Department of Chemical Engineering

Hydrothermal Processing of Biomass and Its Derived Sugar Compounds in Hot-Compressed Gamma-Valerolactone/Water Mixtures

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This thesis is presented for the Degree of

Doctor of Philosophy

of

Curtin University

May 2018

Declaration

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

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: ……………………………………………………

Date: ……05/05/2018……………

To my beloved family

Abstract

The use of fossil fuels such as coal and petroleum is leading us to challenges including the depletion of fuel resources and adverse environmental impacts. Significant research & development efforts have been devoted to developing sustainable, cost effective, and environmentally-friendly renewable fuels, among which biomass-derived biofuels via biorefinery are considered as one of the key alternatives.

Biorefinery is integrated with various cross-discipline technologies for processing feedstocks to produce target products. Hydrothermal processing is being widely regarded as a key technology to participate in various steps in biorefinery. For instance, hydrothermal processing can be used for biomass pretreatment for delignification and fractionation. It may also be applied to convert biomass into platform chemicals such as various sugars and phenols. During hydrothermal processing, reactions of biomass and its derived products may follow wide varieties of pathways. For example, glucose decomposition in hot-compressed water (HCW) may include isomerization, dehydration, retro-aldol condensation, and reversion reactions.

Hydrothermal processing of biomass and its derived products are dependent on reaction conditions (e.g. temperature and pressure), the use of catalysts, and the solvent systems used as reaction media. Various organic solvents have been recently used as reaction media for biomass processing, including polar aprotic solvents, polar protic solvents, and ionic liquids. Gamma-valerolactone (GVL) is one of the most promising solvents because it can be produced from biomass itself. In despite of extensive work on using GVL as a solvent for biomass hydrothermal processing, most of the published work has been on catalytic biomass conversion in GVL-containing solvent systems using acids as catalysts. Unfortunately, there has been no study on the effect of GVL on the hydrothermal treatment of biomass and its derived products under catalyst-free conditions.

Therefore, this PhD program has been designed to conduct a systematic study into understanding the fundamental reaction mechanisms during hydrothermal treatment of

biomass and its derived sugar products in hot-compressed GVL/water (HCGW) under catalyst-free conditions. The key objectives are to (1) investigate the solvent effect of GVL on the reaction mechanisms and kinetics of glucose in HCGW under catalyst-free conditions at various GVL concentrations, in comparison to those under hot-compressed water (HCW) conditions; (2) understand the solvent effect of GVL on the reaction mechanisms and kinetics of cellobiose in HCGW under catalyst-free conditions; (3) further investigate sugar recovery from cellulose and lignocellulosic biomass via hydrothermal processing in HCGW under catalyst-free conditions; and (4) compare the solvent effect of GVL with other organic solvents during hydrothermal processing of fructose and glucose under catalyst-free conditions. The following work has been completed to achieve these objectives.

Firstly, a systematic set of experiments have been carried out to investigate the solvent effect of GVL on hydrothermal processing of glucose in HCGW under catalyst-free conditions at GVL concentrations ranging from 1 to 75% on a volume basis. As the concentration of GVL in the solvent system increases, the yield of fructose decreases (from ~12% in HCW to ~5% in HCGW with 10% of GVL) but the yield of levoglucosan (LGA) increases (from ~2.5% in HCW to ~7.5% in HCGW with 50% GVL). Moreover, the yield of 5-Hydroxymethylfurfural (5-HMF) first increases from ~48% in water only to ~58% in HCGW with 5% GVL, followed by a continuous decrease to ~50% in HCGW with 75% GVL. Further analysis shows that the primary selectivity of fructose decreases but that of LGA increases as the concentration of GVL in HCGW increases. The results suggest that 5-HMF is a primary product of glucose decomposition in HCGW under catalyst-free conditions. Kinetic analysis of glucose decomposition shows that the reaction rate constants of glucose decrease and those of dehydration reactions increase with increasing concentration of GVL in the solvents while those of the isomerization reactions decreases with increasing concentration of GVL in HCGW. Moreover, the activation energy for glucose conversion decreases as concentration of GVL increases. Overall, compared to that under water alone conditions, the presence of GVL in HCGW alters the reaction pathways of glucose decomposition, via suppressing isomerization reactions and

enhancing dehydration reactions. It also changes the main reaction pathway from glucose to 5-HMF from "glucose – fructhose – 5-HMF" under HCW conditions to "glucose – 5-HMF" and "glucose – LGA –LGO– 5-HMF" under HCGW conditions.

Secondly, cellobiose has been used as a model compound of biomass-derived oligomers to study the solvent effect of GVL on the decomposition of glucose oligomers in HCGW under catalyst-free conditions. The maximal yield of glucose is more than double from ~30% in HCW to ~60% in HCGW with only 10% GVL /water. On the other side, the maximal yield of glucosyl-fructose (GF) decreases from ~20% in HCW to ~5% in HCGW with only 1% GVL, and further decreases to 0 with increasing GVL concentration to 10%. The primary selectivity of glucose drastically increases from ~8% in HCW to ~80% in HCGW as the concentration of GVL increases from 0 to ~10%. However, the primary selectivity of GF decreases from ~80% in HCW to approximately 0 in HCGW with 10% GVL because there was no GF peak detected under the current experimental conditions. Kinetic analysis suggests that the reaction rates of cellobiose decomposition increases with increasing GVL concentration in HCGW from 0 to 10%. Further increasing GVL concentration in HCGW leads to decreases in reaction rate constants. There is apparently no change on the overall activation energy of cellobiose decomposition. In summary, the hydrolysis reaction of cellobiose is strongly enhanced but the isomerization reactions are suppressed in HCGW, compared with those in HCW.

Thirdly, experiments have been conducted to understand the solvent effect of GVL on hydrothermal processing of cellulose and lignocellulosic biomass in HCGW under catalyst-free conditions. Results show that the glucose recovery from cellulose is enhanced from ~80% in HCW to ~91% in HCGW. In addition, the reaction time needed for converting the same amount (15 mg) of cellulose is shortened from ~110 min in HCW to ~70 min in HCGW with 10% GVL, indicating that the efficiency for cellulose decomposition is enhanced in HCGW. Moreover, the yields of glucose oligomers at Degree of Polymerization 1 to 5 (i.e. DP1to DP5) is higher in HCGW than that in HCW, suggesting that the decomposition of cellulose derived oligomers

are also enhanced in HCGW. Characterization on the liquid products suggests that the isomerization reactions of cellulose derived glucose oligomers are suppressed in HCGW, which is responsible for the increase of the glucose recovery. Further application of HCGW for biomass hydrothermal processing shows improvements in the reactions via two aspects. One is that HCGW increases the glucose recovery from biomass to ~90% compared with that at ~60% in HCW, leading to an increase in overall sugar recovery from ~74% in HCW to ~93% in HCGW. The other is that HCGW enhances the decomposition of hemicellulose compared with HCW at the same temperature and reaction time.

Fourthly, various organic solvents including protic (water, ethanol, methanol) and aprotic (GVL, acetone and 1,4-dioxane) solvents have been used for the decomposition of fructose and glucose, to understand the effect of solvent type on decomposition mechanisms of glucose and fructose in aqueous organic co-solvents. It is found that the isomerization reactions of both glucose and fructose are enhanced in water, methanol/water and ethanol/water, while the dehydration reactions of glucose and fructose are suppressed. In contrast, the presense of aprotic solvents (e.g., GVL, acetone and 1,4-dioxane) enhances the dehydration reactions of glucose to LGA and 5-HMF and the dehydration of fructose to 5-HMF, but suppresses the isomerization reactions of glucose and fructose. For example, the primary selectivity of fructose from glucose decomposition is higher in protic/water co-solvents, i.e., ~78% in water, ~82% in methanol/water and ~80% in ethanol/water, compared with those in the aprotic/water co-solvents, i.e., ~31% in GVL/water, ~40% in acetone/water and ~41% in 1,4-dioxane/water. In contrast, the primary selectivity of LGA from glucose decomposition is lower in protic solvent/water co-solvents, i.e., ~5% in water, ~7% in methanol/water and ~8% in ethanol/water, compared with those in the aprotic solvent /water co-solvents, i.e., ~20% in GVL/water, ~14% in acetone/water and ~13% in 1,4-dioxane/water. The primary selectivities of 5-HMF in aprotic/water co-solvents are familiar at ~26% as a primary product compared that in protic/water co-solvents at 0%. The results demonstrate that the aqueous organic co-solvent system can be a powerful

tool to tune the reaction pathways of sugar hydrothermal decomposition, greatly enhancing the production of platform chemicals such as 5-HMF.

Overall, this research has discovered new knowledge on and made original contributions to various aspects of hydrothermal processing of biomass and its derived sugars in hot compressed solvents under catalyst-free conditions. It has revealed the fundamental reaction mechanisms during the hydrothermal processing of biomass and its derived sugars in HCGW. It has also clarified the primary reaction pathways of glucose decomposition in HCGW. The solvent effect of GVL on hydrothermal decomposition of cellobiose (as a model compound of biomass-derived glucose oligomers) in HCGW under catalyst-free conditions has also been elaborated. Based on the understanding on glucose and cellobiose, HCGW has then been applied to the hydrothermal processing of microcrystalline cellulose and lignocellulosic biomass for effective sugar recovery. Finally, this study has also compared the solvent effect of GVL with other organic solvents during hydrothermal processing of fructose and glucose as model compounds under catalyst-free conditions.

