg L^{-1}, ~51% of cellobiose is decomposed in 61s at 200 °C, while the decomposed cellobiose is only ~11% when the initial concentration is increased to 10,000 mg L^{-1}.

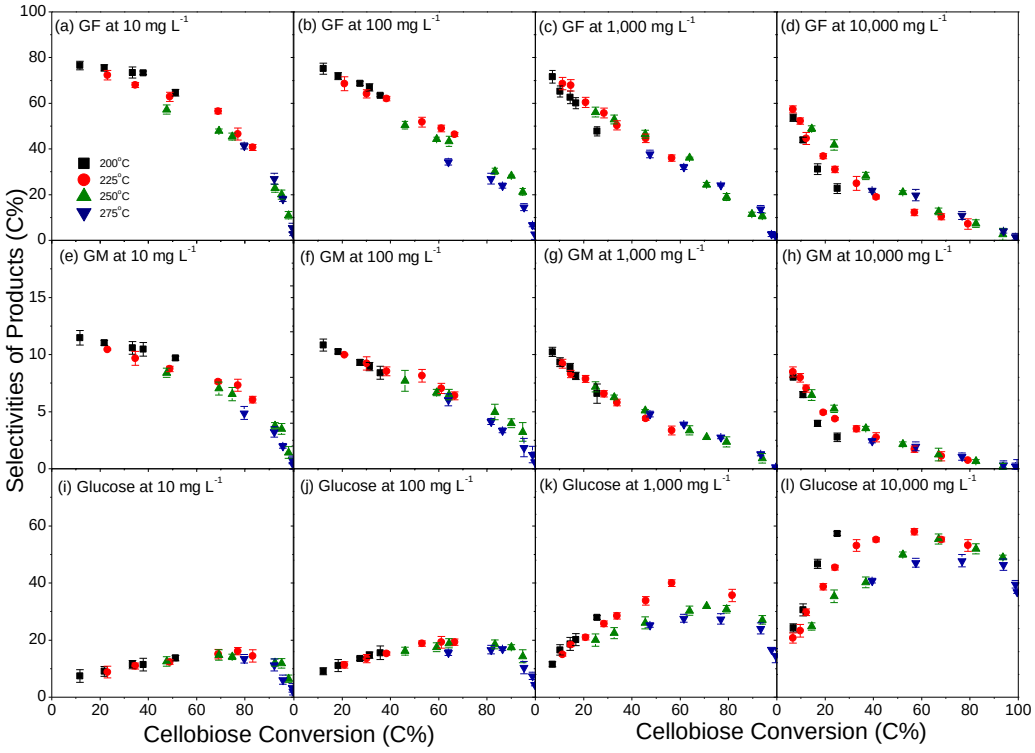

Figure 5- 1: Yields of cellobiose and its primary products from cellobiose decomposition in HCW at various initial cellobiose concentrations, expressed on a carbon basis. (a) cellobiose at 10 mg L^{-1}; (b) cellobiose at 100 mg L^{-1}; (c) cellobiose at 1,000 mg L^{-1}; (d) cellobiose at 10,000 mg L^{-1}; (e) GF at 10 mg L^{-1}; (f) GF at 100 mg L^{-1}; (g) GF at 1,000 mg L^{-1}; (h) GF at 10,000 mg L^{-1}; (i) GM at 10 mg L^{-1}; (j) GM at 100 mg L^{-1}; (k) GM at 1,000 mg L^{-1}; (l) GM at 10,000 mg L^{-1}; (m) glucose at mg L^{-1}; (n) glucose at 100 mg L^{-1}; (o) glucose at 1,000 mg L^{-1}; (p) glucose at 10,000 mg L^{-1}

Chapter 4 showed that GF and GM from isomerisation reactions are the dominant primary products from cellobiose decomposition under hydrothermal conditions. Glucose via hydrolysis reaction is only a minor primary product. It can be seen that the three main primary products (GF, GM, and glucose) of cellobiose decomposition follow completely different trends that are strongly dependent on initial cellobiose concentration. The yields of the isomerisation products (GF and GM) increase with a decrease in the initial concentration. For example, the maximal yields of GF (~39% at 225 °C and 31 s) and GM (~5% at 225 °C and 45 s) are both obtained at the lowest initial concentration (10 mg L^{-1}). In contrast, the yield of glucose (the product of hydrolysis reaction) follows an opposite trend and increases with an increase in initial concentration. The maximal glucose yield (~46% at 250 °C and 86 s) is obtained at the highest initial concentration (10,000 mg L^{-1}). Therefore, the results reported here suggest that isomerisation reactions are favoured at low initial concentrations while hydrolysis reaction is preferable at high initial concentrations.

Figure 5-2 presents the results on the selectivities (on a carbon basis) of GF, GM and glucose as a function of cellobiose conversion under various initial concentrations. The data in Figure 5-2 clearly shows that the initial cellobiose concentration strongly affects the selectivities of primary products during cellobiose decomposition. The selectivities of GF and GM decrease but that of the glucose increase with an increase initial cellobiose concentration. Moreover, the initial cellobiose concentration also has a strong influence on the evolution of the selectivities of those primary products as conversion increases during cellobiose decomposition. At low concentrations (i.e., <100 mg L^{-1}), the selectivities of GF and GM initially reduce slowly as cellobiose conversion increases to ~70% and rapidly decrease as conversion further increases. At 1,000 mg L^{-1}, the selectivities of GF and GM almost reduce linearly as cellobiose conversion increases. However, at high concentrations (i.e., 10,000 mg L^{-1}), the selectivities of GF and GM initially reduce rapidly as cellobiose conversion increases to ~30% conversion and then reduce slowly as conversion further increases. The results suggest that high initial cellobiose concentrations greatly enhance the secondary decomposition of GF and GM even at the early conversion stage, possibly catalysed by some of the decomposition products of cellobiose. On the other hand, the selectivity of glucose increases as cellobiose conversion increases to ~60−80%

(depending on reaction conditions) and then decreases as conversion further increases. A higher initial concentration leads to higher glucose selectivity at an even earlier stage of cellobiose decomposition. It is clear that the formation of glucose is strongly promoted at high initial concentrations, possibly catalysed by some acidic products from cellobiose decomposition. For example, the maximal glucose selectivity at 10 mg L^{-1} is ~16.1% (at 200 °C and a cellobiose conversion of ~77.1%), but increases to ~57.3% at 10,000 mg L^{-1} (at 200 °C and a cellobiose conversion of ~25.1%). It is possible to achieve a higher glucose yield at a higher cellobiose initial concentration.

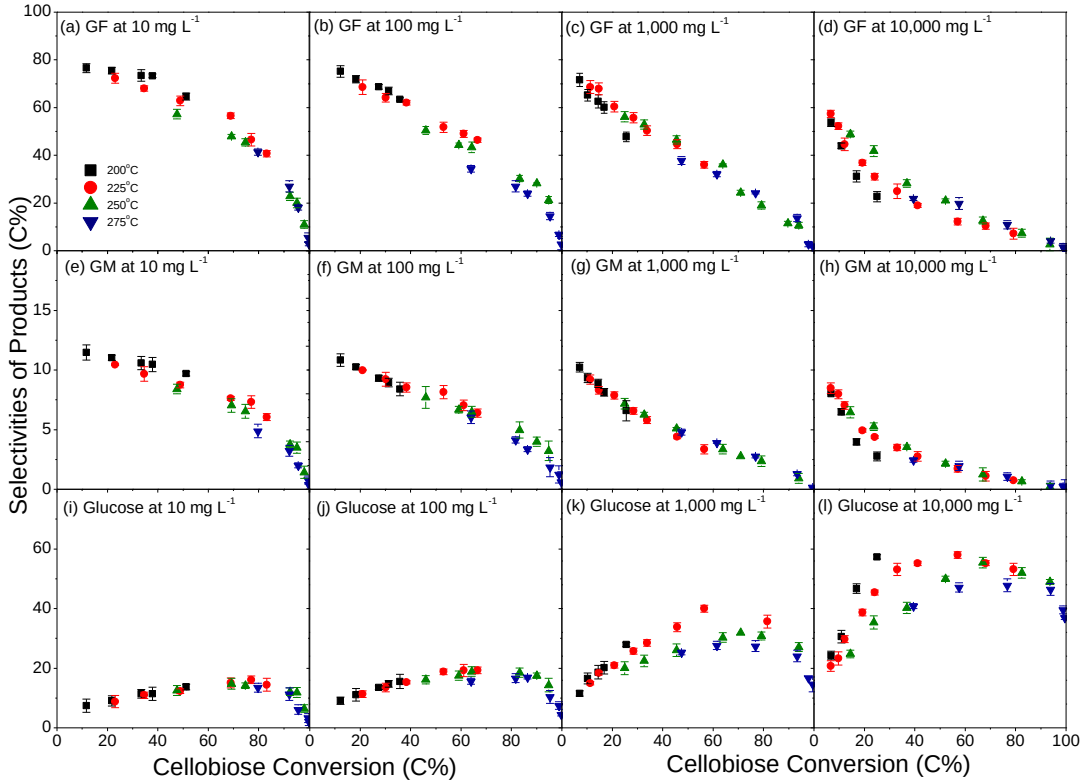

Figure 5- 2: Selectivities of primary products from cellobiose decomposition in HCW at various initial concentrations, calculated on a carbon basis. (a) GF at 10 mg L^{-1}; (b) GF at 100 mg L^{-1}; (c) GF at 1,000 mg L^{-1}; (d) GF at 10,000 mg L^{-1}; (e) GM at 10 mg L^{-1}; (f) GM at 100 mg L^{-1}; (g) GM at 1,000 mg L^{-1}; (h) GM at 10,000 mg L^{-1}; (i) glucose at mg L^{-1}; (j) glucose at 100 mg L^{-1}; (k) glucose at 1,000 mg L^{-1}; (l) glucose at 10,000 mg L^{-1}

The observed different trends in the selectivities of primary products during cellobiose decomposition indicate that the initial cellobiose concentration significantly affects the isomerisation and hydrolysis reactions and the further secondary reactions of these primary products to produce other products. However, the mechanisms responsible for such effects are still unclear. Therefore, further efforts were taken to analyse the kinetics of isomerisation and hydrolysis reactions that are the primary reactions of cellobiose hydrothermal decomposition.

5.3 Kinetics of Cellobiose Decomposition at Various Initial Cellobiose Concentrations

5.3.1 Kinetics of cellobiose

On the basis of the cellobiose yield data in Figure 5-1, the relationships between $-ln[C(t)/C(0)]$ and residence time t at various initial cellobiose concentrations and temperatures are then plotted in Figure 5-3. A linear relationship between $-ln[C(t)/C(0)]$ and residence time t is observed for all reaction conditions except for those at an initial cellobiose concentration of 10,000 mg L^{-1}. The results show that cellobiose decomposition is indeed first order with respect to cellobiose concentration at initial concentrations $\leq$1,000 mg L^{-1}. At higher concentrations such as 10,000 mg L^{-1}, cellobiose decomposition initially follows first-order kinetics, but the reaction rate constant starts to increases at a certain conversion depending on temperature. Such phenomenon further indicates that cellobiose decomposition reactions at 10,000 mg L^{-1} appear to be catalysed by some decomposition products, particularly when the reaction proceeds to increased conversions.

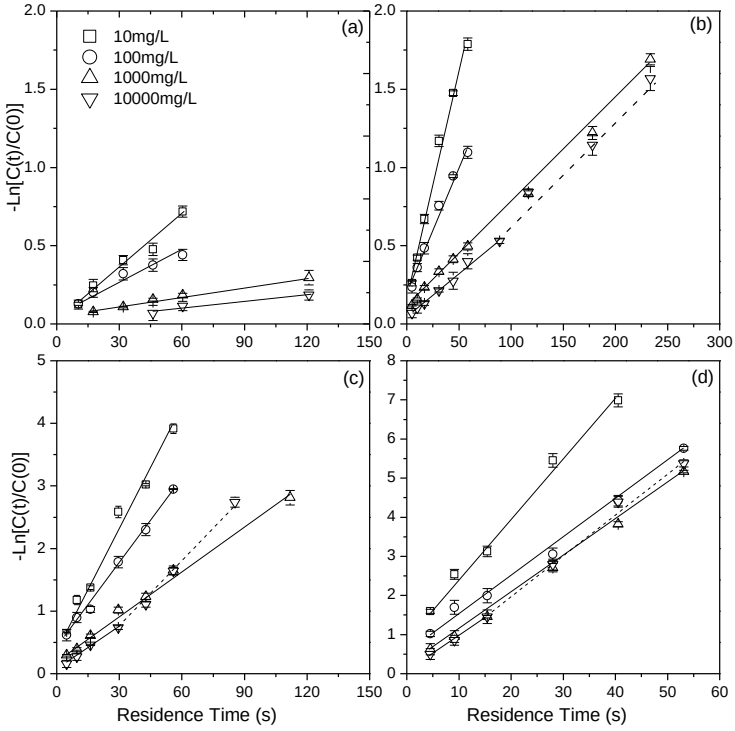

Figure 5- 3: Correlations between –ln[C/C(0)] and residence time at various initial concentration and temperatures. (a) 200 °C; (b) 225 °C; (c) 250 °C; (d) 275 °C

The reaction rate constant of cellobiose decomposition are then calculated and presented in Figure 5-4. It should be noted that only the initial reaction rates constant are considered for the experiments at an initial concentration of 10,000 mg L^{-1}. Clearly, the reaction rate constant of cellobiose decomposition decreases with an increase in initial cellobiose concentration, similar to that reported for glucose decomposition.[138] This can be attributed to the lower molar ratio of ion product and cellobiose (i.e., $([H_3O^+]+[OH^-])/[C]$) at a higher cellobiose concentration, since the hydrogen and hydroxyl ions are good catalysts for cellobiose decomposition.[28, 158, 195] Such a decrease in cellobiose decomposition reaction rate constant becomes significant at low initial cellobiose concentrations (10−1,000 mg L^{-1}) and low temperatures (200−225 °C). For example, at 200 °C, the reaction rate constant reduces by ~78% as the initial concentration increases from 10 to 1,000 mg L^{-1} (by two orders of magnitude) while such a reduction is only ~37% at 275 °C. As the initial concentration increases from 1,000 to 10,000 mg L^{-1}, further reduction in reaction rate constant is minimal at temperatures >250 °C, although such reductions are still high at temperatures <250

°C. Therefore, the kinetics of cellobiose decomposition strongly depends on initial cellobiose concentration and temperature, suggesting the differences in the underlying reaction mechanisms.

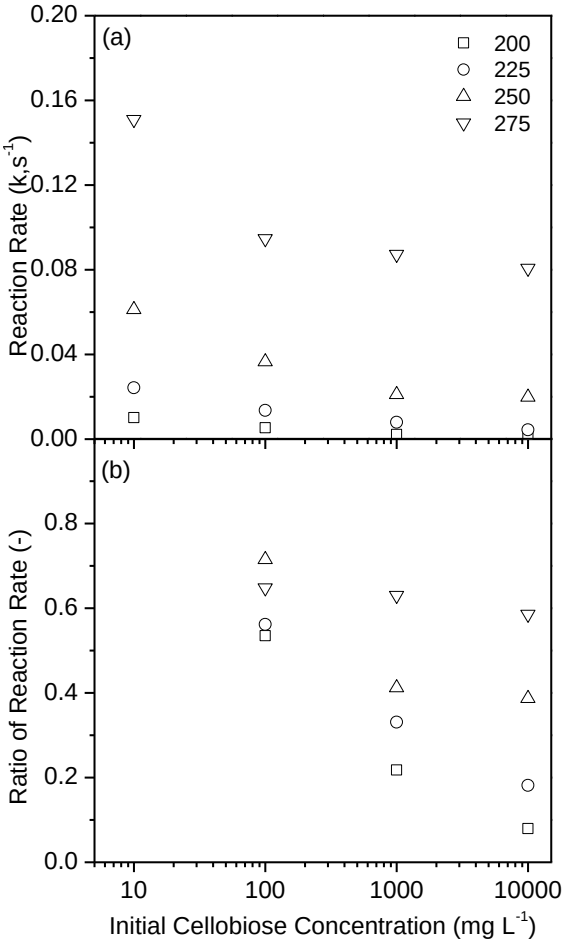

Figure 5- 4: Effect of initial cellobiose concentration on the reaction rate constant of cellobiose decomposition in HCW. (a) Reaction rate constant; (b) ratio of reaction rates to those at 10 mg L^{-1}

5.3.2 Kinetics of isomerisation and hydrolysis reactions

Further efforts are made to derive the kinetics of isomerisation and hydrolysis reactions during cellobiose primary decomposition under various initial cellobiose concentrations and temperatures. According to the delplot method,[189, 191] the ratio of each primary reaction to overall cellobiose decomposition can be determined by the intercept of product selectivity at cellobiose conversion $X \rightarrow 0$ (i.e., $\frac{k_{GF}}{k} = \lim_{X \rightarrow 0} S_{GF}$).

On the basis of selectivities of GF, GM and glucose in Figure 5-2, the ratios of isomerisation and hydrolysis reactions to overall cellobiose decomposition reaction can be obtained and presented in Figure 5-5.