Acknowledgements

I express my warm thanks to my supervisors, Prof. Hongwei Wu and Dr. Yun Yu, for their advices, guidance, inspiration, training, patience and continuous supports during the course of my study. I would like to extend my gratitude to my thesis committee chairperson, Prof. Shaobin Wang, for his assistant and advice throughout this research.

I would like to offer my special thanks to all Chemical Engineering Department lab technical staffs, Ms. Karen Haynes, Mr. Jason Wright, Mr. Xiao Hua, Mr. Araya Abera, Dr. Roshanak Doroushi, Dr. Guanliang Zhou, Mr. Andrew Chan, Ms. Ann Carroll and Ms. Melilna Miralles for their help and technical support in the lab. My special thanks are extended to the members of our research group members, Dr. Suiboon Liaw, Dr. Mingming Zhang, Mr. Matthew Witham, Ms. Wenran Gao, Mr. Xujun Chen, Mr. Mingyang Li, Ms Jinxiu Cao, Ms. Gelareh Nareri, Mr. Yu Long, Mr. Chao Feng, Mr. Changya Deng, and Ms. Qiqing Shen.

Lastly, I would like to thank my friends and families for their continuous support and encouragement. Mr. Samir Yacub and Ms. Maricel Yacub, I really appreciate the family bond, care, and support offered from you.

List of Publication

Papers published in refereed international journals:

- **Song B**, Yu Y, Wu H**.** Effect of Aprotic and Protic Solvents on the Hydrothermal Decomposition of Glucose and Fructose, to be submitted to *Industrial & Engineering Chemistry Research*.
- **Song B**, Yu Y, Wu H**.** Tuning Glucose Decomposition in Hot-Compressed Gamma-valerolactone/Water Mixtures: From Isomerization to Dehydration Reactions, accepted by *Fuel*.
- **Song B**, Yu Y, Wu H. Solvent Effect of Gamma-Valerolactone (GVL) on Cellulose and Biomass Hydrolysis in Hot-Compressed GVL/Water Mixtures. *Fuel*, **2018**, 232, 317-322.
- Long Y, Yu Y, **Song B**, Wu H. Polymerization of glucose during acid-catalyzed pyrolysis at low temperatures. *Fuel*, **2018**, 230, 83-88.
- **Song B**, Yu Y, Wu H. Insights into Hydrothermal Decomposition of Cellobiose in Gamma-Valerolactone/Water Mixtures. *Industrial & Engineering Chemistry Research*, **2017**, *56* (28), 7957-7963.
- Yu Y, **Song B**, Long Y, Wu H. Mass Spectrometry Analysis of Sugar and Anhydrosugar Oligomers from Biomass Thermochemical Processing. *Energy & Fuels*, **2016**, *30* (10), 8787-8789.

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Chapter 1: Introduction

1.1　Background and Motives

Lignocellulosic biomass is a key renewable source which is available widely in the world[1]. Thermochemical processing of biomass followed with biorefinery is regarded as a sustainable way to partially address the challenges of energy security and environmental issues arisen from the use of fossil fuels.[1-4] The main components of lignocellulosic biomass are lignin (10−25%), cellulose (40−60%) and hemicellulose (20−40%).[5] Each of the components is composed by corresponding monomeric units. For example, cellulose is composed by glucose monomers via 1,4-glycosidic bonds at β conformation.[6, 7]

There are various technologies from different disciplines such as pyrolysis,[2] mechanical treatment,[8] hydrothermal processing[9] and aerobic digestion[10] in biorefinery. Hydrothermal processing is one of the promising routes for various purposes.[11] Therefore have been extensive researches conducted on the mechanisms and kinetics of biomass and biomass derived compounds,[12] including those of glucose, cellobiose, and cellulose in hot-compressed water (HCW). Various factors have been considered to influence the kinetics and mechanisms, including the reaction conditions, catalysts, and solvents.[13-16]

Recently, various organic solvents were applied as co-solvent for biomass hydrothermal processing.[17-26] Among those organic solvents, gamma-valerolactone (GVL) has attracted a lot of research interests because it can be produced from biomass itself.[27-29] It was reported that high sugar yields were achieved from biomass processing in hot-compressed GVL/water (HCGW) under moderate conditions (~160−220 °C) with minimized amount of sulfuric acids (0.005 mol/L compared with 0.1

mol/L in water) as catalyst.[30] Moreover, GVL was also used as a medium for the production of GVL from biomass.[31] However, so far most of reports in the open literature concern the conversion of biomass and its model compounds in HCGW using acids as catalysts.[32-34] To understand the fundamental science, it is of critical importance to systematically investigate the solvent effect of GVL on the conversion of biomass and its model compounds under catalyst-free conditions. Therefore, this PhD study has been designed to conduct a systematic investigation into the effect of GVL on the decomposition mechanisms of biomass and its derived sugars in HCGW under catalyst-free conditions.

Among the technologies used for biomass treatment, hydrothermal processing is one of the most common approaches that can be used for biomass pretreatment and further transformation of biomass derived compounds such as lignin, cellulose and hemicellulose.[11] The conditions of hydrothermal processing can be different with changes in temperature, pressure, catalyst, flow type, solvent system, and other factors. Recently, hydrothermal treatment of biomass in organic solvents has attracted research interests, because an optimal solvent system influences the decomposition of biomass and benefits the yields of target products under certain conditions.[13, 14] Thus, further insights on the solvent effect of organic solvents to biomass processing under hydrothermal conditions are of significance for biorefinery.

1.2   Scope and Objectives

This PhD study aims at carrying out a set of systematic experiments for understanding the solvent effect of GVL on the decomposition mechanisms of biomass and its derived sugars in HCGW under catalyst-free conditions. The detailed objectives of this study are as follows:

- To investigate the solvent effect of GVL on the reaction mechanisms and kinetics of glucose in HCGW under catalyst-free conditions at various GVL

concentrations, in comparison to those under hot-compressed water (HCW) conditions;

- To understand the solvent effect of GVL on the reaction mechanisms and kinetics of cellobiose in HCGW under catalyst-free conditions;

- To further investigate sugar recovery from cellulose and lignocellulosic biomass via hydrothermal processing in HCGW under catalyst-free conditions;

- To compare the solvent effect of GVL with other organic solvents during hydrothermal processing of fructose and glucose under catalyst-free conditions.

1.3   Thesis Outline

This thesis consists of 8 chapters including the current chapter. The thesis structure is schematically shown in the thesis map presented as Figure 1.1. The chapters in this thesis are outlined below:

- Chapter 1 introduces the background and objectives of the current research.
- Chapter 2 provides an up-to-date literature review on biorefinery, lignocellulosic biomass, hydrothermal processing, the reaction mechanisms of biomass derived sugars (e.g., glucose, cellobiose, and cellulose) under hydrothermal conditions, the factors influencing the mechanisms and kinetics of biomass derived sugars, and the current studies using GVL as co-solvent for biomass processing. Afterwards, the research gaps and objectives are concluded.
- Chapter 3 provides an overview on the methodology employed to achieve the research objectives and detailed description on the sample preparation, experimental setups and analytical methods.
- Chapter 4 reveals the decomposition mechanisms and kinetics of glucose in HCGW with comparisons with those in HCW under catalyst-free conditions.
- Chapter 5 elaborates the decomposition mechanisms and kinetics of cellobiose in HCGW in comparsion to those in HCW under catalyst-free conditions.

- Chapter 6 reports the decomposition mechanisms of crystalline cellulose in HCGW and applies HCGW for lignocellulosic biomass saccharification with comparisons with those in HCW under catalyst-free conditions.
- Chapter 7 investigates the decomposition mechanisms and kinetics of glucose and fructose in HCGW with comparisons with other organic solvents.
- Chapter 8 summarises the conclusions and lists out future work.

Chapter 1: Introduction
- Research background and motives
- Objectives and scope
- Overall thesis structure

Chapter 2: Literature Review
- Status and current knowledge in this research area
- Research gaps
- Specific objective this research

Chapter 3: Methodology and Analytical Methods
- Sample preparations
- Experimental setup and procedures
- Analytical methods

Chapter 7 Effect of Aprotic and Protic Solvents on the Hydrothermal Decomposition of Glucose and Fructose

- Reaction mechanisms of glucose and fructose in different binary solvents.
- Differences and commons between aprotic and protic organic solvents on the hydrothermal decomposition of glucose and fructose.

Chapter 6 Solvent Effect of Gamma-Valerolactone (GVL) on the Decomposition of Cellulose and Biomass in Hot-Compressed GVL/Water

- Apply GVL/water onto cellulose.
- Insight the solvent effect of GVL on cellulose decomposition.
- Apply GVL/water onto mallee wood biomass for sugar recovery.

Chapter 5 Mechanisms and Kinetics of Cellobiose Decomposition in Hot-Compressed Gamma-Valerolactone/Water

- Difference between water and GVL/water on affecting the chemistry of cellobiose.
- Reaction is shifted from isomerization-predominated to hydrolysis-predominated.
- Influence of GVL on the kinetics of cellobiose decomposition under

Chapter 4 Mechanisms and Kinetics of Glucose Decomposition in Hot-Compressed Gamma-Valerolactone/Water

- Detailed solvent effect of GVL on the chemistry of glucose under hydrothermal conditions.
- Solubility Parameters of binary solvents.
- Correlation between the reaction mechanism and the Hydrogen Bonding Solubility Parameter.

GVL to other solvents   cellobiose to cellulose and biomass   glucose to cellobiose

Chapter 8 Conclusions and Recommendations

To evaluate the objectives

Figure 1.1: Thesis Map

Chapter 2: Literature Review

2.1 Introduction

Hydrothermal processing of biomass is a promising technology to produce biofuels and biochemicals.[35] Organic solvents are used to facilitate biomass hydrothermal conversion to improve the process efficiency.[14] This chapter first reviews the current literatures concerning hydrothermal processing of biomass as a key approach for biorefinery. The fundamental reaction mechanisms of biomass and its model compounds including glucose, cellobiose and cellulose under hydrothermal conditions were summarized, followed by the factors influencing the reaction mechanisms including temperature, pressure, solvent systems, etc. In addition, a detailed review on GVL and its effect on biomass processing is present. Based on the current understanding in biomass processing in GVL/water, the research gaps are identified and corresponding objectives are set for this study in order to provide insights on the solvent effect of GVL on reaction mechanisms of biomass hydrothermal processing under catalyst-free conditions.

2.2 Lignocellulosic Biomass and Its Major Components

Lignocellulosic biomass is the most abundant resource to partially replace the traditional fossil fuels for renewable energy production. The major components of lignocellulosic biomass are cellulose (~40–50%), hemicellulose (~25–35%), and lignin (~10–30%) as shown in Figure 2.1.[36] The structure of each component is briefly introduced as follows.
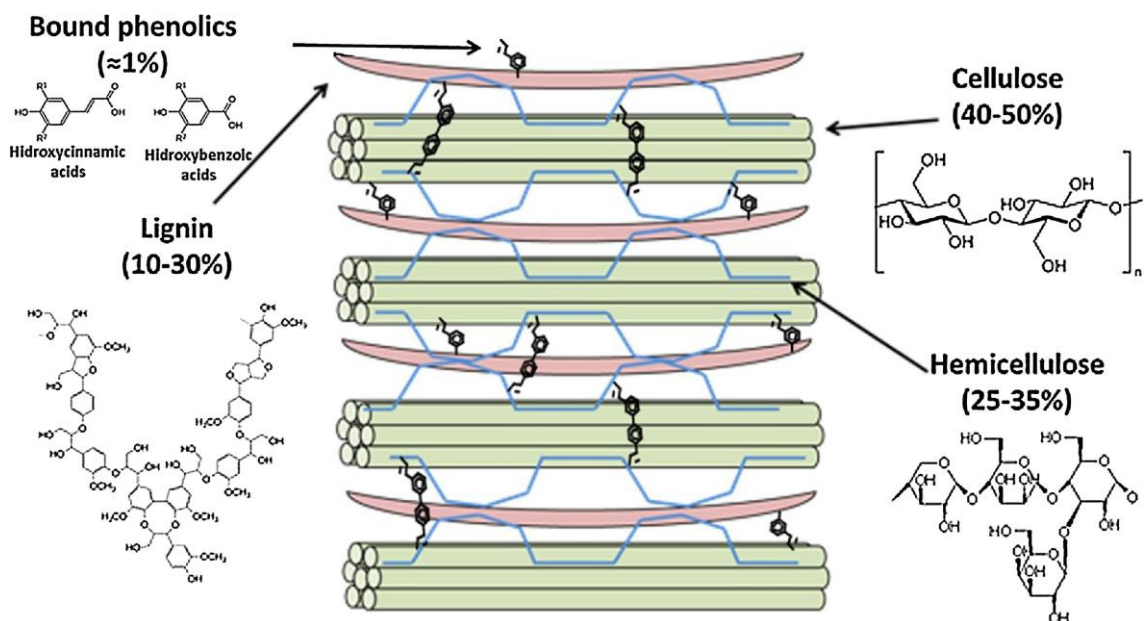
Figure 2.1: The structure of lignocellulosic biomass.[36]

2.2.1 Cellulose

Cellulose is the major component of lignocellulosic biomass. Natural cellulose exists as the combination of both crystalline and amorphous forms,[37] the portions of which are different depending on the biomass type. For instance, the crystalline cellulose accounts for 41% of the dry mass for Scandinavian pine, but 33% for Scarlet oak.[38] The determination of crystalline portions is based on the crystallinity index theory.[39] The structure of crystalline cellulose is shown in Figure 2.2.[40] Crystalline cellulose consists of long glucose chains linked via β-1,4-glycosidic bonds and strong hydrogen bonding networks. The hydrogen bonds can be characterized via semi-quantitative analysis by FT-IR as studied previously.[41] Crystalline cellulose is more difficult to be decomposed compared with amorphous cellulose because of the strong inter- and intra-molecular bonds. Thus, the fraction of crystalline and amorphous cellulose makes significant differences to the decomposition chemistry of cellulose under hydrothermal conditions.[42] Previous studies[43-45] have investigated different methods to enhance the decomposition of cellulose for sugar yields. For example, Asaoka et al. demonstrated that the use of formic acid (0.1 w/w%) enhanced the reaction rate

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constants by 10 times, and the sugar recovery was increased from ~25% in water only to ~50% in water with acid at 230 °C and 50 mins.[46]
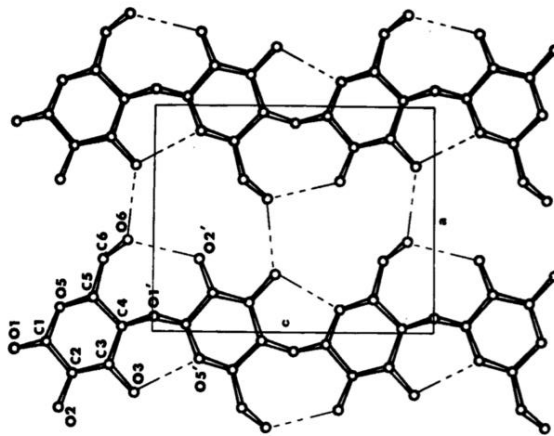
Figure 2.2: Structure of crystalline cellulose (the red dash lines represent the inter-/intra- hydrogen bonds).[37]

During the decomposition of cellulose, the degree of polymerization (DP) can be applied as parameter to present the degradation of cellulose.[47] For example, Roberto et al. demonstrated that a microcrystalline cellulose sample (primary DP_n at 1500) was drastically degraded by ionic liquids with a wide range of DP (10–1000) detected after treatment.[48] Moreover, a previous study by Yun et al. characterized glucose oligomers at DP from 1 to 25 in the liquid products from microcrystalline cellulose decomposition in hot-compressed water (HCW).[49]

The saccharification of cellulose is one of the most important technologies to convert cellulose into glucose and glucose oligomers, which can be used as feedstocks for the production of value-added chemicals such as alcohols, acids and furfurals.[46] For example, decomposition of cellulose to glucose oligomers was demonstrated to enhance the production of acetone, methanol and ethanol through aerobic digestion.[10] In addition, further hydrothermal processing of cellulose derived oligomers to glucose is also of great significance, because glucose can be converted into various value-added chemicals, which will be further discussed in following sections.

2.2.2 **Hemicellulose**

Hemicellulose mainly consists of multiple monosaccharides including hexose (i.e., glucose, galactose and mannose), pentose (i.e., xylose and arabinose). There are also a small amount of 4-O-methyl glucuronic acid and galacturonic acid residues. The representative structures of xylan, arabinoxylan, mannan, and glucomannan are shown in Figure 2.3. Overall, each polymer has the main monomers connected via C-O-C bonds as the backbone, which is substituted with side chains by other saccharides. Among the polymers of hemicellulose, xylan is the most abundant polymer in lignocellulosic biomass. It should be noted that the structure of hemicellulose is amorphous that can be easily decomposed under hydrothermal conditions.
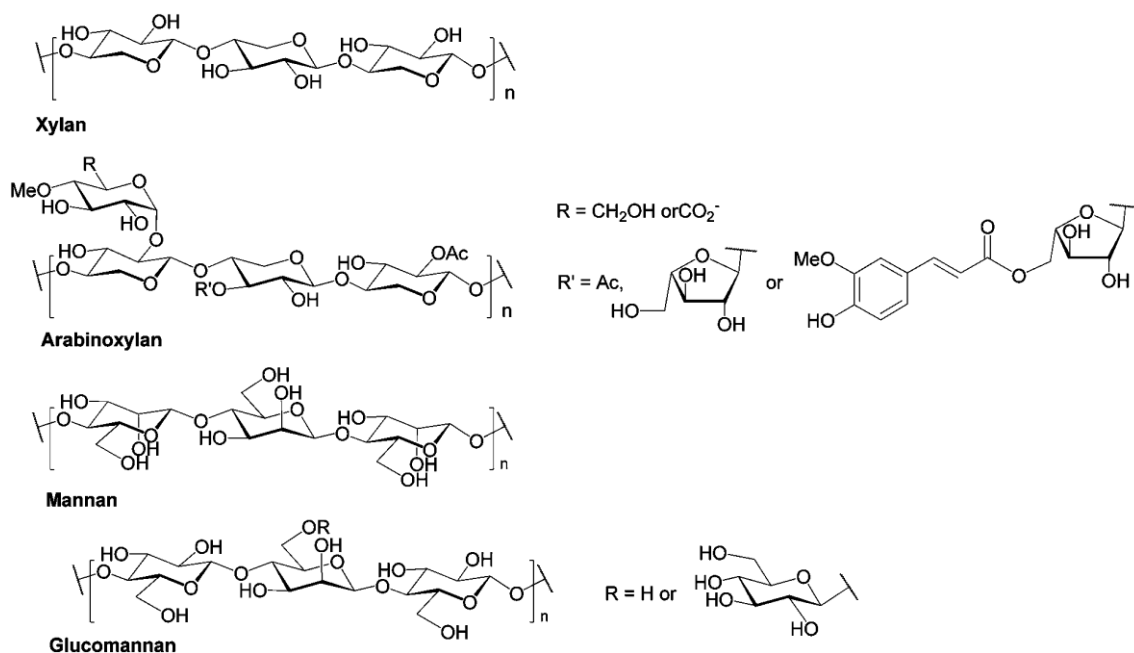
Figure 2.3: Representative structures of hemicellulose.[50]