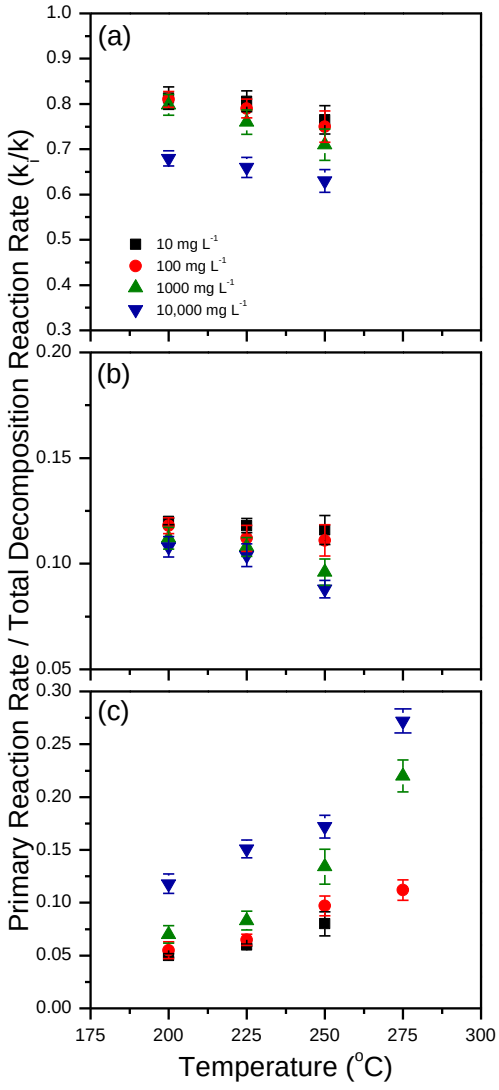

Figure 5- 5: Effect of initial cellobiose concentration on the selectivity of various primary reactions during cellobiose decomposition in HCW. (a) Isomerisation reaction to produce GF (k_{GF}/k); (b) isomerisation reaction to produce GM (k_{GM}/k); (c) hydrolysis reaction to produce glucose (k_G/k)

It can be seen in Figure 5-5 that the reaction rate constant ratios of two isomerisation reactions reduce with an increase in initial concentrations and temperatures. For the isomerisation reaction to produce GF, the value of k_{GF}/k reduces from 0.81 to 0.68

when initial cellobiose concentration increases from 10 to 10,000 mg L^{-1} at 200°C, while such ratio reduces from 0.79 to 0.63 at 250°C. For the isomerisation reaction to produce GM, the value of k_{GM}/k reduces from 0.120 to 0.108 at 200°C when the initial cellobiose concentration increases from 10 to 10,000 mg L^{-1}, while the ratio reduces from 0.116 to 0.083 at 250°C. Oppositely, the ratio of hydrolysis reaction (k_G/k) increases with an increase in initial cellobiose concentration, i.e., from 0.056 to 0.118 at 200°C when initial cellobiose concentration increase from 10 to 10,000 mg L^{-1}, while such ratio increase from 0.075 to 0.272 at 275°C when initial cellobiose concentration increase from 10 to 10,000 mg L^{-1}. The data clearly suggest that high initial cellobiose concentrations suppress the isomerisation reactions but greatly enhance the hydrolysis reaction. The promotion of hydrolysis reaction at high initial cellobiose concentration due to the low molar ratio of ion product and cellobiose at high concentrations, there are insufficient hydroxyl ions to catalyse all the cellobiose molecules. Therefore, more cellobiose molecules have the chance to interact with the hydrogen ion, thereby promoting the hydrolysis reactions. Such promotion effect on hydrolysis reaction becomes more significant at high temperatures due to the reduced affinity of the hydrogen ion for water molecules at high temperatures. The affinity of hydrogen ions to water molecules is reduced because of the weakened hydrogen bonds in water, leading to more protons to be involved in the hydrolysis reaction.

Based on the data in Figures 5-4 and 5-5, the reaction rate constants for isomerisation and hydrolysis reactions can be calculated. Figure 5-6 shows the Arrhenius plots of overall cellobiose decomposition and its three primary reactions at various initial cellobiose concentrations. The two isomerisation reactions decrease with an increase in the initial cellobiose concentration, similar as that for overall cellobiose decomposition. However, an interesting finding was observed for the hydrolysis reaction. At low temperatures (<250 °C), the hydrolysis reaction rate decreases as the initial cellobiose concentration increases, whereas the hydrolysis reaction rate follows an opposite trend at high temperatures (>250 °C). Further analyses indicate that, at low temperatures, although the selectivity of hydrolysis reaction (as shown in Figure 5-5) increases with initial cellobiose concentration, such an increase is less significant than the reduction in the overall reaction rate of cellobiose decomposition as initial

cellobiose concentration increases. For example, at 200 °C, the selectivity of hydrolysis reaction increases by around 2 folds (see Figure 5-5) as the initial cellobiose decomposition increase from 10 to 10,000 mg L^{-1}, but the reaction rate of cellobiose decomposition reduces by ~92% (see Figure 5-4b). This results in a reduction in the hydrolysis reaction rate as initial cellobiose concentration increases. However, under high temperature conditions, the reduction in the overall reaction rate of cellobiose decomposition is much smaller. For example, at 275 °C, the reaction rate of cellobiose decomposition only reduces by ~42% (see Figure 5-4b), when the initial cellobiose decomposition increases from 10 to 10,000 mg L^{-1}, corresponding to over 2 folds increase (see Figure 5-5) in the selectivity of hydrolysis reaction under the same conditions. Therefore, at high temperatures (>250 °C), the reduction in overall cellobiose decomposition becomes slower, eventually leading to the increase in hydrolysis reaction rate. While at low temperatures (<250 °C), there is a substantial reduction in overall cellobiose decomposition, which cannot be offset by the increase in the selectivity of the hydrolysis reaction.

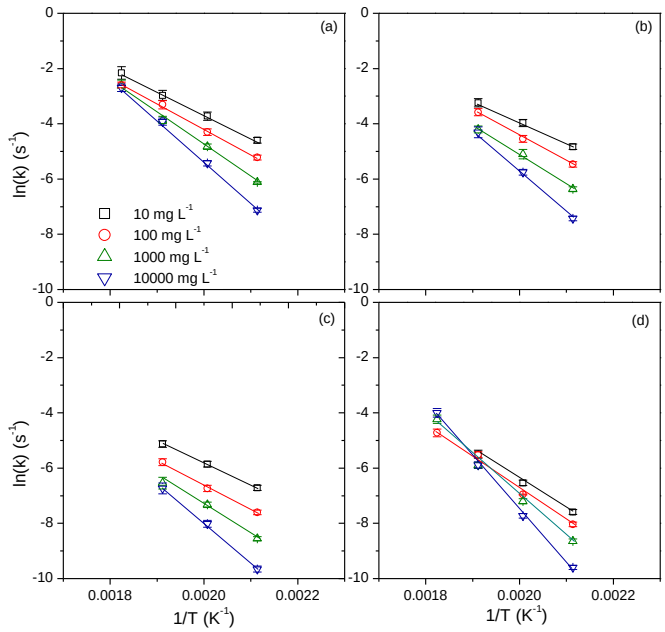

Figure 5- 6: Arrhenius plots of cellobiose decomposition in HCW. (a) cellobiose decomposition reaction (k); (b) isomerisation reaction to produce GF (k_{GF}); (c) isomerisation reaction to produce GM (k_{GM}); (d) hydrolysis reaction to produce glucose (k_G)

Obviously, the reduction of overall cellobiose decomposition becomes slower at increased concentrations (> 1,000 mg L^{-1}), especially at high temperatures (>250 °C). Only the selectivity of the hydrolysis reaction is increased at increased concentrations. Furthermore, there is a significant reduction in the pH values of the reaction solutions (see Figure 5-7) as conversion increases, demonstrating the formation of acidic products. For example, at an initial cellobiose concentration of 10,000 mg L^{-1}, the pH value reduces from ~7 to ~5 even at an early conversion stage (~7%). Therefore, cellobiose decomposition actually occurs under acidic conditions. The formation of acidic products is largely promoted at increased initial cellobiose concentration, as the pH values at high concentrations are lower when compared at the same cellobiose conversion. Therefore, the increased formation of acidic products is likely to be responsible for the increased selectivity of hydrolysis reactions.

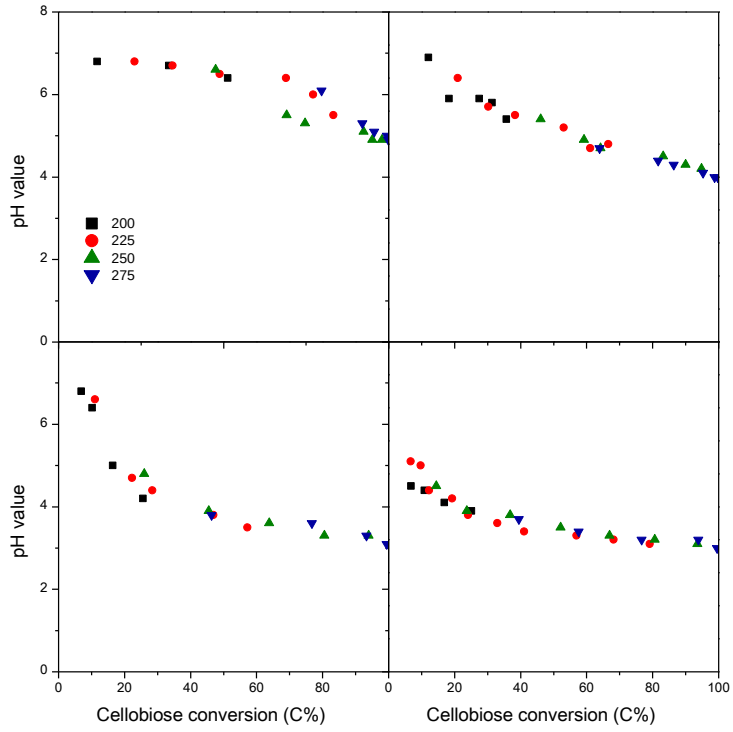

Figure 5- 7: pH value of liquid product as a function of cellobiose conversion at various initial concentrations. (a) 10 mg L^{-1}; (b) 100 mg L^{-1}; (c) 1,000 mg L^{-1}; (d) 10,000 mg L^{-1}

5.3.3 Kinetics parameters

The activation energy and pre-exponential factor are also determined by further processing of the data in Figure 5-8. Among the three primary reactions during cellobiose decomposition, isomerisation to produce GM has the lowest activation energy, increasing from 68 to 122 kJ mol^{-1} when the initial cellobiose concentration increases from 10 to 10,000 mg L^{-1}. The activation energy of the other isomerisation to produce GF is slightly higher, i.e., 68−133 kJ mol^{-1} at an initial cellobiose concentration range of 10−10,000 mg L^{-1}. Compared to the two isomerisation reactions, hydrolysis reaction has a much higher activation energy of 81−151 kJ mol^{-1} at the same initial cellobiose concentration range. Overall, cellobiose decomposition has an apparent activation energy range of 73−131 kJ mol^{-1} at an initial cellobiose concentration range of 10−10,000 mg L^{-1}. Furthermore, the activation energy of three primary reactions increases with initial cellobiose concentration, due to the reduced molar ratio of ion product and cellobiose at increased initial cellobiose concentrations.

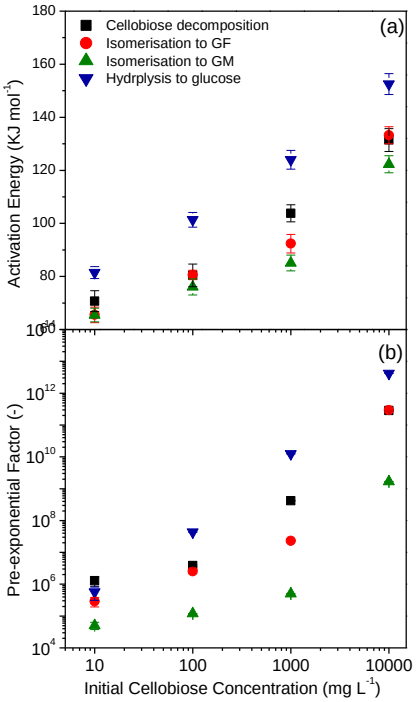

Figure 5- 8: Effect of initial cellobiose concentration on the activation energy and pre-exponential factor of various reactions during cellobiose decomposition in HCW. (a) Activation energy; (b) pre-exponential factor

5.4 Mechanisms Responsible for Cellobiose Primary Decomposition in HCW at Various Initial Cellobiose Concentrations

The results from this study have provided some insight into cellobiose decomposition in HCW. First, the selectivity of isomerisation reactions reduced at a high cellobiose concentration, but hydrolysis reaction to produce glucose is increased. Chapter 4 suggested that unlike hydrogen ions which have a high affinity for water molecules, hydroxyl ions are readily available to catalyse the isomerisation reactions during cellobiose decomposition in HCW. However, high cellobiose concentrations reduce the molar ratio of ion product and cellobiose. Accordingly, it reduces the amount of cellobiose molecules to be catalysed by hydroxyl ions but increases the possibility of cellobiose molecules to interact with hydrogen ions for hydrolysis reaction. As a result, the contribution of the hydrolysis reaction is increased at high cellobiose concentrations. Figure 5-9 summarises the effect of initial cellobiose concentration on the reaction pathways of cellobiose decomposition in HCW.

Second, an increase in initial cellobiose concentration suppresses the cellobiose decomposition in HCW. This is due to the catalytic effect of ion products in HCW. As cellobiose concentration increases, the molar ratio of ion product and cellobiose reduce. Hence, reduce the availability of hydrogen and hydroxyl ions for catalysing cellobiose decomposition reactions. Although the overall cellobiose decomposition decreases with increasing the cellobiose concentration for various temperatures, the trends are slightly different. At low temperatures (<250 °C), as the cellobiose decomposition is almost dominantly contributed by isomerisation reactions, the overall reaction rate of cellobiose decomposition reduce significantly as cellobiose concentration increases. At high temperatures (>250 °C), the overall reaction rate of cellobiose decomposition reduces more slowly, particularly at high concentrations, due to the increased contribution of hydrolysis reaction at high temperatures and high concentrations.

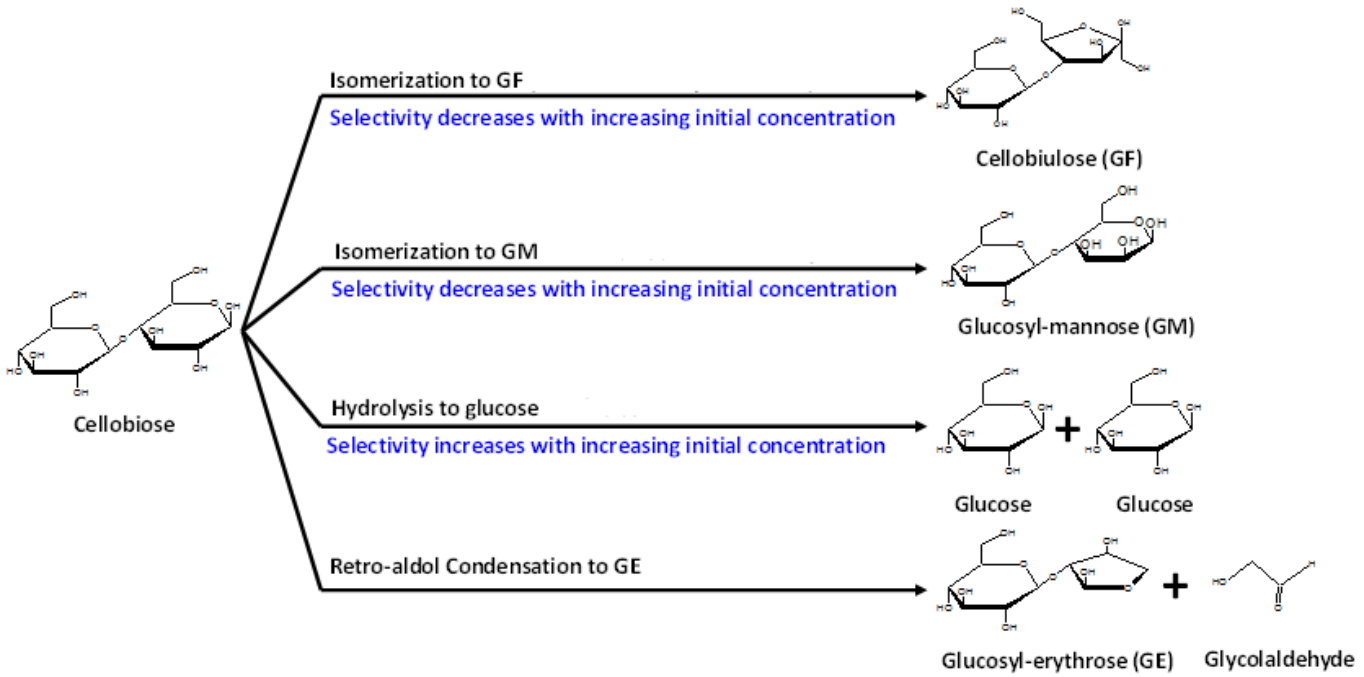

Figure 5- 9: Effect of initial cellobiose decomposition on the reaction pathways of cellobiose decomposition in HCW

Third, it should be noted that significant acidic products are produced during cellobiose decomposition, even at the early stage. Such acidic products may have a little effect on the primary reactions of cellobiose decomposition at low concentrations (<1,000 mg L^{-1}) as the cellobiose decomposition still follows the first-order kinetics. However, at high concentrations (i.e., 10,000 mg L^{-1}), those acidic products not only promote the decomposition of GF and GM but also catalyse the primary reactions of cellobiose decomposition, as reflected by the increase of reaction rate at the middle stage of cellobiose decomposition (see Figure 5-3). This finding may have important applications to improve the glucose yield during cellobiose or cellulose decomposition under hydrothermal conditions.