2.2.3 **Lignin**

Lignin mainly includes syingyl (S) units with two methoxyl groups, guaiacyl (G) units with one methoxyl and p-hydroxyphenyl (H) units without methoxyl groups. These

units are combined with multiple aryl ether and C–C bonds. In biomass, lignin is linked with hemicellulose and cellulose by different bonds, such as phenyl glycosides, benzyl ethers and gamma-esters. A schematic diagram of lignin structure is shown in Figure 2.4. Researches in lignin are attracting more and more interests recently, because lignin can be a valuable source of chemicals if it is broken into smaller molecular units. However, the intermolecular bonds between lignin monomeric unites are difficult to be decomposed (> 350 °C in HCW), although the structure of lignin is amorphous.[36]
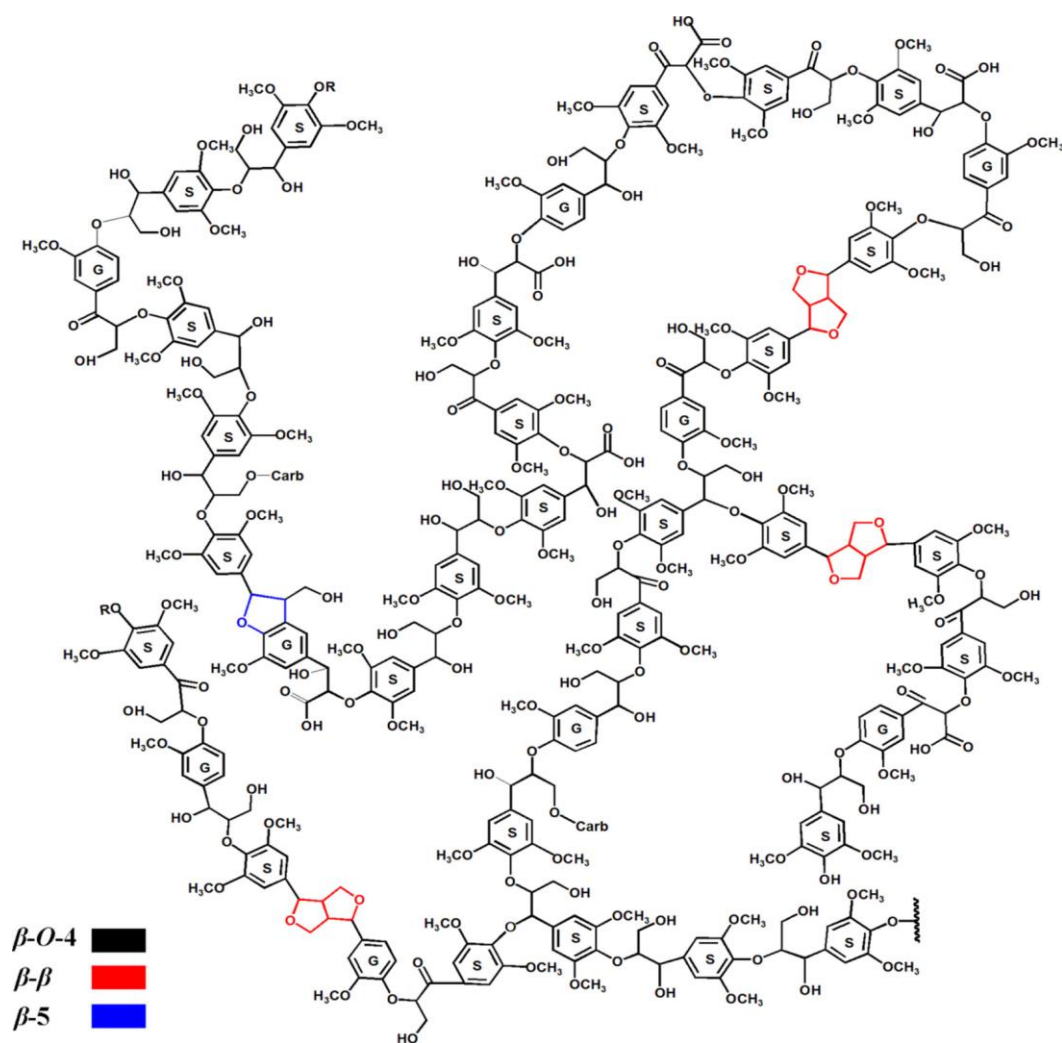
Figure 2.4: Potential structural diagram of lignin in plant cell wall of lignocellulosic biomass.[51]

2.2.4   **Other components**

Besides the three main components, biomass also contains organic extractives and inorganic species. These minor components were recently reported to have impact on the conversion of biomass.[52-56] For example, alkali and alkaline earth metallic (AAEM) species widely exists in lignocellulosic biomass. Previous studies by Wu et al. quantified the amount of alkali and alkaline earth metallic (AAEM) species in mallee wood (less than 2%) and demonstrated that these inorganics influences the emission of particulates during combustion.[57, 58] Moreover, a further study from the same group correlated the release of AAEM species with the decomposition of hemicellulose in HCW and suggested that the existence of AAEM influences the hydrothermal decomposition of biomass.[59] In addition, the AAEM species were demonstrated to have effect on the reaction mechanisms and kinetics of cellobiose under hydrothermal conditions (200–275 °C and 10 MPa).[60]

2.3   **Hydrothermal Treatment of Biomass and Its Derived Compounds**

As one of the key technologies for biomass conversion, hydrothermal processing can be used for biomass pretreatment, decomposition, and production of monomers such as glucose, fructose and xylose. Hydrothermal processing of biomass is related to multiple subjects such as material science and biology. For instance, the hydrothermal processing of biomass generates value-added chemicals or composites that are applicable as new materials (e.g., organic acids, furfural, and cellulose nanofiber).[61] Moreover, hydrothermal pretreatment of biomass is a key method for the feedstock preparation for fermentation or aerobic digestion.[62] Following review gives a detailed understanding on the use of hydrothermal treatment in biorefinery.

To achieve the decomposition of biomass or its derived compositions and compounds, water at high temperature (> 150 °C) is needed to reach the activation energies of various reactions; and the pressure of water should be high enough to ensure the water at liquid phase. Moreover, the reaction temperature and pressure are critical factors

influencing the mechanisms and kinetics of biomass hydrothermal processing, which are further reviewed in following sections. This section first gives a brief introduction of the physicochemical properties of water at different temperatures and pressures. In addition, a review on the decomposition of biomass compositions and corresponding mechanisms are concluded.

2.3.1 Properties of Hot-Compressed Water

Hot-compressed water (HCW) has been widely used as an ideal and environmental friendly reaction medium because it is non-toxic, non-flammable and widely distributed.[63] HCW can be widely applied into multiple biorefinery steps such as liquefaction and gasification.[64] The properties of hot-compressed water (HCW) are strongly influenced by temperature and pressure. Moreover, the changes in properties of HCW were expressed by different parameters such as density, dielectric constant and ionic products. For example, Figure 2.5 gives the changes of these parameters with the change of temperatures (0–600 °C) and pressures (25–100 MPa). [16] As shown, with the increase of temperature under the same pressure, the density and dielectric constant of water decreases; while the ionic products increase from 0 to ~350 °C and followed by a decrease. The properties of water are responsible for the selectivity of products, and the reaction kinetics of hydrothermal reactions.[16]
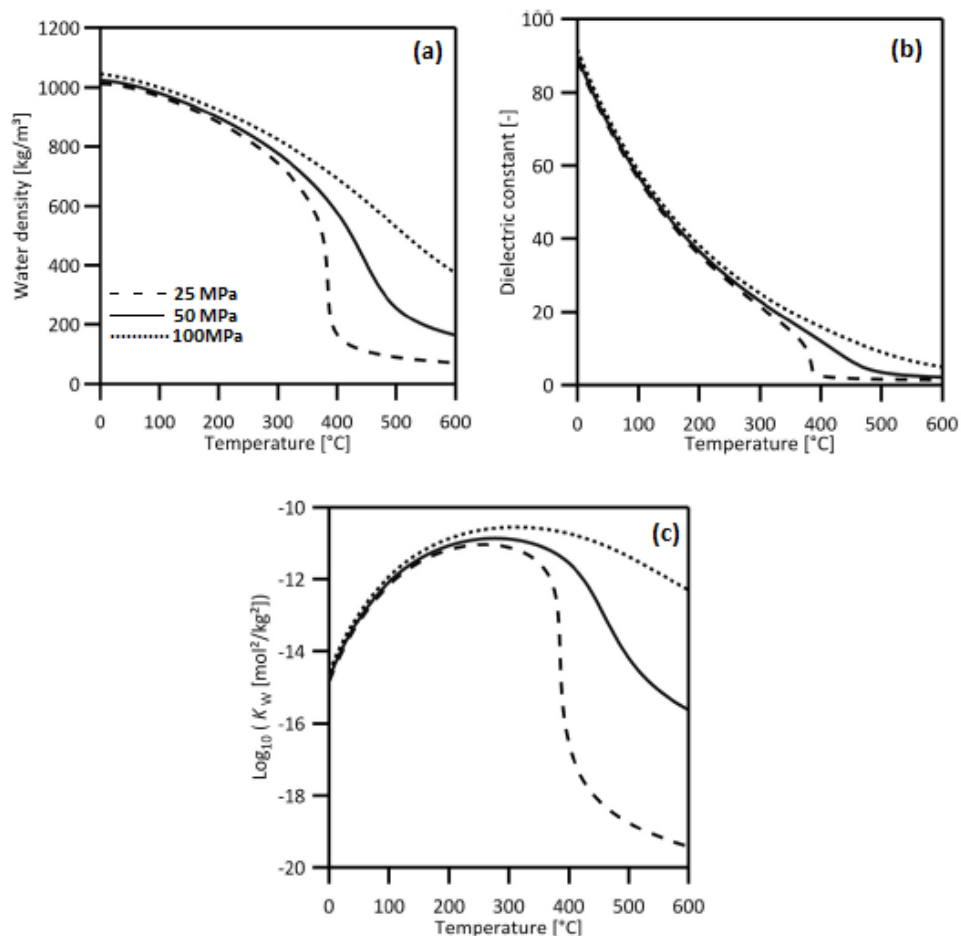
Figure 2.5: The density (a), dielectric constant (b), and ionic products (c) of HCW at various conditions.[16]

Based on the changes in properties, hot-compressed water (HCW) is classified into subcritical (374 °C < T < 100 °C, 22.1 MPa > P > 0.1 MPa) and supercritical (> 374 °C, > 22.1 MPa) water,[65] and the properties under subcritical and supercritical conditions are drastically different. For instance, the density, dielectric constant and other properties of water under several certain conditions are presented in Figure 2.5. For example, supercritical water has higher temperature (400 °C) than subcritical water (250 °C), and therefore enables faster biomass decomposition.[66] Moreover, the dielectric constant of supercritical water (5.9 at 400 °C and 25 MPa) is lower than that of subcritical water (27 at 250 °C and 5 MPa), which suggests that subcritical water is preferred for the acid catalyzed reactions such as hydrolysis, compared to supercritical water.[16]

Table 2.1: Properties of water under various conditions[67]

Properties	Ordinary	Subcritical	Supercritical	
Temperature T (°C)	25	250	400	400
Pressure P (MPa)	0.1	5	25	50
Density ρ (gcm^{-3})	1	0.80	0.17	0.58
Dielectric constant ε	78.5	27.1	5.9	10.5
pkw	14.0	11.2	19.4	11.9
Heat capacity C_p(kJkg^{-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 (mWm^{-1}K^{-1})	608	620	160	438

2.3.2 Hydrothermal Treatment of Lignocellulosic Biomass

The hydrothermal treatment of biomass was studied for different purposes. For example, various monosaccharides and oligomers can be produced through biomass hydrothermal treatment in HCW.[68, 69] In addition, direct treatment of biomass can liquefy biomass into bio-oil or bio-crude.[70] Phillip et al. studied that hydrothermal liquefaction of microalgae achieved the yield of bio-oil at ~60% at ~350 °C with various heterogeneous catalysts.[71] Moreover, the same group studied the hydrothermal gasification of biomass at 200–500 °C. However, the direct conversion of biomass is hard to optimize the yield of target products mainly because of the complexity of biomass compositions.[72]

The decomposition of the major components in HCW strongly depends on the reaction conditions because the required conditions for each of the main components are different. Compared with the other components, hemicellulose is easier to be decomposed. A study by Jussi et al. demonstrated that hemicellulose could be extracted from biomass at as low as 90 °C given enough time (24–48 h).[73] In addition, ~70% of the hemicellulose in biomass was fractionated from biomass at ~160 °C with HCW.[74] Moreover, the decomposition of the cellulose in lignocellulosic biomass requires a minimal temperature at ~240 °C, which depends on the specific structures and the effect of other components.[36] The decomposition of lignin requires the highest

temperature (~350 °C).[36] Based on the different requirements of decomposition temperature, it is plausible that the fractionation of the major components of biomass can be achieved under hydrothermal conditions. Herein, based on the previous studies, the fractionation of biomass can be achieved by three stages in HCW, i.e., 180–210 °C for hemicellulose, 240–300 °C for cellulose, and > 350 °C for lignin[36, 59, 74].

Moreover, other solvents were also studied for biomass fractionation recently. For example, hydrothermal processing with binary solvents such as acetone/water, ethanol/water, and gamma-valerolactone/water were studied for lignin extraction from biomass.[61, 75, 76] The hydrothermal treatment with aqueous organic solvents was considered as promising techniques for biomass treatment and will be further discussed on following sections. In general, the separation of biomass into single components (i.e., lignin, hemicellulose and cellulose) is a complex process that contains two or more steps. For example, a pretreatment with ethanol can separate a large portion of lignin from lignocellulosic biomass.[76] At the same time, most of the hemicellulose is also removed together with lignin. Hence, a further step to separate of lignin from hemicellulose is needed.

2.3.3 Hydrothermal Treatment of Cellulose and Cellobiose

The hydrothermal treatment of cellulose has been widely studied recently.[77-79] One of the key purposes of cellulose hydrothermal processing is to convert cellulose into saccharides. For instance, the hydrothermal treatment of microcrystalline cellulose in subcritical water can achieve the glucose recovery at maximally ~80% at ~270 °C and 10 MPa in a HCW.[42, 43, 49, 80-82] Moreover, hydrothermal processing of cellulose can also generate hydrochar, which was used to absorb the pollutants in water.[83] After decomposition into glucose, various value-added products can be produced with glucose as platform chemical. Previous studies demonstrated that there are various value-added chemicals such as organic acids[84], furfurals[85], liquid fuels[86], and gases[87]. Hydrothermal treatment of cellulose was also used to produce cellulose nanofibres (CNF).[88]
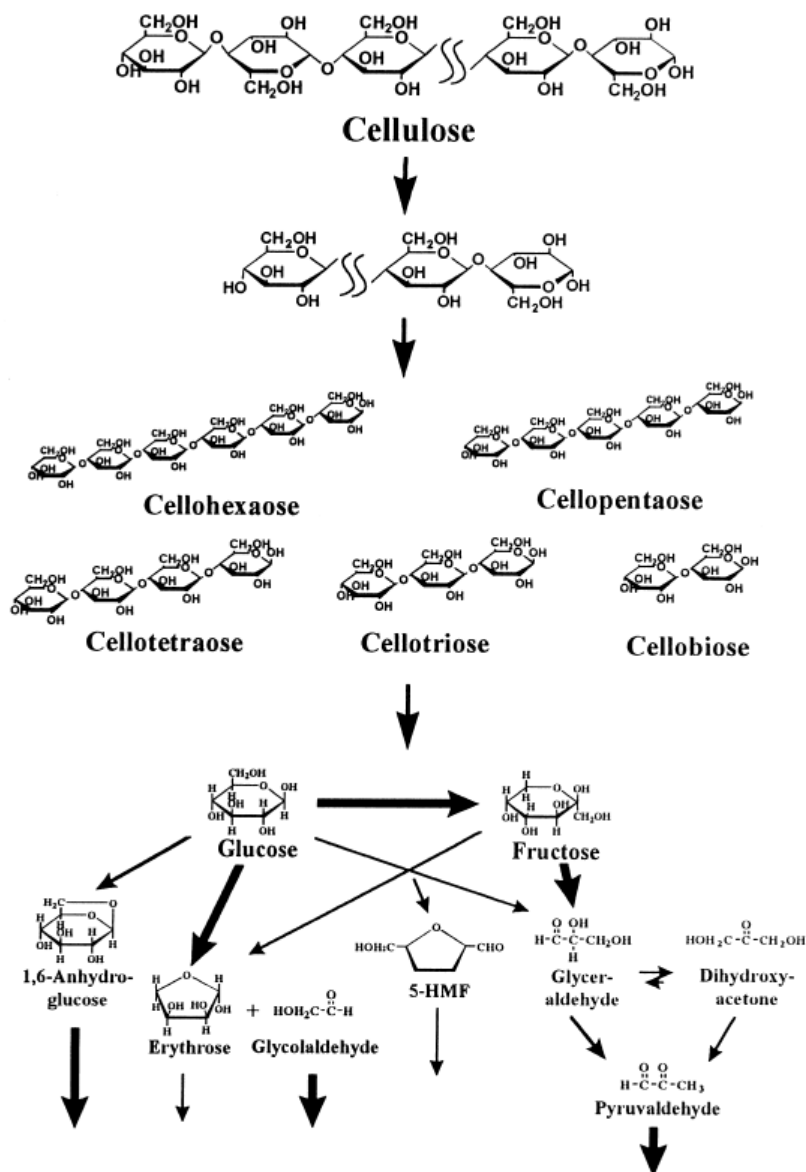
Figure 2.6: Cellulose hydrolysis pathways in HCW.[89]

The mechanisms of cellulose decomposition in HCW were widely studied, in order to optimise the treatment for different products. For example, Sasaki et al. carried out a set of works to understand the decomposition mechanisms of cellulose in HCW at 290–400 °C and 25 MPa.[89, 90] The hydrolysis of cellulose in HCW is present in Figure 2.6. As shown, various glucose oligomers are produced during the decomposition of cellulose, and the oligomers are further hydrolysed to glucose, which goes through the reaction pathways of glucose.