5.5 Conclusion

This study investigates the mechanism and kinetics of cellobiose decomposition in HCW at various initial concentrations (10−10,000 mg L^{-1}) and temperatures (200−275 °C). The reaction rate constant of cellobiose decomposition is found to decrease with an increase in initial cellobiose concentration. Isomerisation reactions to produce GF and GM are still the dominant reactions at an initial cellobiose concentration of 10 – 10,000 mg L^{-1}. However, as the initial cellobiose concentration increases, the selectivities of isomerisation reactions decrease while the selectivity of hydrolysis reaction increases. The promotion of hydrolysis reaction at high initial cellobiose concentrations is likely due to the low molar ratio of ion product and cellobiose, which reduces the amount of hydroxyl ions to catalyse cellobiose decomposition, thus increases the chance of hydrogen ions to interact with cellobiose for hydrolysis reaction. The increase in the hydrolysis reaction at high initial cellobiose concentrations may also be related to the formation of acidic products at the early stage of cellobiose decomposition. The apparent activation energy of cellobiose decomposition increases with increasing initial cellobiose concentration, due to the reduced molar ratio of ion product to cellobiose.

CHAPTER 6 EFFECT OF INITIAL PH ON CELLOBIOSE DECOMPOSITION UNDER WEAKLY ACIDIC CONDITIONS

6.1 Introduction

It can be observed from Chapter 4 and 5 that the pH value of liquid product reduces substantially to a pH value of ~4 even at the early stage of cellobiose decomposition in HCW. This indicates that the reaction condition during cellobiose decomposition changes from non-catalytic to weakly acidic (i.e., pH = 4−6) as cellobiose decomposition proceeds. There are substantial studies on cellulose [157, 165, 198], glucose [118, 145, 150] and cellobiose [126] hydrolysis in dilute acid. However, most of the previous studies were conducted under acidic conditions with pH < 3, where acid-catalysed reaction plays a dominant role. Under weakly acidic conditions (i.e., pH of 3−7), the cellobiose decomposition was reported to follow a distinctly different reaction mechanism as those under stronger acidic conditions (i.e., pH < 3) [126], but such a mechanism is still unresolved. Therefore, the purpose of this study is to compare cellobiose decomposition at 200−250 °C under non-catalytic (pH = 7) and weakly acidic (i.e., pH = 4−6) conditions. This study will provide a mechanistic understanding of the reaction mechanism of cellobiose decomposition to build a linkage between non-catalytic and acidic conditions.

6.2 Effect of Initial pH on the Yields of Primary Products from Cellobiose Decomposition

Figure 6-1 demonstrates the effect of initial pH on the yields of cellobiose and its main primary products as a function of residence times at 200 – 250 °C. It is clearly shown that the cellobiose yield decreases when the initial pH of cellobiose solution reduces from 7 (water only) to 4 for all the temperatures in this study. Obviously, the addition

of acid promotes the cellobiose hydrothermal conversion. It is also interesting to see that the isomerisation reaction products GF and GM are also produced as major primary products even under weakly acidic conditions, indicating that isomerisation reactions also play important roles during cellobiose hydrothermal conversion under acidic conditions.

However, the initial pH of cellobiose solution greatly influences the yields of three main primary products from cellobiose decomposition. A reduction in the initial pH leads to an increased formation of glucose via hydrolysis reaction, at the expense of the isomerisation reactions to form GF and GM. For example, at 250 °C and a residence time of ~30 s, a reduction in the initial pH from 7 to 4 decreases the GF yield from ~22% to ~12% and the GM yield from ~2.3% to ~1.3%, but increases in the glucose yield from ~17% to ~31%.

Another interesting observation from Figure 6-1 is that the yields of GF and GM both increase with residence time until a cellobiose conversion of ~60% is reached. A further increase in residence time results in the reduction of both yields. It should be noted that the decreases in the yields of GF and GM are more significant at lower initial pH conditions, clearly suggesting that the secondary decomposition of GF and GM is favoured under acidic conditions. For glucose, its yield follows similar trends as those of GF and GM under acidic conditions (i.e., pH < 7). However, under non-catalytic conditions (pH = 7), the glucose yield continuously increases with residence time until a higher cellobiose conversion of ~80% is reached, indicating that glucose decomposition is suppressed under non-catalytic conditions.

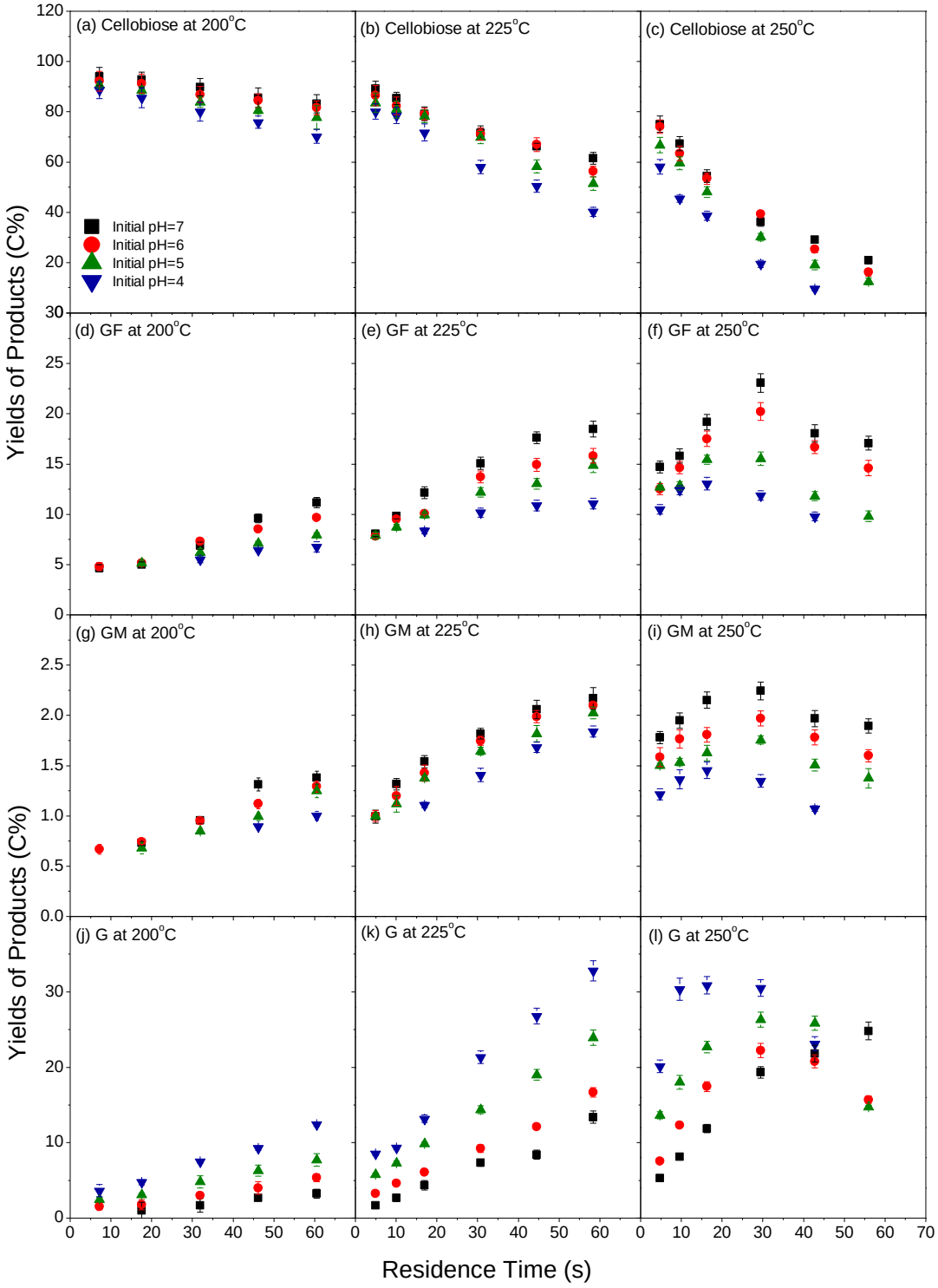

Figure 6- 1: Effect of initial pH on the yields of cellobiose and its primary products at temperature 200 – 250 °C. (a) Cellobiose at 200 °C; (b) cellobiose at 225 °C; (c) cellobiose at 250 °C; (d) GF at 200 °C; (e) GF at 225 °C; (f) GF at 250 °C; (g) GM at 200 °C; (h) GM at 225 °C; (i) GM at 250 °C; (j) glucose at 200 °C; (k) glucose at 225 °C; and (l) glucose at 250 °C

The selectivities of three primary products were further calculated. Figure 6-2 presents the selectivities of three main primary products as a function of cellobiose conversion at various temperatures and initial pH conditions. It can be seen that both the GF and GM selectivities decrease as cellobiose conversion increases, whereas the glucose selectivity increases with cellobiose conversion. The initial pH significantly affects the selectivities of three primary products. At reduced pH conditions, the selectivities of GF and GM reduce considerably, but the glucose selectivity increases greatly. The higher glucose selectivity under more acidic conditions is at least due to the following reasons. First, the isomerisation reactions to produce GF and GM are largely suppressed under acidic conditions. Another reason is that the secondary hydrolysis reactions of GF and GM to produce glucose are promoted under acidic conditions.

However, the glucose selectivity starts to decrease at increased cellobiose conversions. For example, at 250 °C and an initial pH of 4, the glucose selectivity starts to decrease at a cellobiose conversion of ~58%, achieving a maximal glucose selectivity of ~52%. While at an initial pH of 7, the glucose selectivity starts to decrease at a cellobiose conversion of ~71%, although the maximal glucose selectivity is only ~35%. It also can be seen that the glucose selectivity reduces more rapidly under acidic conditions. This indicates that it is difficult to achieve high glucose selectivity at high conversions under acidic conditions. Therefore, although acidic conditions strongly promote the hydrolysis reaction to form glucose, the glucose decomposition is also favoured, resulting in the rapid reduction in glucose selectivity at increased conversion under acidic conditions.

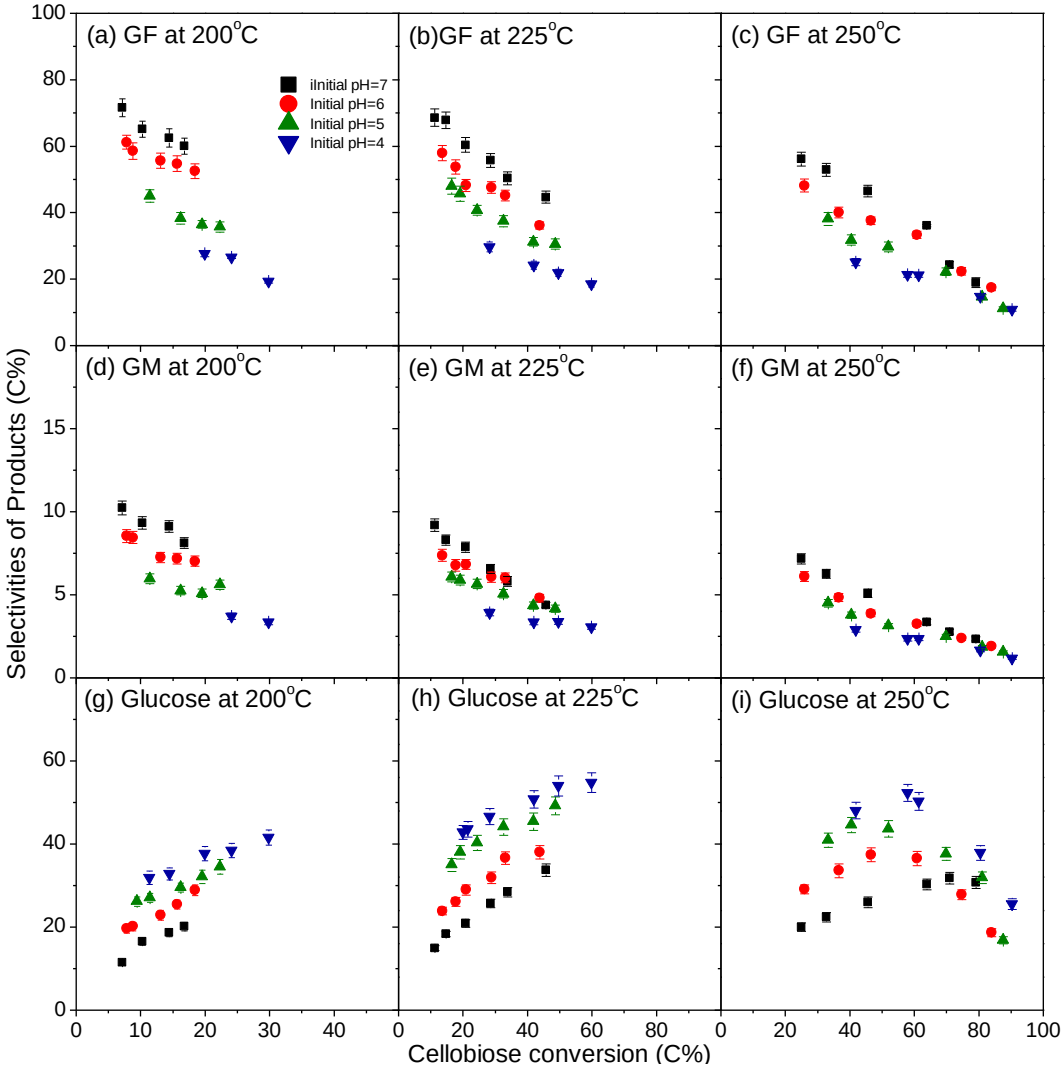

Figure 6- 2: Effect of initial pH on the primary products of cellobiose decomposition at temperature 200 – 250 °C. (a) GF at 200 °C; (b) GF at 225 °C; (c) GF at 250 °C; (d) GM at 200 °C; (e) GM at 225 °C; (f) GM at 250 °C; (g) glucose at 200 °C; (h) glucose at 225 °C; and (i) glucose at 250 °C

6.3 Effect of Initial pH on the Kinetics of Cellobiose Decomposition

Based on the cellobiose concentration *C(t)* at various residence times *t*, the rate constant *k* (s^{-1}) of cellobiose decomposition reaction can be determined using equation 3.7 in Chapter 3, assuming the cellobiose decomposition reaction follows the first-order kinetics. The correlation between –ln[C(t)/C(0)] versus residence times for all the conditions are then plotted in Figure 6-3. A linear correlation is observed for all the condition, indicating that cellobiose decomposition under acidic conditions also follows the first order reaction kinetics. The reaction rate constant of cellobiose

decomposition increases with decreasing the initial pH of cellobiose solution. Obviously, cellobiose decomposition is accelerated under acidic conditions. Compared to those at an initial pH of 7, the rate constants at an initial pH of 4 are almost doubled for all the temperature conditions.

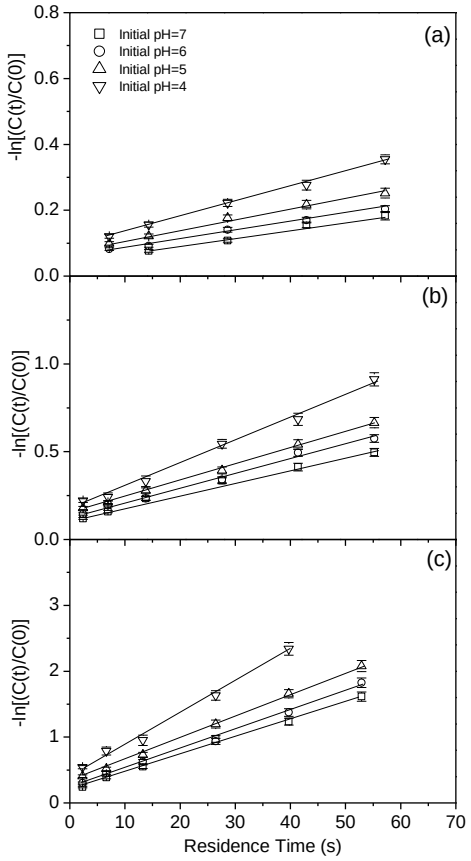

Figure 6- 3: Correlations between –ln[(C(t)/C(0)] and residence time at various temperatures and initial pH conditions during cellobiose decomposition in HCW. (a) 200 °C; (b) 225 °C; and (c) 250 °C

The reaction rate constants of the three main primary reactions of cellobiose decomposition can then be determined. Based on the delplot method[189-191], the reaction rate constant ratio of each primary reaction to overall cellobiose decomposition is equal to the intercept of product selectivity at cellobiose conversion $X \rightarrow 0$. Based on the data in Figure 6-2, the reaction rate constant ratios of each primary reaction rate to overall cellobiose decomposition reaction rate are obtained. Figure 6-4 presents the

effect of initial pH on the ratios of three primary reaction rates to overall cellobiose decomposition reaction rate. It can be found that the contribution of isomerisation reaction to produce GF reduces when the initial pH of cellobiose solution reduces. For example, at 200 °C, the value of k_{GF}/k reduces significantly from 0.77 to 0.46 when the initial pH reduces from 7 to 4. A similar trend can be seen for the isomerisation reaction to produce GM. For example, the value of k_{GM}/k reduces from 0.112 to 0.051 when the initial pH reduces from 7 to 4 at 200 °C. In contrast, the contribution of hydrolysis reaction to produce glucose increases with a reduction in the initial pH of cellobiose solution. For example, the value of k_G/k increases from 0.08 to 0.26 when the initial pH reduces from 7 to 4 at 200 °C. Obviously, the contribution of hydrolysis reaction to cellobiose decomposition increases substantially at reduced pH conditions.

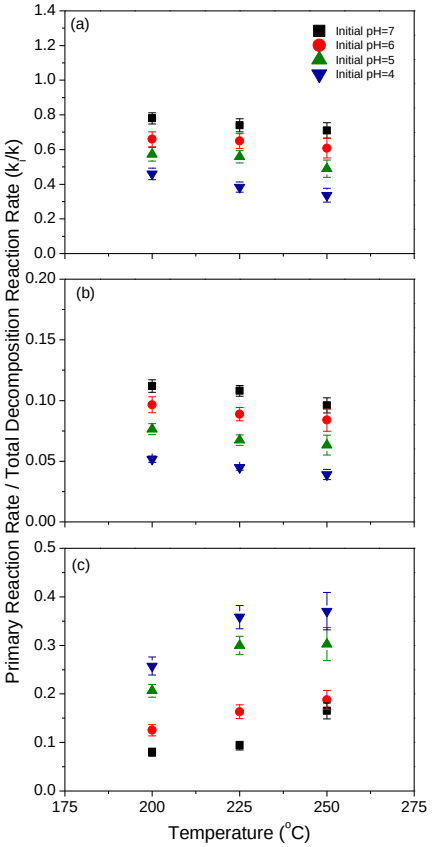

Figure 6- 4: Effect of initial pH on the selectivity of main primary reactions during cellobiose decomposition in HCW: (a) isomerisation reaction rate to produce GF (k_{GF}/k); (b) isomerisation reaction rate to produce GM (k_{GM}/k); and (c) hydrolysis reaction rate to produce glucose (k_G/k)

Based on the above data, the rate constants of three primary reactions of cellobiose decomposition can be estimated. Figure 6-5 plots the reaction rate constants as a function of the hydrogen ion concentration at the reaction temperature, which was calculated according to equation 3.11 to 3.14 in Chapter 3. It is noteworthy that the hydrogen ion concentrations for both water and sulphuric acid at reaction temperature rather than at room temperature are considered, as recommended by Kupiainen et al. [118] If the hydrogen ion concentration at room temperature is used, it cannot explain that the hydrolysis reaction rate constant is non-zero under non-catalytic conditions (pH = 7). Several important findings can be observed from Figure 6-5. First, the reaction rate constants of isomerisation reactions to produce GF and GM almost remain constant under various initial pH conditions. Therefore, the increase in hydrogen ion concentration doesn't affect the isomerisation reaction rate constants, demonstrating that the isomerisation reactions are not acid-catalysed reactions. However, the reaction rate constants of isomerisation reactions increase with reaction temperature, i.e., from ~0.0018 and ~0.00025 s^{-1} at 200 °C to ~0.0173 and ~0.00225 s^{-1} at 250 °C for the isomerisation reaction to produce GF and GM, respectively. Second, the rate constant of hydrolysis reaction increases almost linearly with the hydrogen ion concentration at the reaction temperature. It suggests that the hydrolysis reaction of cellobiose under non-catalytic conditions is indeed catalysed by the hydrogen ion dissociated from water at high temperatures. Under acidic conditions, the hydrolysis of cellobiose to produce glucose is truly dependent on the available hydrogen ion concentration at the reaction temperature. Third, the overall reaction rate constant of cellobiose decomposition also increases almost linearly with the hydrogen ion concentration at the reaction temperature. Obviously, the increase in overall reaction rate constant at higher hydrogen ion concentrations is mainly due to the increased contribution of the hydrolysis reaction, since the reaction rate constants of isomerisation reactions do not change with the hydrogen ion concentration.

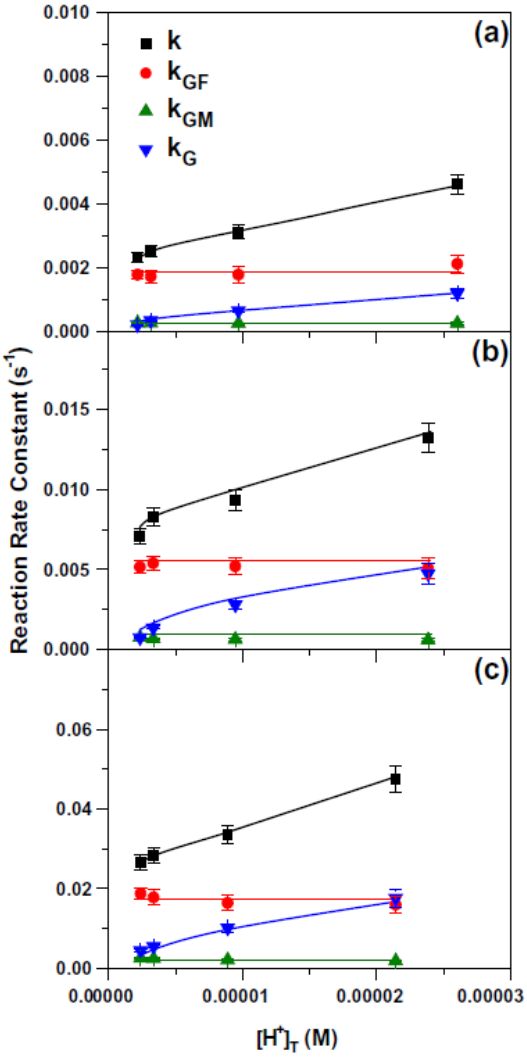

Figure 6- 5: Reaction rate constant of cellobiose decomposition in HCW as a function of hydrogen ion concentration at reaction temperature: (a) 200 °C; (b) 225 °C; and (c) 250 °C.

6.4 Modelling of Cellobiose Decomposition under Various Initial pH Conditions

The above results clearly demonstrate that the rate constant of cellobiose hydrolysis reaction is strongly dependent on the hydrogen ion concentration at the reaction temperature. The rate constant of hydrolysis reaction was fitted to the modified Saeman equation[118]:

$$k_G = k_{0,G}[H^+]_T^m e^{-E_{a,G}/RT} \qquad \text{Equation 6.1}$$

where $k_{0,G}$ is the pre-exponential factor (M^{-1} s^{-1}) of the hydrolysis reaction, $E_{a,G}$ is the activation energy (kJ mol^{-1}) of the hydrolysis reaction, and m is the power of the hydrogen ion concentration at the reaction temperature. The values for each parameter were estimated by nonlinear regression analysis. Based on the data in Figure 5, it was found that an m value of 0.68 is best fitted to the equation (13). The activation energy and pre-exponential factor were further estimated to be ~116 kJ mol^{-1} and ~9.3×10^{12} M^{-1} s^{-1}, respectively.

Therefore, the rate constant of cellobiose decomposition under various initial pH conditions can be estimated based on the following equation:

$$k = k_{0,GF}e^{-E_{a,GF}/RT} + k_{0,GM}e^{-E_{a,GM}/RT} + k_{0,G}[H^+]_T^m e^{-E_{a,G}/RT} \qquad \text{Equation 6.2}$$

where $k_{0,GF}$ and $k_{0,GM}$ are the pre-exponential factor (s^{-1}) of isomerisation reactions to produce GF and GM, respectively; $E_{a,GF}$ and $E_{a,GM}$ are the activation energy (kJ mol^{-1}) of isomerisation reactions to produce GF and GM, respectively. Since the rate constants of isomerisation reactions do not change with initial pH, the activation energy and the pre-exponential factor remains unchanged under various initial pH conditions. According to the Arrhenius plots, the activation energy of isomerisation reactions are ~90 and ~84 kJ mol^{-1} for GF and GM formation respectively, and the pre-exponential factor are ~1.3×10^7 s^{-1} and ~2.5×10^5 s^{-1} for GF and GM formation respectively.

The modelling results based on equation 6.2 are compared with experimental results in Figure 6-6. The model can well predict the reaction rate constant of cellobiose decomposition at 200 and 225 °C at various initial pH conditions, but the modelling results are lower than the experimental results at 250 °C. It seems that some other reactions are responsible for the primary decomposition of cellobiose under acidic conditions at a higher temperature of 250 °C. The retro-aldol condensation reaction to produce GE is also a minor primary reaction (with selectivity < 5%) under non-catalytic conditions, but is suppressed under acidic conditions based on analysis (data not shown). One of the possible reactions take place under acidic conditions is the reversion reaction[145, 150, 199], which is a polymerisation reaction to produce oligomers.

The reversion reaction is known to increase with an increase in hydrogen ion concentration [199], which seems to explain the increased gap between experimental and simulation results as the hydrogen ion concentration increases.

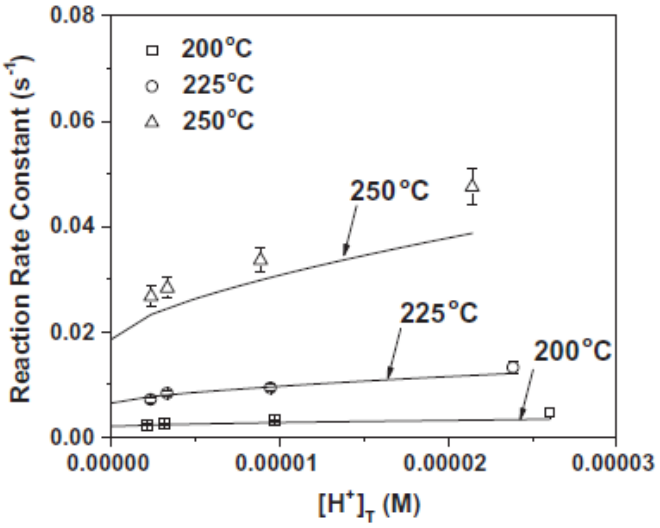

Figure 6- 6: Comparisons of reaction rate constants of cellobiose decomposition between experimental results (points) and modelling results (lines) at various pH and temperature conditions.

6.5 Further Discussions on Cellobiose Decomposition under Hydrothermal Conditions

The results of this study have important applications on cellobiose decomposition under non-catalytic or acidic conditions. First, it improves the understanding of cellobiose decomposition mechanism under non-catalytic condition. The data in this work show that a reduction in initial pH from 7 to 4 leads to an increase in the rate constant of cellobiose decomposition by a factor of ~2. Chapter 4 and 5 reported a reducing pH from ~7 to ~4 (due to the formation of organic acids) with increasing conversion during cellobiose decomposition under non-catalytic conditions. However, an increase in rate constant with increasing conversion was not found at initial concentrations less than 1,000 mg L^{-1}. Only at high initial cellobiose concentrations (i.e., 10,000 mg L^{-1}), an increase in rate constant was found at increased conversions. Obviously, such an increase in rate constant is due to the contribution of the hydrolysis reaction, as isomerisation reactions do not change with the pH condition. It seems that

the formed organic acids have little catalytic effects on the primary cellobiose decomposition at low cellobiose concentrations. Unlike the acids which were directly added into the cellobiose solution, the formed acids may be difficult to interact with cellobiose molecules in a mixture of compounds. Rather, the formed acids seem to have more chances to catalyse the secondary decomposition of GF and GM, as suggested in Chapter 5. At high cellobiose concentrations, the formed acids may have a high possibility to interact with cellobiose molecules, leading to an increase in the reaction rate of cellobiose decomposition at increased conversions.

Second, this study builds a linkage between the cellobiose decomposition mechanism under non-catalytic and acidic conditions. The above results clearly show that the rate constant of hydrolysis reaction substantially increases under acidic conditions, significantly contributing to the cellobiose decomposition. In contrast, the rate constants of isomerisation reactions almost remain unchanged. Although the isomerisation reactions still play important roles under non-catalytic or weakly acidic conditions (i.e., pH = 4−7), their contributions under strongly acidic conditions are greatly reduced, because the rate constants of isomerisation reactions do not increase with hydrogen ion concentration. For example, at an initial pH of 2, the rate constant of the hydrolysis reaction is calculated to be ~40 times higher than that of isomerisation reaction for GF formation, according to the kinetics parameters in this study. Therefore, under strongly acidic conditions, the rate constants of isomerisation reactions for GF and GM can be removed from the equation (14) due to their negligible contribution to cellobiose decomposition, and the overall rate constant of cellobiose decomposition can be directly simulated using modified Saeman equation. However, it should be noted that some other reactions (i.e., reversion reaction) may play an increasing role during cellobiose decomposition under strongly acidic conditions. An improved understanding of those reactions is helpful to simulate the cellobiose decomposition under strongly acidic conditions.

6.6 Conclusions

This study investigates the effect of initial pH on cellobiose hydrothermal decomposition at 200 – 250 °C under weakly acidic conditions with an initial pH range of 4−7. Similar as cellobiose decomposition under non-catalytic conditions, the isomerisation reactions to produce GF and GM and the hydrolysis reaction to produce glucose are the main primary reactions of cellobiose decomposition under weakly acidic conditions. However, the selectivity of hydrolysis reaction increases remarkably under acidic conditions, at the expense of isomerisation reactions. Compared to those under non-catalytic conditions, the rate constants of isomerisation reactions almost remain unchanged under various pH conditions, but the rate constant of hydrolysis reaction increases significantly with reducing the initial pH of cellobiose solution. Therefore, the acceleration of cellobiose decomposition under acidic conditions is mainly due to the increased contribution of the hydrolysis reaction, which is truly dependent on the hydrogen ion concentration at the reaction temperature. A kinetic model including the isomerisation and hydrolysis reactions, can well predict the cellobiose hydrothermal decomposition under various initial pH conditions at low temperatures (i.e., < 225 °C), but underestimates the rate constant of cellobiose hydrothermal decomposition at higher temperatures (i.e., 250 °C), probably due to the increased contribution of other reactions such as reversion reaction.

CHAPTER 7 EFFECT OF ALKALI AND ALKALINE EARTH METAL CHLORIDES ON CELLOBIOSE DECOMPOSITION IN HCW

7.1 Introduction

Chapter 4 - 6 in this thesis provide some new insights into the reaction mechanism of cellobiose decomposition in HCW under various conditions. Isomerisation reactions to produce cellobiulose (glucosyl-fructose, GF) and glucosyl-mannose (GM) have been revealed to be the dominant primary reactions during cellobiose decomposition in HCW at 200−275 °C. Compared to isomerisation reactions, hydrolysis reaction to produce glucose is only a minor primary reaction during cellobiose decomposition in HCW, but the hydrolysis reaction is promoted at increased temperatures and initial concentrations. Hydrolysis reaction also increases under weakly acidic conditions. The contribution of retro-aldol condensation reaction to produce GE (glucosyl-erythrose) and glycolaldehyde is even lower at 200−275 °C.

It is known that biomass contains abundant alkali and alkaline earth metallic (AAEM) species, such as Na, K, Mg and Ca. Previous studies[200-203] have shown that AAEM species have an influence on biomass or sugar conversion in HCW. However, the effect of AAEM species on cellobiose decomposition is little known. Therefore, the purpose of this work is to investigate the effect of AAEM chlorides on the reaction pathways and mechanism of cellobiose decomposition in HCW. A series of systematic experiments were performed using a continuous reactor at 200 – 275 ^{o}C and cellobiose concentration of 1000 mg L^{-1}. The concentration of salt was prepared at a salt to cellobiose molar ratio of 10.

7.2 Effect of AAEM Chlorides on the Kinetics of Cellobiose Decomposition in HCW

Assuming the cellobiose decomposition follows the first-order kinetics, the reaction rate k (s^{-1}) of cellobiose decomposition can be determined by the equation 3.5 (Chapter 3). Based on the cellobiose concentration in the liquid product at various residence times, the relationship between $-ln[C(t)/C(0)]$ and residence time t at various temperatures can be plotted in Figure 7-1. A linear relationship between $-ln[C(t)/C(0)]$ and residence time t is observed for all reaction conditions.