Recently, the isomerization reactions of glucose oligomers in HCW were proposed as another important reaction pathway.[91] Thus, a reaction pathway of cellulose in HCW was updated with hydrolysis and isomerization as the major reactions. The schematic of cellulose hydrolysis and isomerization is present in Figure 2.7. There are other reaction pathways for the cellulose decomposition in HCW, such as dehydration and retro-aldol reactions.[92, 93] The decomposition of cellulose is also influenced by various factors that will be further reviewed.
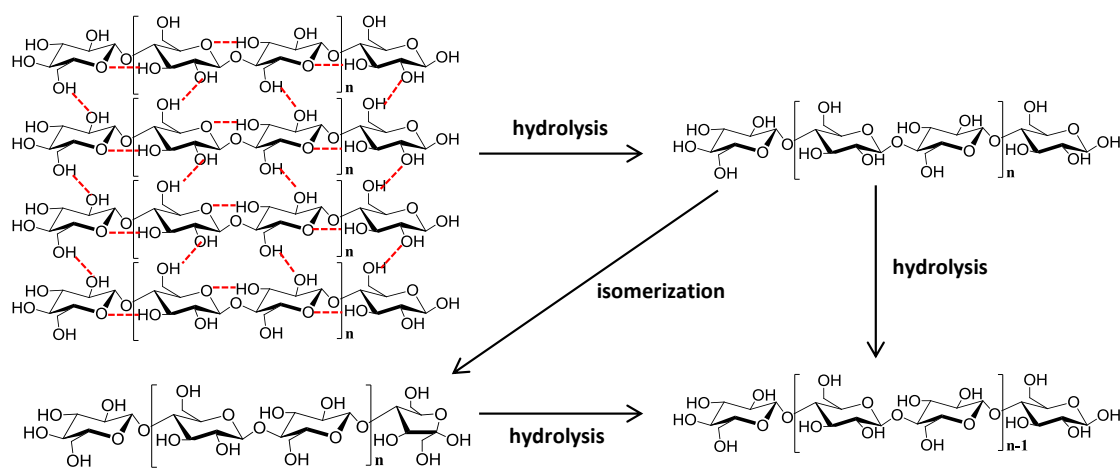
Figure 2.7: Major reaction pathways of cellulose decomposition in HCW.[91, 94]

Moreover, studies were conducted to understand the decomposition mechanisms of cellulose in HCW with cellulose derived oligomers. Cellobiose has been widely studied as the simplest cellulose derived oligomer.[91, 95-99] Previous studies of cellobiose under subcritical and supercritical water (at 300–400 °C and 25–40 MPa) concluded the major reaction pathways of cellobiose decomposition in HCW as shown in Figure 2.8.[95, 96] As shown, under such reaction conditions, the main primary reactions are hydrolysis from one cellobiose molecule to two glucoses and retro-aldol condensation reactions from one cellobiose molecule to one glucosyl-erythrose (GE) and one glycolaldehyde, or one glucosyl-glycolaldehyde (GG) and one erythrose. GE and GG are further hydrolysed to glucose and erythrose or glucose and glycolaldehyde. Moreover, the glucose follows the reaction pathways proposed on the above section.

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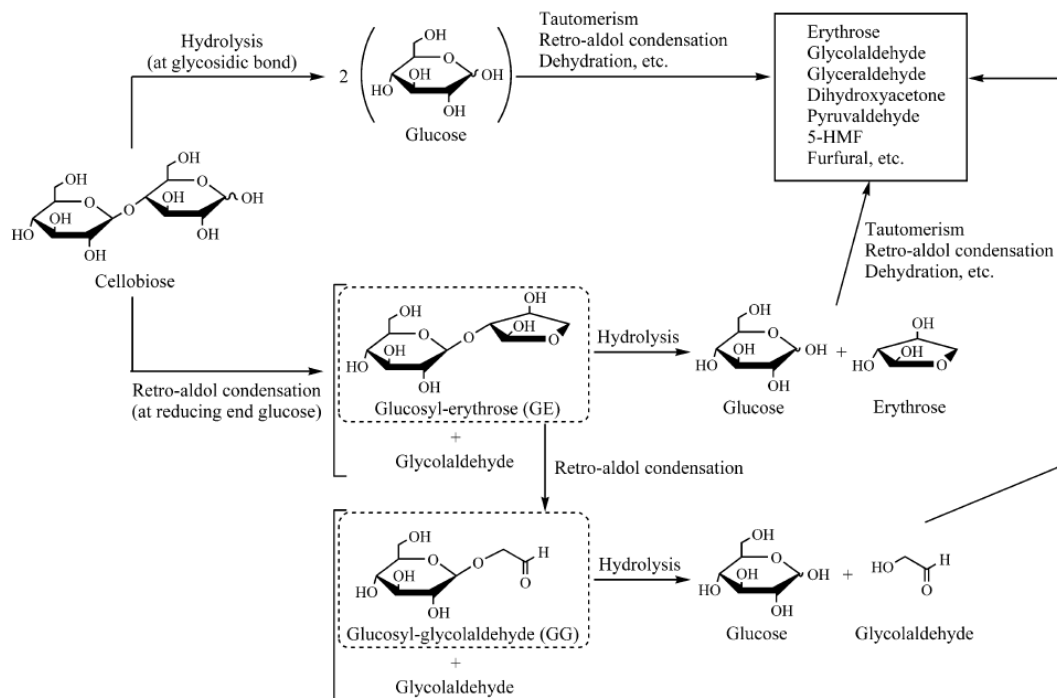
Figure 2.8: Major reaction pathways of cellobiose decomposition in HCW.[95]

Furthermore, the recent study by Kimura et al. suggested that glucose oligomers, including cellobiose, decompose mainly via isomerization of glucose at the reducing end to fructose (100–140 ℃). The isomers are further hydrolysed to glucose oligomers at the next DP and fructose.[94] The reaction pathways are present in Figure 2.9.
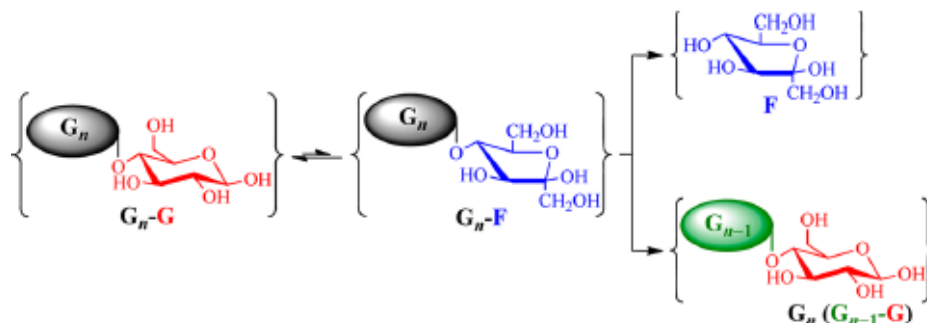
Figure 2.9: Major reaction pathways of cellobiose decomposition in HCW.[94]

More recently, Zainun et al. further studied the mechanism of cellobiose decomposition in HCW at 200–275 ℃ and 10 MPa. As shown in Figure 2.10, the dominant primary reaction for cellobiose decomposition under such conditions is the

isomerization from cellobiose to glucosyl-fructose (63–81%); while the hydrolysis (6–27%) and retro-aldol reactions (less than 5%) are shown to be minor reactions.[100]
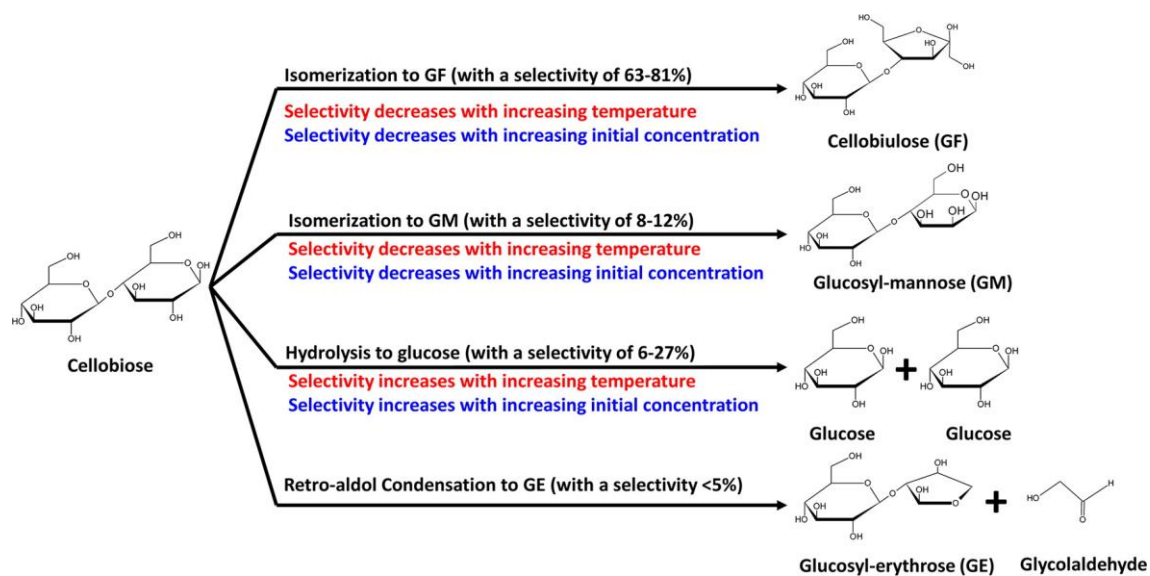
Figure 2.10: Major primary reaction pathways of cellobiose decomposition in HCW.[100]