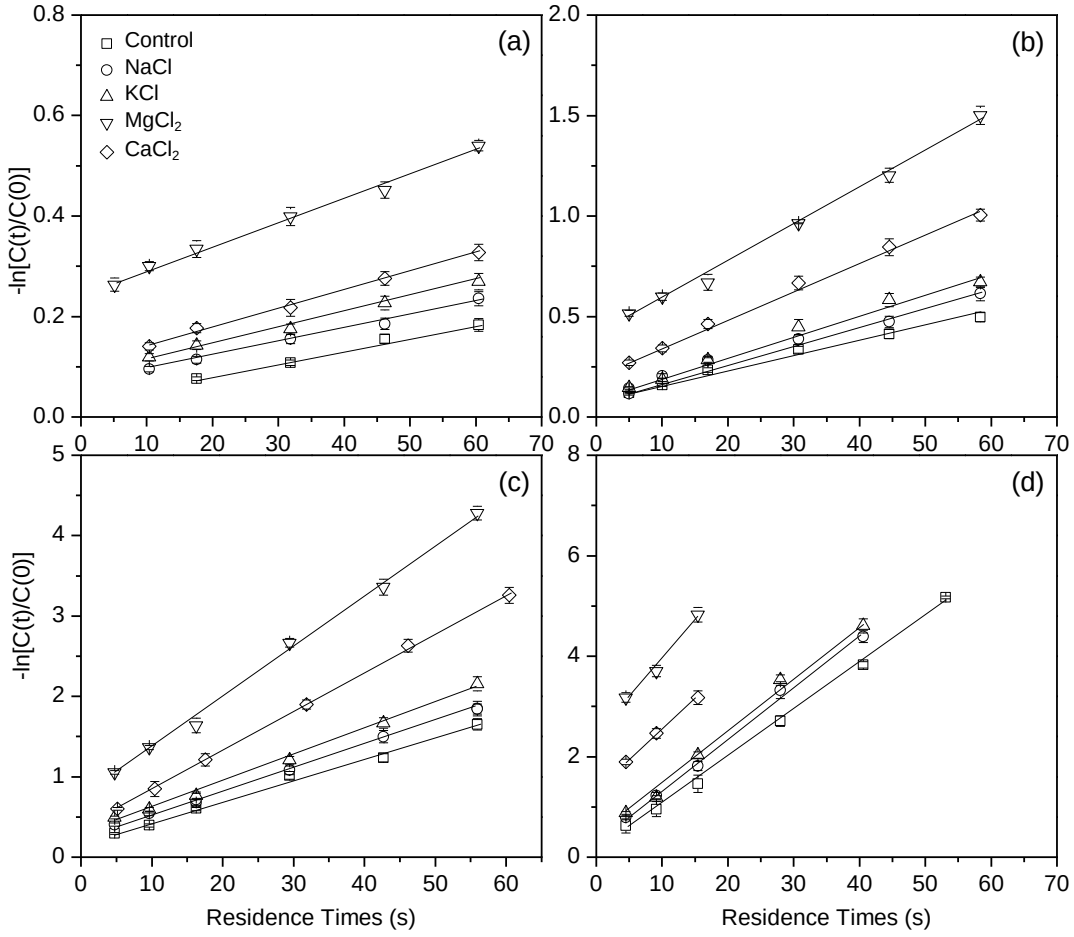

Figure 7- 1: Correlations between –ln[C(t)/C(0)] and residence time at various temperatures during cellobiose decomposition in HCW with the addition of various salts at a salt-to-cellobiose molar ratio of 10. (a) 200 °C; (b) 225 °C; (c) 250 °C; (d) 275 °C

Based on the slope of the linear curve, the reaction rate of cellobiose decomposition under various reaction conditions can be determined, and the results are shown in Table 7-1. The addition of AAEM chlorides indeed accelerates cellobiose decomposition in HCW. At the same temperature and salt concentration, the reaction rate of cellobiose decomposition follows an order of $MgCl_2$ > $CaCl_2$ > KCl > NaCl. Compared to the reaction rate of control experiment (water only), the reaction rate of cellobiose decomposition is almost doubled in the $MgCl_2$ solution at all temperatures. Based on the reaction rates at various temperatures, the activation energy and pre-exponential factor of cellobiose decomposition in various AAEM chloride solutions can be also estimated, and the results are also listed in Table 7-1. Without salt addition, the cellobiose decomposition has an apparent activation energy of ~104.9 KJ mol^{-1}. The addition of salt reduces the apparent activation energy of cellobiose decomposition in HCW, i.e., to ~103.9 KJ mol^{-1} for NaCl, ~101.7 KJ mol^{-1} for KCl, ~99.0 KJ mol^{-1} for $MgCl_2$ and ~101.0 KJ mol^{-1} for $CaCl_2$.

Table 7- 1: Reaction rates and kinetics parameters of cellobiose decomposition at various reaction conditions

	Reaction rate (s^{-1})				Kinetic Parameters	
	200 °C	225 °C	250 °C	275 °C	Activation energy (KJ mol^{-1})	Pre-exponential factor
Control (water only)	0.0025	0.0069	0.0263	0.0936	104.9	8.33×10^8
NaCl	0.0027	0.0085	0.0283	0.1013	103.9	7.35×10^8
KCl	0.0030	0.0112	0.0328	0.1071	101.7	5.10×10^8
$CaCl_2$	0.0037	0.0139	0.0522	0.1167	101.0	5.46×10^8
$MgCl_2$	0.0049	0.0184	0.0593	0.1510	99.0	4.29×10^8

7.3 Effect of AAEM Chlorides on the Primary Products of Cellobiose Decomposition in HCW

The above results clearly demonstrate that cellobiose decomposition reaction is largely accelerated in AAEM chloride solutions, especially for the $MgCl_2$ solution. However, it is not clear which primary reaction of cellobiose decomposition is affected by AAEM chlorides, since Chapter 4 presented that cellobiose decomposes via a series of main primary reactions, i.e., isomerisation reactions to from GF and GM, hydrolysis reaction to form glucose, and retro-aldol reaction to from GE and glycolaldehyde. Using their concentrations in the liquid products, the yields of cellobiose and its main primary decomposition products GF, GM and glucose were calculated on a carbon basis. Figure 7-2 compares the effect of AAEM chlorides on the yields of cellobiose and its main primary decomposition products at 200 – 275 °C and a salt concentration of ~29 mM. It can be found that the yields of three main primary products are all enhanced in AAEM chloride solutions. Therefore, three main primary reactions of cellobiose decomposition are all promoted by AAEM chlorides, and such promotion effect of AAEM chlorides also follow a similar trend of $MgCl_2 > CaCl_2 > KCl > NaCl$. However, at high temperatures (>250 °C), the yields of primary products are easily degraded even at short residence times. As the primary products of cellobiose decomposition are not stable, the primary products can further decompose to other secondary products, depending on the catalytic effects of AAEM chlorides on the secondary reactions. Therefore, the yields of GF, GM and glucose depend on the trade-off between their formation from cellobiose decomposition and their decomposition to other products. A careful comparison the cellobiose conversion and the yields of primary products at the same residence time suggests that GF and GM start to decompose at a cellobiose conversion of ~60%, while glucose starts to decompose at a higher cellobiose conversion of ~80%. The data clearly indicate that the addition of AAEM chlorides not only promote the formation of primary products from cellobiose decomposition but also enhance their secondary decomposition.

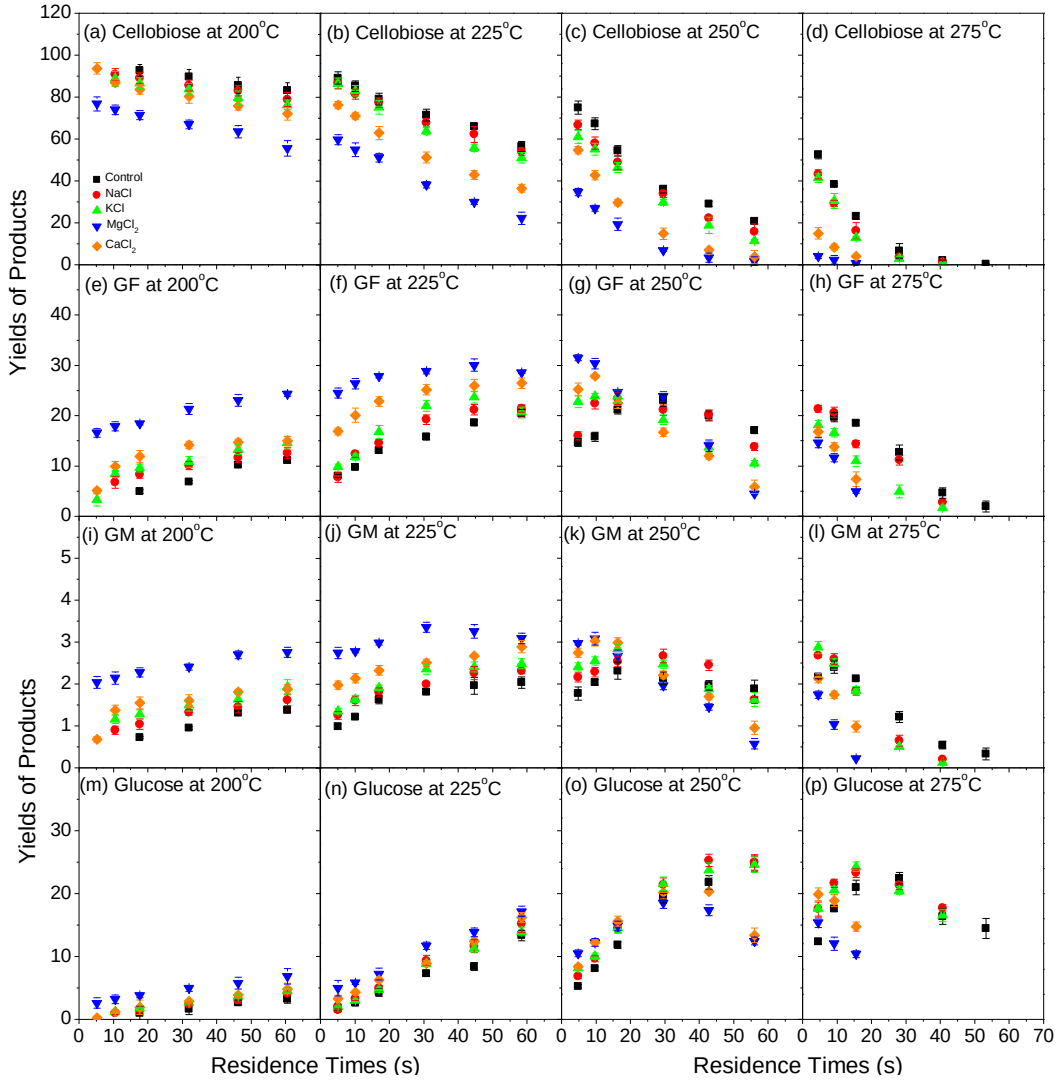

Figure 7- 2: Effect of alkali and alkaline earth metal chlorides on the yields of cellobiose and its primary products from cellobiose decomposition at various temperatures, expressed on a carbon basis. (a) cellobiose at 200 °C; (b) cellobiose at 225 °C; (c) cellobiose at 250 °C; (d) cellobiose at 275 °C; (e) GF at 200 °C; (f) GF at 225 °C; (g) GF at 250 °C; (h) GF at 275 °C; (i) GM at 200 °C; (j) GM at 225 °C; (k) GM at 250 °C; (l) GM at 275 °C; (m) glucose at 200 °C; (n) glucose at 225 °C; (o) glucose at 250 °C; (p) glucose at 275 °C

The AAEM chlorides exhibit a different catalytic effect on the secondary decomposition of GF, GM and glucose. For GF and GM, the secondary decomposition is promoted in all AAEM chloride solution, following an order of $MgCl_2$ > $CaCl_2$ > KCl > NaCl. For example, at 250 °C, the yields of GF and GM in the $MgCl_2$ solution

are initially highest but become lowest when the residence time increases to ~56 s. When the temperature increases to 275 °C, the yields of GF and GM in the $MgCl_2$ solution are lowest even at a short residence time. Since $MgCl_2$ has the strongest effects on the formation and decomposition of GF and GM, the maximal yields of GF and GM are obtained in the $MgCl_2$ solution. For example, the maximal GF yield of ~32% is obtained at 250 °C and a residence time of ~5 s, while the maximal yield of GM is ~3% at 250 °C and a residence time of ~10 s. For glucose, only the alkaline earth metal chlorides exhibit strong catalytic effects on its decomposition, while such effects of alkali metal chlorides are weak. Therefore, the maximal glucose yields in the alkali metal chloride solutions are quite similar as that in water. It is also noteworthy that the maximal glucose yield is obtained at a longer residence time than those for GF and GM. This is because glucose is both a primary product (from cellobiose hydrolysis) and a secondary product (from the hydrolysis of GF and GM) during cellobiose decomposition in HCW.

The above data clearly suggest that three major primary reactions are all enhanced in AAEM chloride solutions. However, such enhancement can be different for each primary reaction, which can be reflected by the selectivity of each primary reaction. Therefore, the selectivities of three primary products were further analysed, and the results are shown in Figure 7-3. It can be found that the addition of AAEM chlorides increases the selectivities of isomerisation reactions to produce GF and GM, but decreases the selectivity of hydrolysis reaction to produce glucose. Therefore, although AAEM chlorides enhance all three primary reactions, such effects are more significant for isomerisation reactions, leading to higher selectivities for isomerisation reactions. Among all AAEM chlorides, the alkaline earth metal chlorides have more significant effects to promote the isomerisation reactions, because the selectivities of isomerisation reactions are higher in the alkaline earth metal chloride solutions. Compared to GF and GM which show decreasing selectivities as cellobiose conversion increases, the glucose selectivity initially increases as cellobiose conversion increases, then starts to decrease at a late stage of cellobiose decomposition (i.e., >80% conversion). The increase of glucose selectivity is mainly due to that glucose is also a secondary product from the hydrolysis of GF and GM. Another reason is that cellobiose decomposition also results in the formation of organic acids, which may

catalyse the hydrolysis reactions of cellobiose or its primary products to produce glucose. However, glucose is further decomposed to other products, leading to the reduction in glucose selectivity at increased cellobiose conversions.

Figure 7-3 also demonstrates that AAEM chlorides not only influence the initial selectivity of glucose but also affect the evolution of selectivity during cellobiose conversion. In the alkali metal chloride solution, the glucose selectivity is initially lower but increases to similar levels to those in water. The increased selectivity of glucose is more likely due to the formation of organic acids. Figure 7-4 compares the effect of AAEM chlorides on the pH values of liquid products after reactions at various cellobiose conversions. It can be seen that the pH value rapidly reduces from ~7 to ~5 in AAEM chloride solutions even at the early stage of cellobiose conversion (i.e., with a conversion of ~10−20%). The formed organic acids may further catalyse the hydrolysis reaction, leading to the increase in glucose selectivity in the alkali metal chloride solution. Furthermore, the similar glucose selectivity also indicates the little catalytic effects of alkali metal chlorides on glucose decomposition. While in the alkaline earth metal chloride solutions, the glucose selectivity is much lower than those in water or the alkali metal chloride solutions. Although the addition of the alkaline earth metal chlorides also promotes the organic acid formation (see the pH value in Figure 7-4), the lower glucose selectivity is probably due to the much stronger catalytic effects of the alkaline earth metal chlorides on glucose decomposition, especially for $MgCl_2$.