2.3.4 Hydrothermal Processing of Hemicellulose

Hydrothermal decomposition of hemicellulose can start at ~150 °C, much lower than that (i.e., ~270 °C) for cellulose.[59] The hydrothermal treatment of hemicellulose can also generate various value-added chemicals, such as organic acids and furfurals.[71, 72] Due to the complicated structure of hemicellulose, hydrothermal decomposition of hemicellulose is less studied compared with cellulose and lignin. As the most abundant polysaccharide from hemicellulose, xylan has been studied as a model compound of hemicellulose.[101, 102] Xylan decomposition mechanism in HCW was presented in Figure 2.11. Various products can be generated from xylan decomposition, including sugar monomers, acids, and furfural.
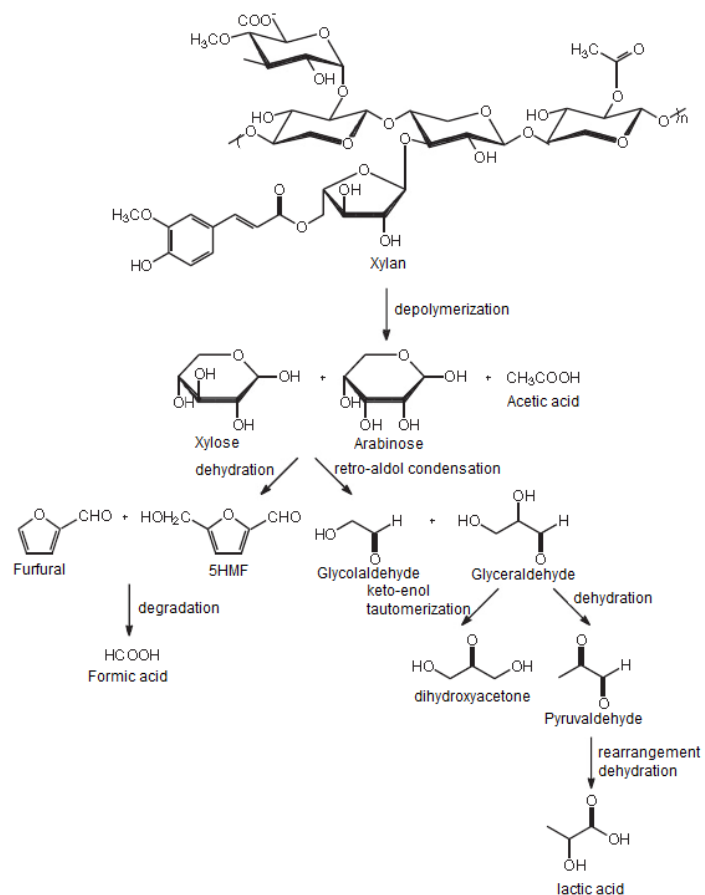
Figure 2.11: Decomposition of xylan and its derived chemicals in HCW.[102]

2.3.5 Hydrothermal Processing of Lignin

As aforementioned, lignin mainly consists of three monomeric units, which are combined by various intermolecular linkages.[36] These monomeric units are renewable commodity chemicals that can be produced via lignin hydrothermal decomposition.[103] For example, the hydrothermal decomposition of lignin was previously studied for producing phenolic units.[104-106] A considerable amount (~30%) of phenolic compounds can be generated from lignocellulosic biomass via hydrothermal processing in subcritical water (~400 °C, 25 MPa).[107] Moreover, further studies indicated that hydrothermal treatment of lignin was enhanced in ethanol/water (~40%) with more phenolic compounds production compared with that in water (~10%) at

260–300 °C.[106, 108] As shown in Figure 2.12, a simplified decomposition process of lignin in subcritical water was recently proposed.[35]
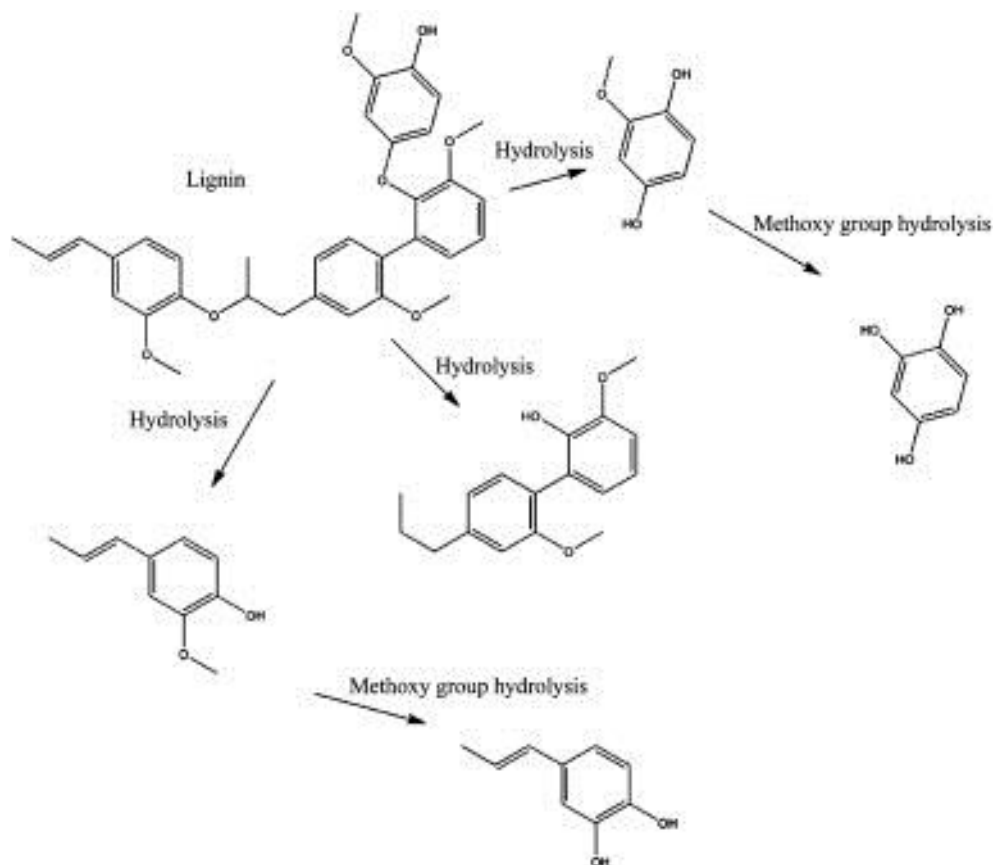
Figure 2.12: Simplified lignin decomposition process in subcritical water.[35]

2.3.6 Hydrothermal Processing of Biomass Derived Sugar Monomers

As aforementioned, more than 60% of lignocellulosic biomass is hemicellulose and cellulose, which can be further decomposed to sugar monomers including arabinose, xylose, galactose, mannose, and glucose. All these monomers are important biomass derived chemicals. The decomposition of these monomers under hydrothermal conditions is shown in Figure 2.13, where various value-added chemicals such as furfural, formaldehyde and organic acids, can be produced.[12] Thus, understanding the reaction mechanisms of biomass derived monomers are of great significance.
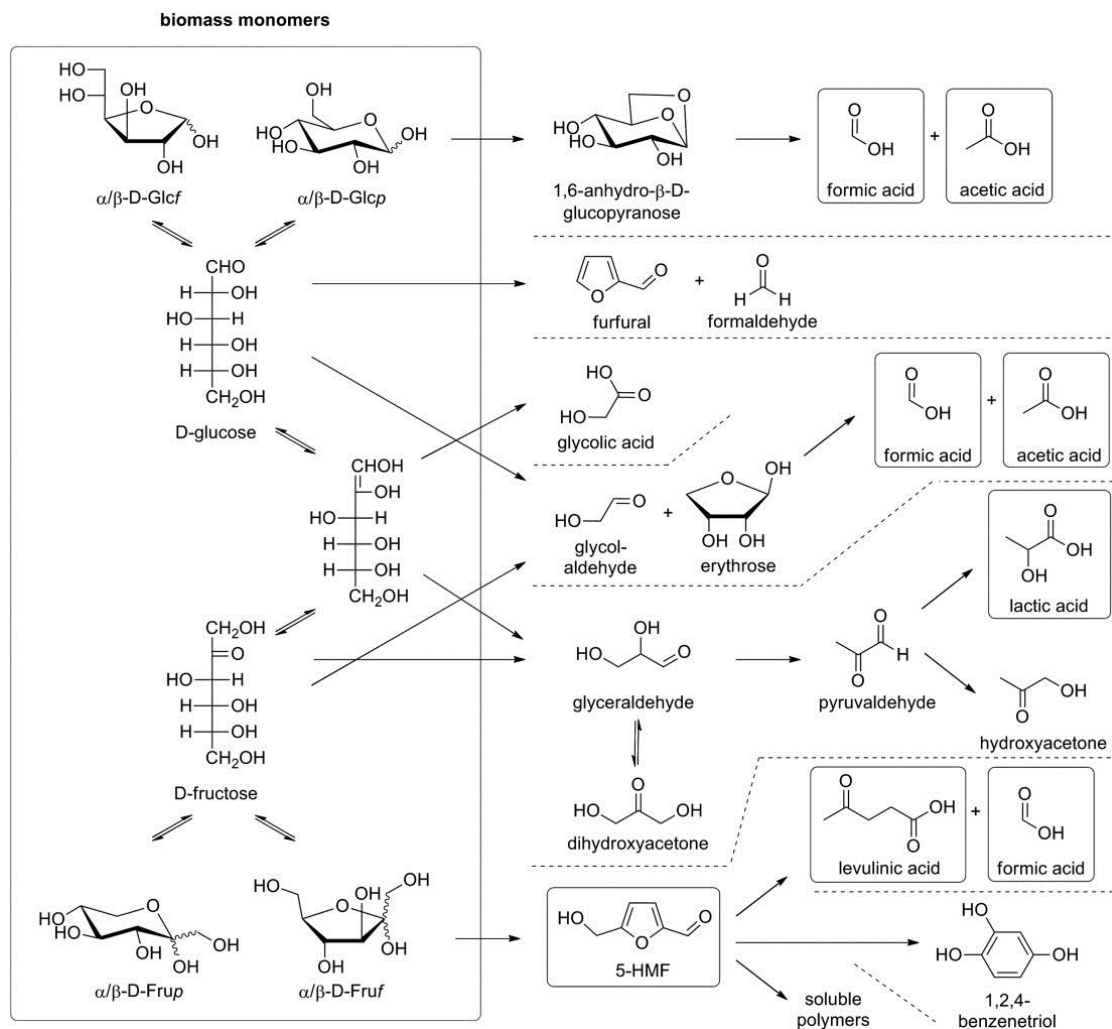
Figure 2.13: Biomass derived monomers and corresponding products under hydrothermal conditions.[12]