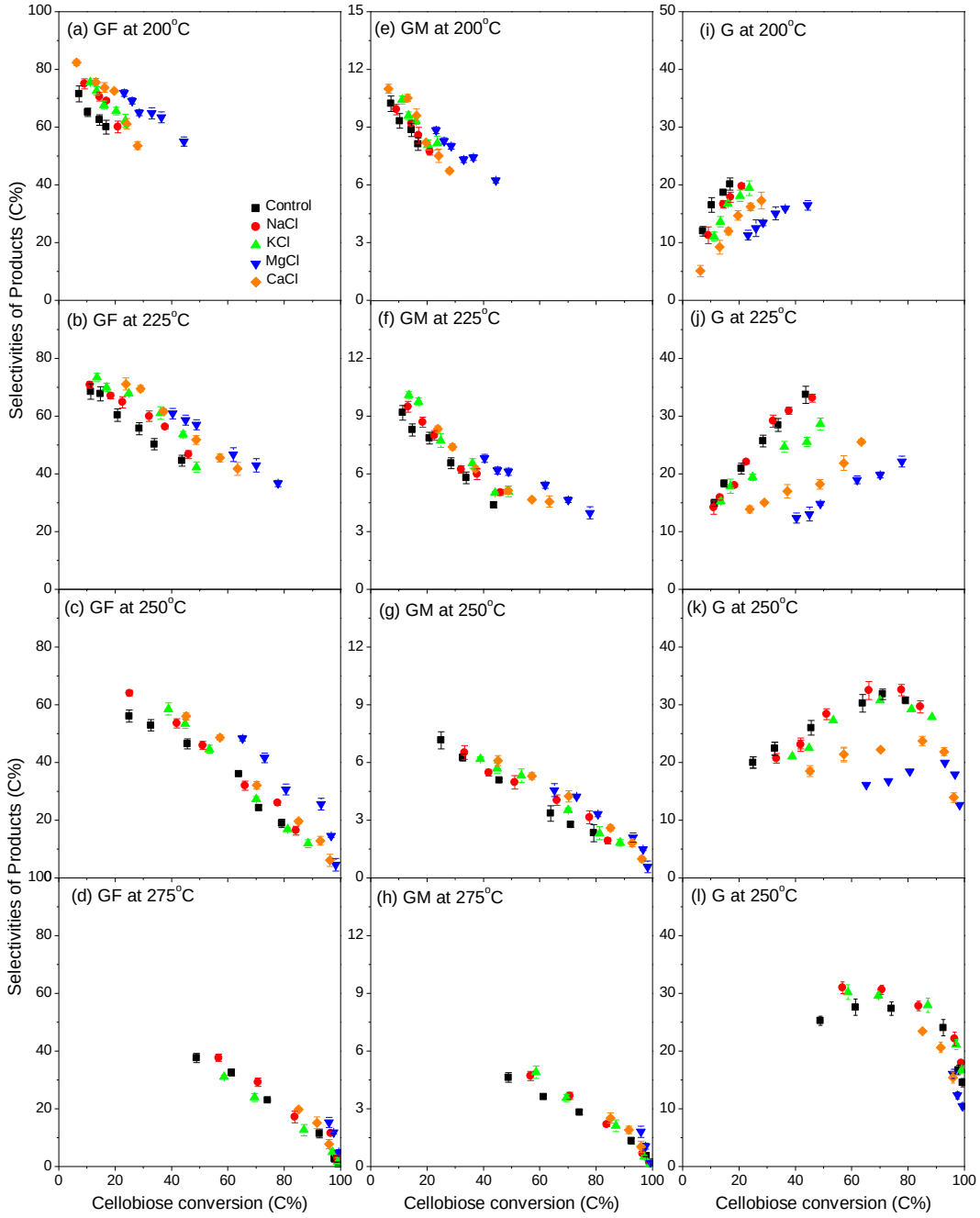

Figure 7- 3: Effect of alkali and alkaline earth metal chlorides on the selectivities of primary products from cellobiose decomposition at various temperatures, expressed on a carbon basis. (a) GF at 200 °C; (b) GF at 225 °C; (c) GF at 250 °C; (d) GF at 275 °C; (e) GM at 200 °C; (f) GM at 225 °C; (g) GM at 250 °C; (h) GM at 275 °C; (i) glucose at 200 °C; (j) glucose at 225 °C; (k) glucose at 250 °C; (l) glucose at 275 °C.

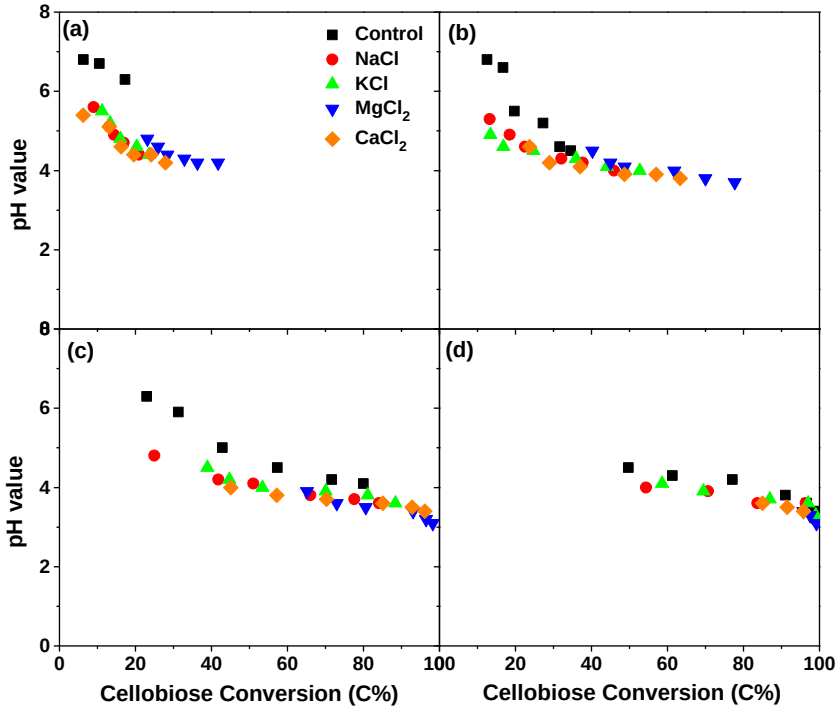

Figure 7- 4: Effect of alkali and alkaline earth metal chlorides on the pH value of the liquid product at various cellobiose conversions. (a) 200 °C; (b) 225 °C; (c) 250 °C; (d) 275 °C

Chapter 4 also identified that retro-aldol condensation reaction to form GE and glycolaldehyde is also a primary reaction of cellobiose decomposition, but its contribution is small compared to other primary reactions. Although the yield of GE is not quantified in this study due to the unavailability of the standard, the relative selectivity of GE was analysed according to the method in Section 3.5.1. The results in Figure 7-5 demonstrate that retro-aldol condensation reaction to form GE and glycolaldehyde is also promoted in AAEM chloride solutions, following a similar order of $MgCl_2$ > $CaCl_2$ > KCl > NaCl. However, the AAEM chlorides also promote the decomposition of GE, resulting in the rapid decrease in the GE selectivity as cellobiose conversion increases.

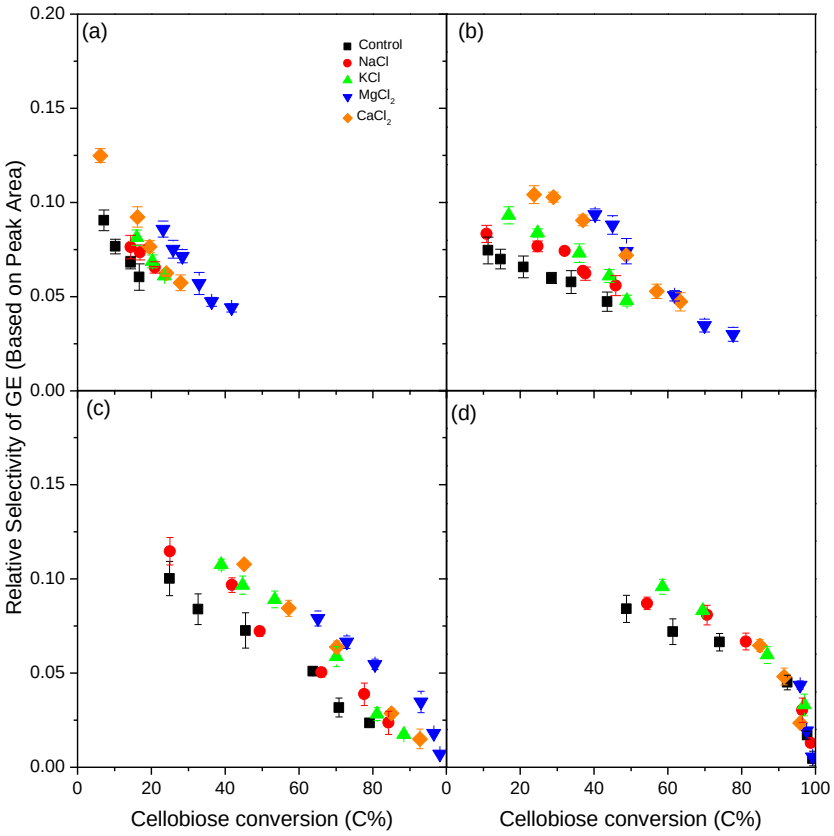

Figure 7- 5: Effect of alkali and alkaline earth metal chlorides on the relative selectivity of primary products from cellobiose decomposition at various temperatures, expressed on a carbon basis. (a) GE at 200 °C; (b) GE at 225 °C; (c) GE at 250 °C; and (d) GE at 275 °C

Therefore, above results indicate that the addition of AAEM chlorides accelerates all cellobiose primary decomposition reactions, but the catalytic effects are more significant for the isomerisation and retro-aldol condensation reactions, resulting in their higher selectivities in AAEM chloride solutions. Unlike the alkaline earth metal chlorides which show strong catalytic effects on the secondary decomposition of all primary products, the alkali metal chlorides only catalyse the secondary decomposition of GM and GF, and their catalytic effects on glucose decomposition are weak.

7.4 Effect of AAEM Chlorides on the Secondary Products of Cellobiose Decomposition in HCW

This study also analyses the yields and selectivities of typical products from the secondary decomposition of the primary products from cellobiose decomposition in HCW. The effect of AAEM chlorides on the yields and selectivities of fructose and mannose are compared in Figure 7-6. Fructose and mannose are typically hydrolysis products of GF and GM. The AAEM chlorides increase the formation of fructose and mannose at low temperatures (i.e., <225 °C). At high temperatures (i.e., >250 °C), the fructose and mannose are easily degraded, particularly in the alkaline earth metal solutions. However, it is interesting to see that the selectivities of fructose and mannose as a function of cellobiose conversion are not significantly affected by the addition of AAEM chlorides at all temperatures. The above results have shown that the selectivities of GF and GM are increased in all AAEM chloride solutions (see Figure 7-3). As the main hydrolysis product of GF and GM, the selectivities of fructose and mannose are expected to increase in the AAEM chloride solutions. Moreover, the selectivities of fructose and mannose are much lower than those of glucose. For example, the maximal selectivity of fructose in the NaCl solution is ~5% at 250 °C, compared to that of ~30% for glucose under the same condition. It is known that the decomposition of fructose is much easier than glucose.[85] Therefore, it seems that both the formation and decomposition of fructose and mannose are promoted at similar levels. Thus, the selectivities of fructose and mannose are not significantly affected by AAEM chlorides. Since the alkaline earth metal chlorides have more important effects on the fructose formation, their effects on fructose decomposition are also more significant.

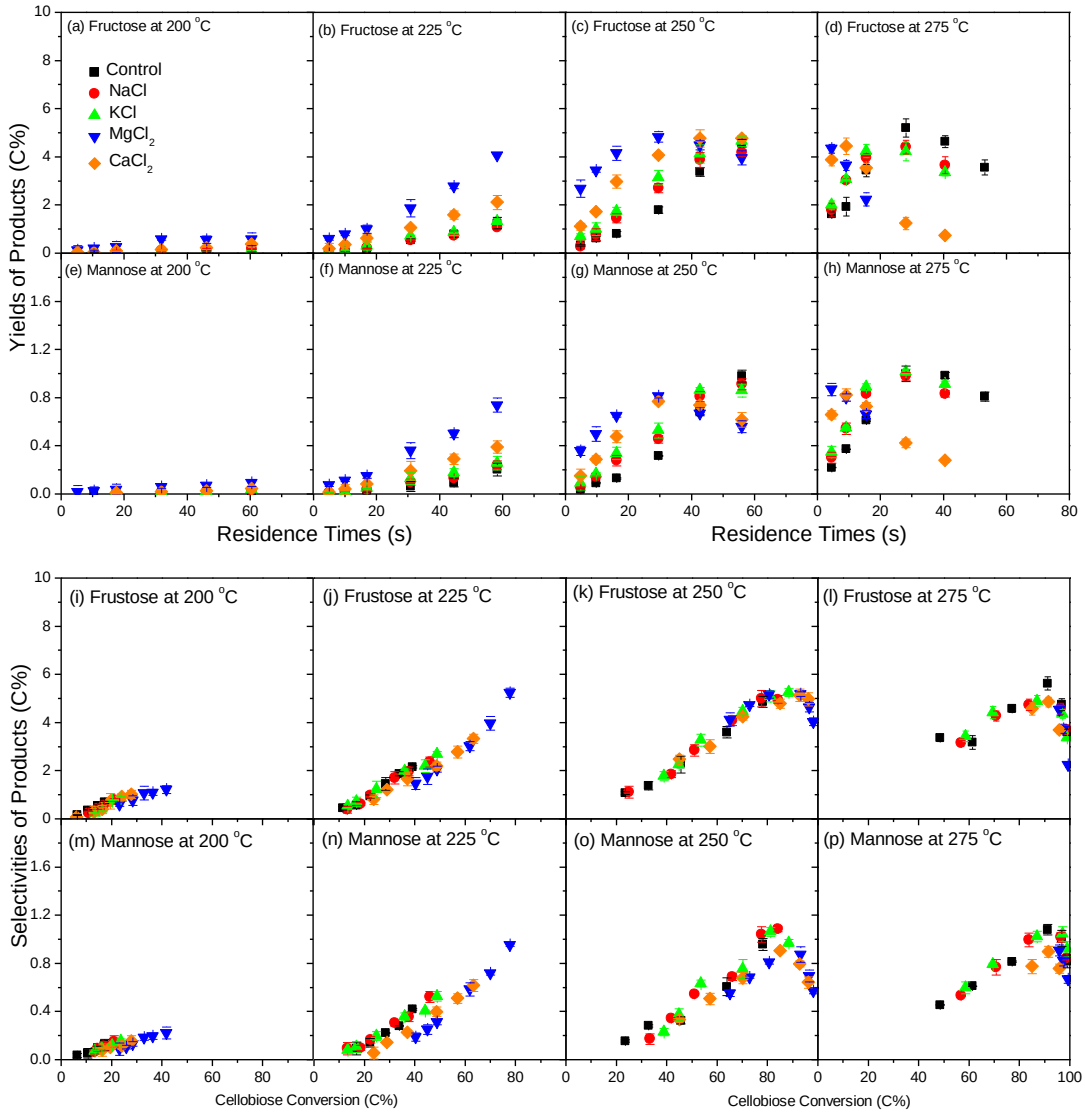

Figure 7- 6: Effect of alkali and alkaline earth metal chlorides on the yields and selectivities of fructose and mannose from cellobiose decomposition at various temperatures, expressed on a carbon basis. (a) yield of fructose at 200 °C; (b) yield of fructose at 225 °C; (c) yield of fructose at 250 °C; (d) yield of fructose at 275 °C; (e) yield of mannose at 200 °C; (f) yield of mannose at 225 °C; (g) yield of mannose at 250 °C; (h) yield of mannose at 275 °C; (i) selectivity of fructose at 200 °C; (j) selectivity of fructose at 225 °C; (k) selectivity of fructose at 250 °C; (l) selectivity of fructose at 275 °C; (m) selectivity of mannose at 200 °C; (n) selectivity of mannose at 225 °C; (o) selectivity of mannose at 250 °C; (p) selectivity of mannose at 275 °C

For the typical dehydration products 5-HMF and cellobiosan, the AAEM chlorides show different effects on their yields and selectivities (see Figure 7-7). The yield and selectivity of 5-HMF at 200 °C are low but increase with temperature. At increased temperatures (> 225 °C), of AAEM the 5-HMF yield is substantially increased in AAEM chloride solutions. The maximal 5-HMF yield is ~24% at 275 °C in the $CaCl_2$ solution, indicating that 5-HMF is a major secondary product from cellobiose decomposition. The addition of alkaline earth metal chlorides has more significant effects on the 5-HMF formation, but also strongly influences the degradation of 5-HMF. Compared to that for the alkaline earth metal chlorides, the addition of the alkali metal chlorides only promotes the 5-HMF formation. Thus, the addition of the alkali metal chlorides results in an increase in the 5-HMF selectivity, whereas the addition of the alkaline earth metal chlorides leads to a reduction in the 5-HMF selectivity.

While for cellobiosan, the yield is relatively low (<1.4%), so it is only a minor secondary product. The addition of AAEM chlorides initially increases its yield. A further increase in residence time reduces the cellobiosan yield in the alkaline earth metal chloride solutions, but not in the alkali metal chloride solutions. This indicates that the addition of alkali metal chlorides has little influence on the decomposition of cellobiosan. Although the addition of the alkali metal chlorides increases the cellobiosan yield, its selectivity is not significantly affected by the alkali metal chlorides. The addition of the alkaline earth metal chlorides greatly decreases the cellobiosan selectivity, especially for $MgCl_2$.

There are also different trends for the yields of glycolaldehyde and erythrose (see Figure 7-8), which are typical products of retro-aldol condensation reactions. The maximal yield of glycolaldehyde is ~17% achieved at 275 °C in the $CaCl_2$ solution, indicating that glycolaldehyde is also an important secondary product from cellobiose decomposition. The addition of AAEM chlorides not only increases the glycolaldehyde yield, but also increases the glycolaldehyde selectivity, following an order of $MgCl_2$ > $CaCl_2$ > KCl > NaCl. For erythrose, it has a maximal yield of ~2.6% at 275 °C in the NaCl solution. The addition of alkali metal chlorides increases its yield but doesn't greatly affect its selectivity. While the addition of alkaline earth metal chlorides initially increases the erythrose yield but reduces its yield at increased

conversions. Obviously, the alkaline earth metal chlorides have more significant catalytic effects on erythrose decomposition.

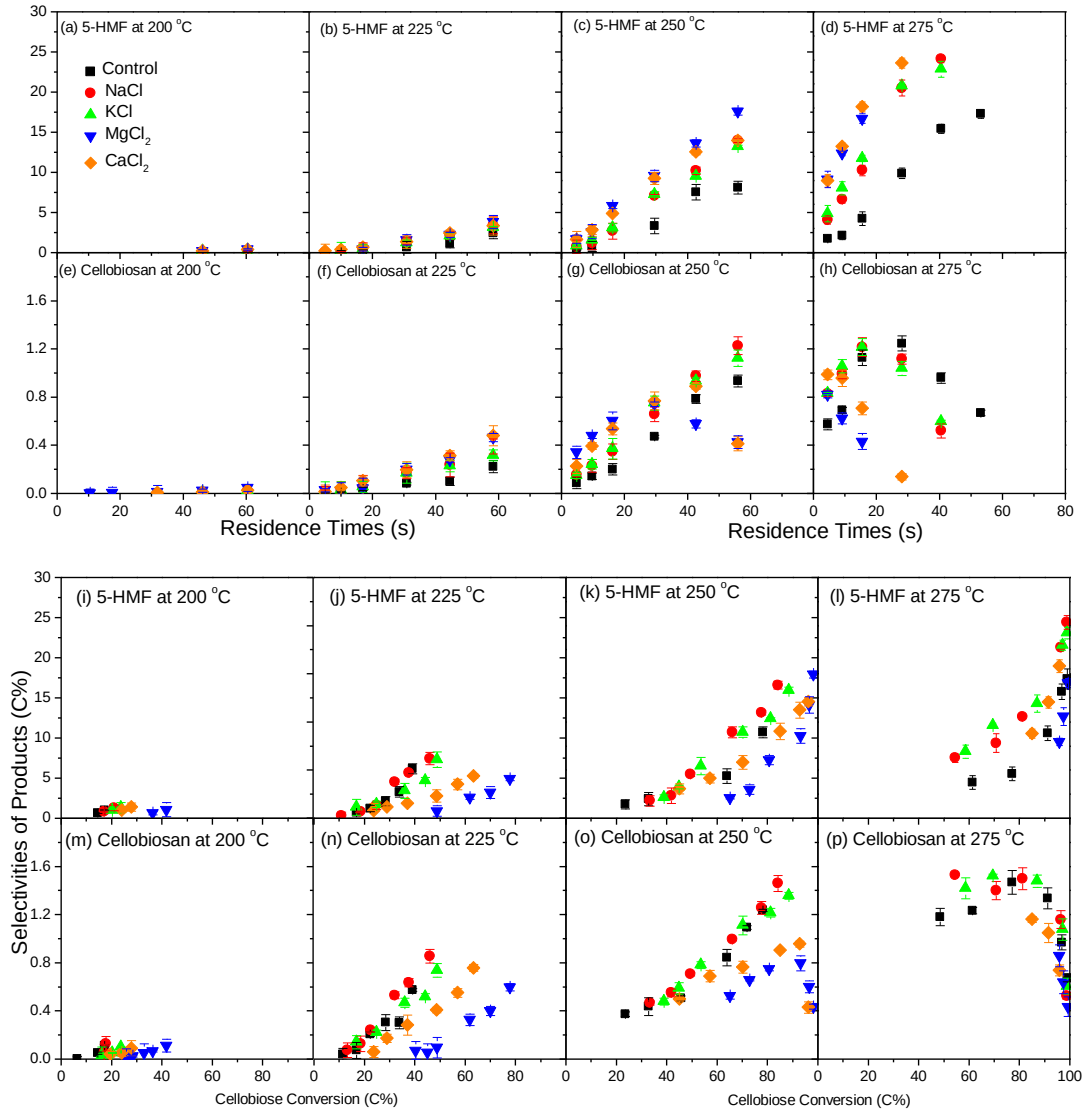

Figure 7- 7: Effect of alkali and alkaline earth metal chlorides on the yields and selectivities of 5-HMF and cellobiosan from cellobiose decomposition at various temperatures, expressed on a carbon basis. (a) yield of 5-HMF at 200 °C; (b) yield of 5-HMF at 225 °C; (c) yield of 5-HMF at 250 °C; (d) yield of 5-HMF at 275 °C; (e) yield of cellobiosan at 200 °C; (f) yield of cellobiosan at 225 °C; (g) yield of cellobiosan at 250 °C; (h) yield of cellobiosan at 275 °C; (i) selectivity of 5-HMF at 200 °C; (j) selectivity of 5-HMF at 225 °C; (k) selectivity of 5-HMF at 250 °C; (l) selectivity of 5-HMF at 275 °C; (m) selectivity of cellobiosan at 200 °C; (n) selectivity of cellobiosan at 225 °C; (o) selectivity of cellobiosan at 250 °C; (p) selectivity of cellobiosan at 275 °C

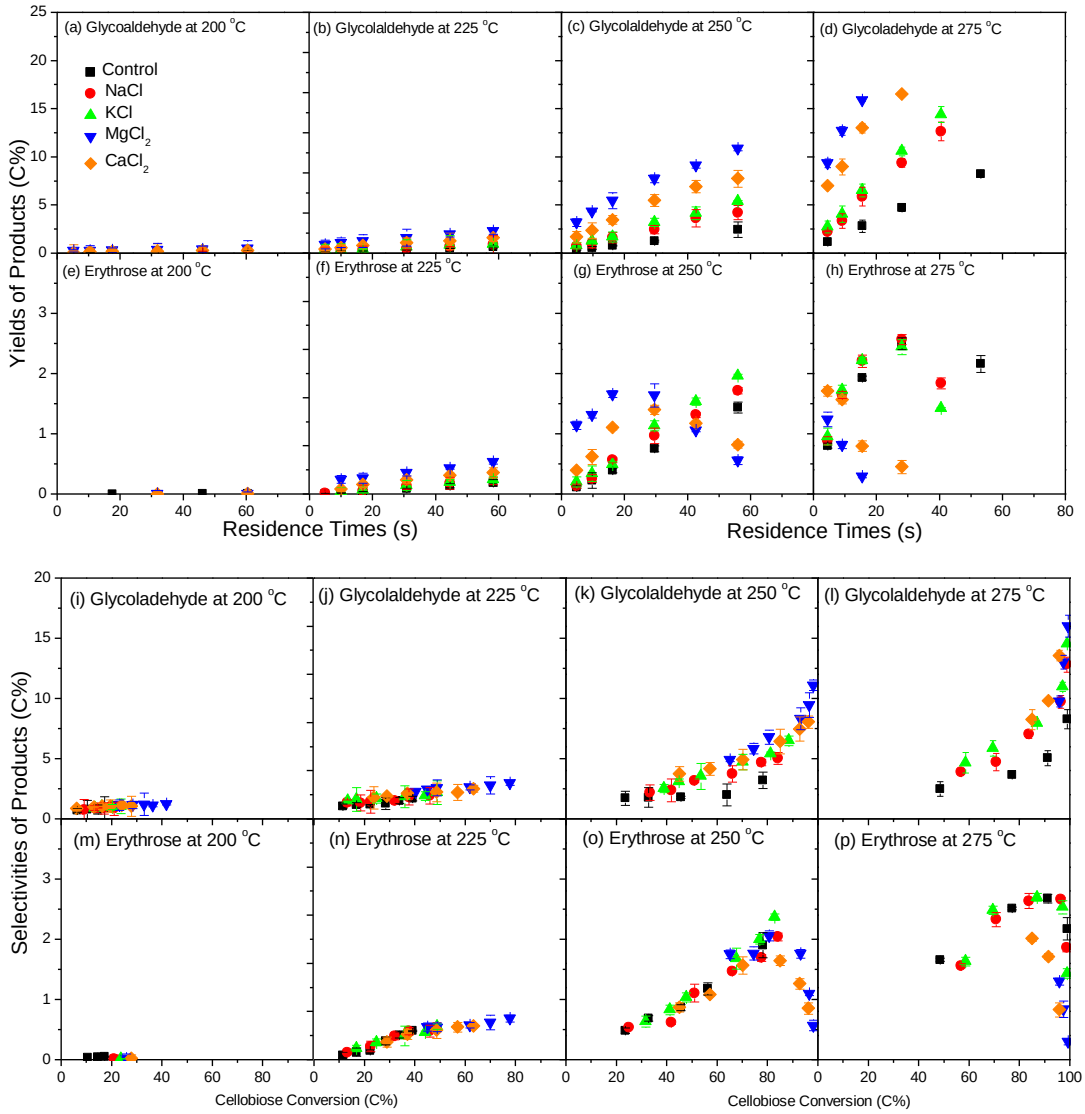

Figure 7- 8: Effect of alkali and alkaline earth metal chlorides on the yields and selectivities of glycolaldehyde and erythrose from cellobiose decomposition at various temperatures, expressed on a carbon basis. (a) yield of glycolaldehyde at 200 °C; (b) yield of glycolaldehyde at 225 °C; (c) yield of glycolaldehyde at 250 °C; (d) yield of glycolaldehyde at 275 °C; (e) yield of erythrose at 200 °C; (f) yield of erythrose at 225 °C; (g) yield of erythrose at 250 °C; (h) yield of erythrose at 275 °C; (i) selectivity of glycolaldehyde at 200 °C; (j) selectivity of glycolaldehyde at 225 °C; (k) selectivity of glycolaldehyde at 250 °C; (l) selectivity of glycolaldehyde at 275 °C; (m) selectivity of erythrose at 200 °C; (n) selectivity of erythrose at 225 °C; (o) selectivity of erythrose at 250 °C; (p) selectivity of erythrose at 275 °C.

7.5 Discussion on the Mechanism of the Catalytic Effect of AAEM Chlorides on Cellobiose Decomposition

The results clearly show that the addition of AAEM chlorides enhances the cellobiose decomposition in HCW, depending on the AAEM species. At the same salt concentration, the effect of AAEM chlorides follow an order of $MgCl_2$ > $CaCl_2$ > KCl > NaCl. Another important finding of this study is that the addition of AAEM chlorides greatly affects the primary and secondary reactions of cellobiose decomposition in HCW. The addition of all AAEM chlorides enhances the selectivities of the isomerisation reactions but reduces the selectivity of hydrolysis reaction during the primary decomposition of cellobiose in HCW. Some secondary reactions are also promoted in AAEM chloride solutions. For example, the secondary decomposition of all primary products of cellobiose decomposition is favoured in the alkaline earth metal solutions, whereas only the secondary decomposition of GF and GM is promoted in the alkali metal chloride solutions. Those secondary products further decompose to other products, such as 5-HMF and glycolaldehyde. The 5-HMF formation is promoted in the alkali metal chloride solutions, but is suppressed in the alkaline earth metal chloride solutions. It seems that the degradation of 5-HMF is also favoured in the alkaline earth metal chloride solution, resulting in a lower 5-HMF selectivity. The addition of both alkali and alkaline earth metal chlorides promotes the retro-aldol condensation to form glycolaldehyde, and such promotion effects are more significant for the alkaline earth metal chlorides. For some minor secondary products, the selectivities of cellobiosan and erythrose are less affected in the alkali metal chloride solutions, while their decomposition is strongly promoted in the alkaline earth metal chloride solutions.

The effect of AAEM chlorides on cellobiose decomposition are complex, at least due to the following reasons. First, the addition of AAEM chlorides changes the water properties (i.e., dielectric constant, ion product), which may influence cellobiose decomposition in HCW. Generally, for a reaction with a transition state more polar than the reactant, an increase in the solvent polarity can increase the reaction rate.[204] In some previous works, the effect of salt on hydrothermal decomposition was explained by the increase in the solvent polarity,[203, 204] as suggested by a Kirkwood analysis[205] via the following equation:

$$lnK_H = lnK_O + constant \times \frac{\varepsilon - 1}{\varepsilon}$$ (Equation 7.1)

where K_H and K_O are the rate constants with and without the catalyst, and ε is the dielectric constant of the solution. Huppert et al[206] suggested that the addition of NaCl increases the dielectric constant, thus leading to an increase in the reaction rate. Torry et al[204] calculated the dielectric constant of NaCl solution based on the equation by Uematsu and Franck,[207] which shows an increasing dielectric constant with an increase in density. However, there is no validation if the equation by Uematsu and Franck is suitable for the salt solution, since the equation was initially developed for water and steam.[207] In fact, some recent works[208-210] reported the salt addition actually reduces the dielectric constant at low temperatures (<100 °C). There is a lack of knowledge on the dielectric constant of various salt solutions under subcritical and supercritical conditions. In this study, the salt concentration (0.029 M) is very small. Thus, the change in dielectric constant is expected to be small. However, a significant increase in reaction rate can be still observed, especially for the alkaline earth metal chlorides. Therefore, it seems that the increase in reaction rate cannot be well explained by the increase in the solvent polarity. Another important property for HCW to catalyse the sugar decomposition is ion product. The salt addition slightly increases the ion product of water,[211] which can be good catalysts for cellobiose decomposition. However, there is limited data on the ion product of various salt solutions under subcritical and supercritical conditions. Therefore, in order to understand the effect of salt on sugar decomposition, it is of critical importance to have a clear understanding of the changes of HCW properties with the addition of various salts.

Second, it is known that sugar form complexes with cations in aqueous solution at room temperature, particularly with the alkaline earth metal cations.[212-215] At increased temperatures, it is believed that such interactions between sugar and cations strongly affect the cellobiose decomposition reaction. The complexation between cations and cellobiose creates positively charged molecules that could promote various cellobiose decomposition reactions, depending on the coordination of cations. Recently, Lewis acids (i.e., $CrCl_3$) were reported to catalyse the isomerisation reaction of aldoses to

ketoses (i.e., glucose to fructose,[33] xylose to xylulose[216]) via the coordination of Cr^{3+}, mostly like in the form of $[Cr(OH)]^{2+}$.[33] It is known that AAEM cations are weak Lewis acids. The isomerisation reaction is more likely catalysed by AAEM cations to form complexes with cellobiose. The Lewis acidity of the alkaline earth metal cations is stronger than that of the alkali metal cations, leading to a more significant effect on the formation of GF and GM in the $MgCl_2$ and $CaCl_2$ solutions.

It is noteworthy that the formation of glucose is slightly enhanced in AAEM chloride solutions. This is probably because that cations also forms hydrated complexes (i.e., $[M(H_2O)_n]^{z+}$) in aqueous solution. Such hydrated complexes undergo hydrolysis reactions to release H_3O^+, via the following reaction

$$[M(H_2O)_n]^{z+} + H_2O \rightarrow [M(H_2O)_{n-1}OH]^{(z-1)+} + H_3O^+ \qquad \text{(Equation 7.2)}$$

Therefore, hydrated metal complexes act as Brønsted acids, which can catalyse the hydrolysis reaction. The dissociation constant (pK_a) of the cation is related to the charge and the radius of the cation. Compared to those of divalent cations (i.e., 11.4 for Mg^{2+} and 12.8 for Ca^{2+}), the pK_a values for monovalent cations are higher (i.e., 14.2 for Na^+ and 14.5 for K^+). Therefore, more H^+ can be generated in the $MgCl_2$ and $CaCl_2$ solutions. This explains the larger effects of $MgCl_2$ and $CaCl_2$ on glucose formation. Although both isomerisation and hydrolysis reactions are promoted, such promotion effects are more significant for isomerisation reactions, leading to the increased selectivities of isomerisation reactions. It is also interesting to see that the alkaline earth metal cations have more significant effects to promote the isomerisation reactions. Thus, more substantial increases in the selectivities of isomerisation reactions occur in the alkaline earth metal chloride solutions.

A recent work[33] indicated that the dehydration of fructose to 5-HMF and the decomposition of 5-HMF to levulinic acid and formic acid, are also catalysed by Brønsted acids. Therefore, the stronger Brønsted acidity derived from the alkaline earth metal cations not only catalyses the hydrolysis reactions (i.e., GF to glucose and fructose, GM to glucose and mannose), but also favours the dehydration reactions

(fructose to 5-HMF), and the decomposition of 5-HMF to levulinic acid and formic acid. This explains the lower selectivities of 5-HMF in the alkaline earth metal chloride solutions. Compared to that of the alkaline earth metal cations, the ability of alkali metal cations to generate H_3O^+ is weak. Therefore, the degradation of 5-HMF is not favoured in the alkali metal chloride solutions, resulting in higher 5-HMF selectivities.

Third, the anion Cl^- may also have some interactions with sugar during cellobiose decomposition. It was reported that Cl^- enhances furfural formation from xylose in dilute aqueous acidic solution, due to the promotion of 1,2-enediol formation from xylose.[217] A ^{13}C NMR study indicated that Cl^- anions donated electrons to C1, C3 and C5 carbons of glucose in a saturated solution of $MgCl_2$,[218] thus affecting the glucose decomposition reaction. Therefore, it seems that the anion Cl^- also plays a role during cellobiose decomposition in HCW, i.e., promoting isomerisation reaction. However, under the reaction condition in this study, the role of Cl^- is expected to be much smaller than that of cation, since the reaction rate of cellobiose in the $MgCl_2$ solution is much faster than that in the $CaCl_2$ solution at the same salt concentration.

Therefore, the effect of AAEM chlorides on the main reaction of cellobiose decomposition in HCW can be summarised in Figure 7-9. Cellobiose decomposition in HCW mainly proceeds via the isomerisation reactions to from GF and GM, which are catalysed by AAEM cations as Lewis acids, due to the coordination of AAEM cations to form complexes. The stronger Lewis acidity of the alkaline earth metal cations is largely responsible for the higher selectivities of cellobiose isomerisation reactions in the alkaline earth metal chloride solutions. Further hydrolysis of GF and GM requires the action of H^+ to produce glucose, fructose, and mannose. Once glucose is formed, it is further catalysed by the alkaline earth metal cations to fructose or mannose via isomerisation reactions.

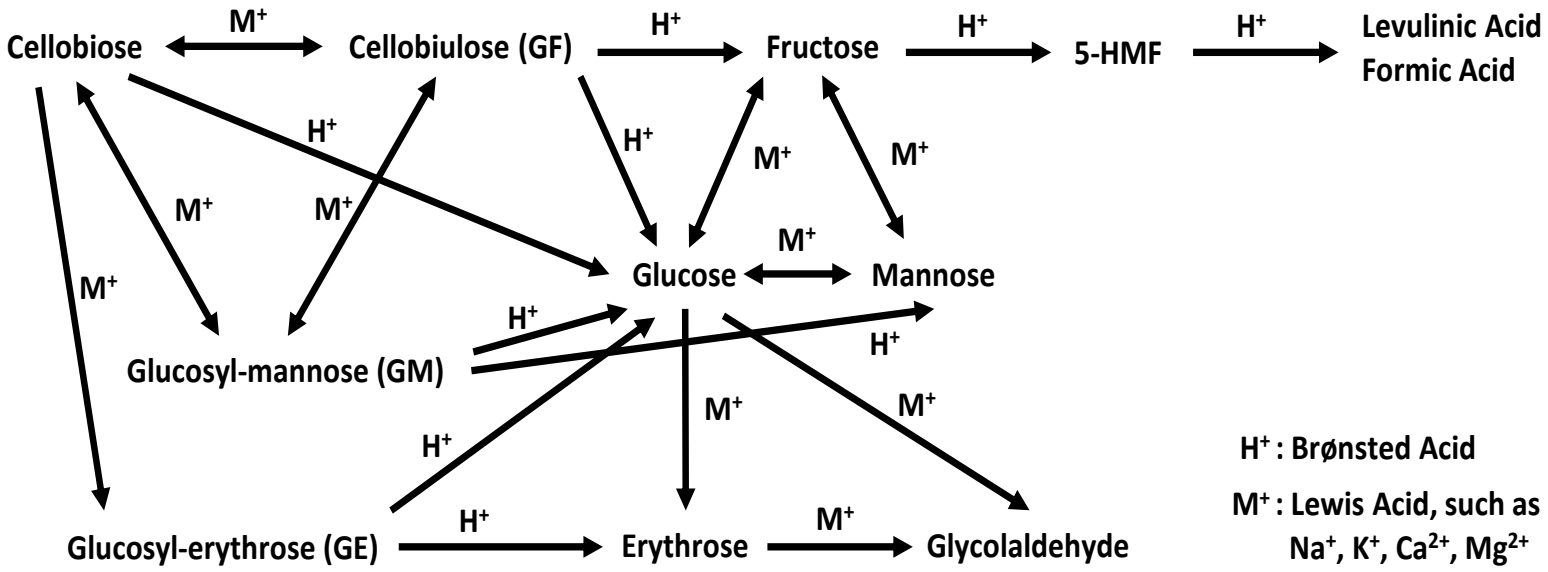

Figure 7- 9: The main reaction network of cellobiose decomposition in HCW, as catalysed by Lewis acids (i.e., AAEM cations) and Brønsted acid (i.e., H^+)

The catalytic effects of the alkali metal cations on glucose isomerisation are weak, probably due to the weak Lewis acidity of the alkali metal cations to form a complexes with glucose. Fructose is rapidly dehydrated to 5-HMF, and then to levulinic acid. Both reactions are catalysed by H^+. The hydrolysis of hydrated metal complexes of the alkaline earth metal cations generates more H^+, thus promoting the transformation of fructose to levulinic acid via 5-HMF. It should be mentioned that the retro-aldol condensation to form GE is also promoted in the AAEM chloride solutions. Further hydrolysis of GE leads to the formation of glucose and erythrose. Erythrose is then decomposed into glycolaldehyde, which is most likely catalysed by the AAEM cations, eventually resulting in the increase in the selectivity of glycolaldehyde.

7.6. Conclusions

This study investigates the effect of AAEM chlorides on cellobiose decomposition in HCW at 200 – 275 °C. The addition of AAEM chlorides enhances cellobiose conversion in an order of $MgCl_2$ > $CaCl_2$ > KCl > NaCl. The reaction rate of cellobiose decomposition in HCW is almost doubled in $MgCl_2$ solution. Such an enhancement in cellobiose conversion can be explained by the catalysis of cations as Lewis acids to form sugar-metal complexes which favour the isomerisation reactions, and the hydrolysis of the hydrated metal complexes to generate H_3O^+ as Brønsted acids which promote the hydrolysis reactions. The promotion effect of AAEM chlorides on isomerisation reactions are more significant, resulting in increases in the selectivities of isomerisation reactions. Compared to Na^+ and K^+, Mg^{2+} and Ca^{2+} have stronger Lewis acidity, thus leading to higher selectivities of isomerisation reactions in the $MgCl_2$ and $CaCl_2$ solutions. The alkali metal chlorides have less influence on glucose selectivity, probably due to the weak Lewis acidity of the alkali metal cations to from complexes with glucose. The stronger Brønsted acidity derived from the alkaline earth metal cations also catalyses the dehydration of fructose to 5-HMF and the further degradation of 5-HMF, resulting in reduced 5-HMF selectivities in the $MgCl_2$ and $CaCl_2$ solutions. In contrast, the 5-HMF selectivity is increased in the NaCl and KCl solutions, because the weak Brønsted acidity of alkali metal cations suppresses the degradation of 5-HMF. Both the alkali and alkaline earth metal chlorides promote the retro-aldol condensation reaction to form glycolaldehyde.

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Introduction

This chapter highlights the key research outcomes from the present study. Overall, a new understanding of the chemical principles of cellobiose decomposition in HCW can be obtained from this study. This study clearly showed that there are two major primary reactions; those are isomerisation reaction to produce cellobiulose and glucosyl-mannose, and hydrolysis reaction to produce glucose. Isomerisation reactions are the dominant reaction during cellobiose decomposition in HCW. Furthermore, the formation of glucosyl-mannose as the second cellobiose isomers was proven in this study, which is firstly reported in this field. These findings are greatly important to elucidate the reaction mechanism of cellobiose decomposition in HCW. This study further examined the effect of temperature, initial cellobiose concentration, initial pH and alkali and alkaline earth metal (AAEM) species on the cellobiose decomposition kinetics and mechanism in HCW. This chapter also provides recommendations for future study in this research area.

8.2 Conclusions

8.2.1 New Insights into the Mechanism of Cellobiose Decomposition in HCW

- Cellobiose is primarily decomposed into cellobiulose (glucosyl-fructose, GF) and glucosyl-mannose (GM) via isomerisation reactions and only a small portion of cellobiose is hydrolysed into glucose. Compared to the isomerisation and hydrolysis reactions, the retro-aldol reaction to produce glucosyl-erythrose (GE) and glycolaldehyde is even lower at 225−275 °C.

- As the water molecules have a high affinity for proton, it easier to transfer the proton from cellobiose to water than from water to cellobiose. Thus, the isomerisation reactions that produced GF and GM are promoted and suppressed the hydrolysis reaction that produced glucose.

- As the hydrogen bonding in water molecules grow weaker at higher temperatures, water affinity for proton is decreased. Therefore, more protons are available to catalyse hydrolysis reaction at higher temperatures.

- Based on the results, it can be concluded that the organic acids produced from cellobiose decomposition at early conversion promoting the secondary reactions but the effect on the primary reactions of cellobiose decomposition are insignificant.

8.2.2 Effect of Initial Cellobiose Concentration on Primary Decomposition Mechanism of Cellobiose in HCW

- Hydrolysis reaction that produced glucose is increased as the initial cellobiose concentration increased from 10 to 10, 000 mg L^{-1} at the temperature range of 200 to 275 ^{o}C, but the GF and GM formed from isomerisation reaction still remain the main products of cellobiose decomposition in HCW.

- At higher initial cellobiose concentrations, there are not enough hydroxyl ions to catalyse the isomerisation reactions as the molar ratio of ion products and cellobiose is small. Therefore, enhance the possibility of hydrogen ions to react with cellobiose to produce glucose.

- Furthermore, the organic acids produced at the beginning of cellobiose conversion may also increase the selectivity of hydrolysis reaction at higher initial cellobiose concentrations.

- At low initial cellobiose concentrations (i.e. <1,000 mg L^{-1}), the effect of organic acids produced from cellobiose decomposition on cellobiose decomposition reaction rate is negligible. On the other hand, the formed organic acids increase the cellobiose decomposition reaction rate at initial cellobiose concentration of 10,000 mg L^{-1}.

- The molar ratio of ion product to cellobiose is reduced with the increase of initial cellobiose concentration resulting the increase in the apparent activation energy of cellobiose decomposition in HCW.

8.2.3 Effect of Initial pH on Cellobiose Decomposition under Weakly Acidic Conditions

- GF and GM produced from isomerisation reactions and glucose from hydrolysis reaction remain major products of cellobiose decomposition in HCW as the pH of the solution changed from natural to acidic.

- Under weakly acidic conditions, the isomerisation reactions are suppressed but the hydrolysis reaction is promoted.

- As the initial pH decrease, hydrolysis reaction rate constant increase but the isomerisation reactions rate constant almost unaffected. The amount of hydrogen ion in the solution greatly affects the rate of hydrolysis reaction.

- The increase in the rate of cellobiose decomposition mainly contributed by the increment of the hydrolysis reaction rate.

- The kinetic model developed from this study containing the isomerisation and hydrolysis reactions is suitable to determine the rate constant of cellobiose decomposition at low temperature (i.e. < 225 ^{o}C) under acidic condition. However, the model is unsuitable for predicting the cellobiose decomposition rate constant at higher temperatures as the predicted value is lower than the real value. This happens probably because of contribution from other reactions for example reversion reaction.

8.2.4 Effect of Alkali and Alkaline Earth Metal (AAEM) Chlorides on Cellobiose Decomposition in Hot-Compressed Water

- The reaction rate of cellobiose decomposition in HCW increase by adding AAEM chlorides with an order of MgCl2> $CaCl_2$>KCl>NaCl.

- The cellobiose conversion rate in HCW increases nearly two times when $MgCl_2$ is added into the cellobiose solution.

- An increment in cellobiose conversion can be explained by the catalysis of cations as Lewis acids to form sugar-metal complexes which favour the isomerisation reactions, and the hydrolysis of the hydrated metal complexes to generate hydrogen ion as Brønsted acids which promote the hydrolysis reaction.

- The selectivities of isomerisation reactions are increased with the addition of AAEM chlorides.

- Compared to alkali metal cations (Na^+ and K^+), alkaline earth metal cation (Mg^{2+} and Ca^{2+}) have stronger Lewis acidity, thus leading to higher selectivities of isomerisation reactions in the $MgCl_2$ and $CaCl_2$ solutions.

- The alkali metal chlorides have weak Lewis acidity make its less influence on glucose selectivity.

- The selectivity of 5-HMF is reduced with the addition of alkaline earth metal chlorides ($MgCl_2$ and $CaCl_2$), probably because of they have stronger Brønsted acidity. Even though, the Brønsted acid catalysed the conversion of fructose to 5-HMF, the effect of Brønsted acid on the degradation of 5-HMF is more significant.

- 5-HMF selectivity is increased in the NaCl and KCl solutions because the weak Brønsted acidity of the alkali metal cations suppresses the degradation of 5-HMF.

- Both the alkali and alkaline earth metal chlorides promote the retro-aldol condensation reaction to form glycolaldehyde.

8.3 Recommendations

Based on the results and conclusions of this study, new research gaps have been identified for future research as follows:

1. The present study revealed that isomerisation reactions are the main primary reactions of cellobiose decomposition in subcritical water. However, there is still large unknown the role of isomerisation reactions during cellobiose decomposition in supercritical water which relevant to hydrothermal gasification process.

2. Detail reaction mechanism of cellobiose primary products (GF, GM and GE) decomposition is still unclear. Unfortunately, experimental studies cannot be carried out as cellobiose isomer (GF and GM) are expensive chemicals and unavailability of GE. Therefore, simulation studies should be conducted to gain some insights into the fundamental decomposition mechanism of these products.

3. The effect of initial pH on the primary reactions of cellobiose decomposition under weakly acidic conditions has been clearly demonstrated. However, there has been a few report on the effect of initial pH on cellobiose decomposition under weakly alkaline conditions.

4. AAEM chlorides have strong catalytic effects on cellobiose decomposition in HCW. Further studies are required to evaluate the effect of different concentrations of AAEM chlorides on the mechanism of cellobiose decomposition in HCW.

5. It is known that biomass contains abundant of inorganic anions (e.g. SO_4^{2-}, PO_4^{3}, and Cl^-). However, the effect of this inorganic anion on cellobiose decomposition in HCW still unclear. Therefore, systematic studies are needed to understand the role of this inorganic anion on the mechanism of cellobiose decomposition in HCW.

6. Future research is also needed on the detail decomposition reaction mechanism and kinetic of glucose oligomers other than cellobiose. Detail kinetic modelling on the decomposition of glucose oligomers would provide a robust understanding on secondary reaction of cellulose decomposition in HCW

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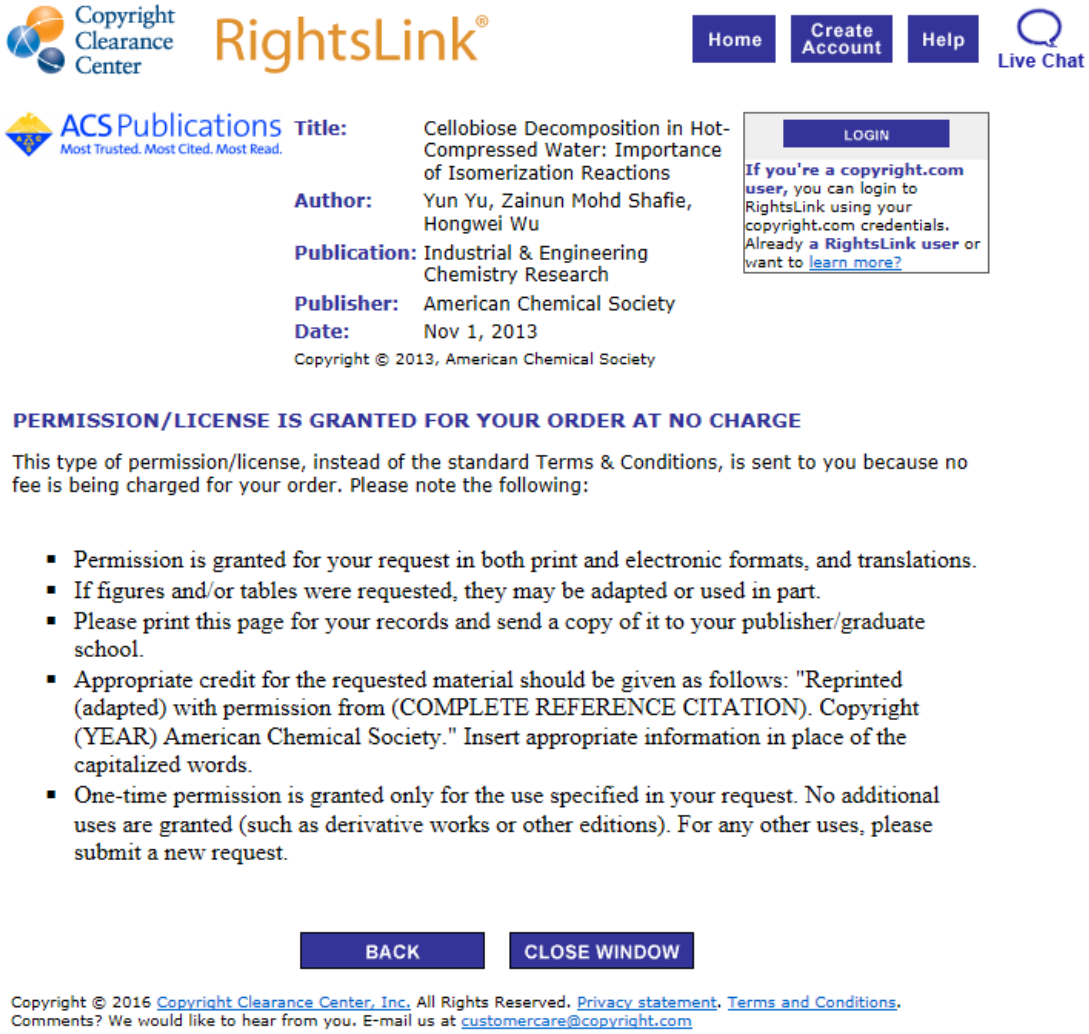

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