Among all the biomass derived monomers, glucose is the most abundant biomass derived sugar monomer and one of the most studied platform chemicals.[91, 94, 95, 109-112] With the use of glucose as feedstock, there are multiple value-added products produced such as 5-HMF[113], erythrose[114], levulinic acid[115], fructose and mannose[110] produced under hydrothermal conditions. Thus, to enhance the yield of different target products, it is necessary to understand the reaction mechanism of glucose. The main reaction pathways of glucose HCW processing are shown in Figure 2.14. In general, the major reaction pathways of glucose decomposition in HCW can be concluded as following three major approaches.

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1. Glucose dehydrates to levoglucosan (LGA) by losing one water molecule between the C1 and C6 hydroxides of the glucose molecule. The LGA is further decomposed to acids as suggested in the figure. Recent studies demonstrated that the dehydration of glucose to LGA is suppressed under the water-rich conditions in HCW.[116, 117]

2. Glucose isomerizes to fructose through open-chain forms, which process was demonstrated as the dominant primary reaction of glucose decomposition with the primary selectivity at higher than 90% in HCW at 175–275 ℃ and 10 MPa.[80] Moreover, with the increase of temperature and pressure to 350 ℃ and 25 MPa, the isomerization (contribution at higher than 50%) was also demonstrated to be the major primary reaction. Furthermore, it was previously demonstrated that fructose could be easily dehydrated to 5-HMF, which is an important biomass derived value-added chemical.[117]

3. Glucose decomposes to erythrose and glycolaldehyde, or glyceraldehyde and dihydroxyacetone, via retro-aldol condensation reaction. Moreover, one erythrose molecule is decomposed to two glycolaldehyde.[111]

As suggested on above, the major reaction pathways of glucose decomposition are initiated with dehydration, retro-aldol condensation, and isomerization as primary reactions under the conditions (temperature 175–350 ℃, pressure 10–25MPa) in the previous studies.[80, 111, 116, 117]
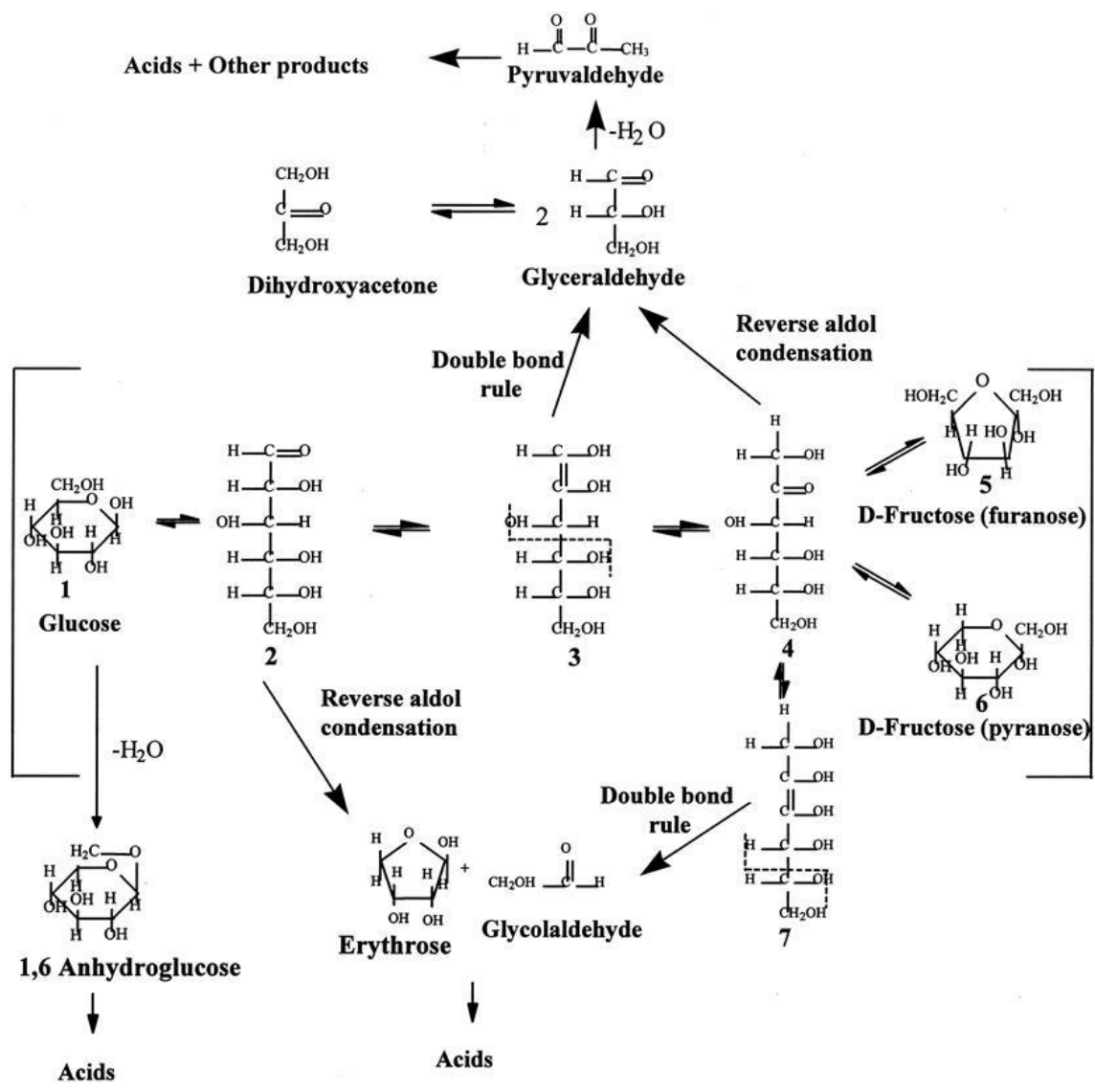
Figure 2.14: Major reaction pathways of glucose decomposition in HCW.[118]

Moreover, with the change of reaction conditions to 400–500 °C and 40 MPa, other reaction pathways were proposed in previous studies.[119-121] As shown in Figure 2.15, the glucose first dehydrates and decarbonizes to furfurals, followed by dehydration into phenols. Meanwhile, glucose, furfurals, and phenols all transform to acids and aldehydes via different reactions. The acids are further decomposed to gases.
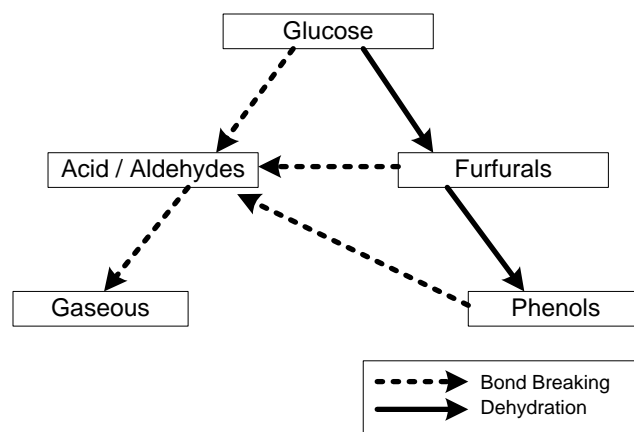
Figure 2.15: Mechanism of glucose decomposition in HCW under supercritical conditions[121]

2.4 Kinetics of Glucose, Cellobiose, and Cellulose Decomposition in HCW

As reviewed in the previous sections, the mechanisms of each model compound are different with the changes in temperatures and pressures. Moreover, the kinetics of model compounds in HCW was also studied. The recent studies on the kinetics of glucose, cellobiose, and cellulose were concluded in Table 2.2. As shown, the kinetic parameters of model compounds are influenced by reactor types, primary concentrations, reaction temperatures and pressures in HCW. The kinetics of each compound are discussed as follows.

1. **Glucose.** The kinetics of glucose decomposition in HCW water was studied in continuous and batch reactors with a wide range of initial concentrations (0.01–162 g/L) at different temperatures (175–460 °C) and pressures (10–40 MPa).[80, 111, 122-125] The study by Yun et al. demonstrated that the reaction rate constants of glucose decomposition in HCW decrease with the increase of initial concentrations under the same temperature and pressure. Moreover, the reaction rate constants increase with the increase of temperatures at the same initial concentrations. In addition, with the increase of initial concentration from 0.01 to 1000 mg/L, the activation energy slightly increases from 90 to 105 kJ/mol. Meanwhile, the frequency factor increases from 2×10^8 to 9×10^8 s^{-1}.[80] Another study by Matsumara et al. further

demonstrated that the frequency factor decreases with the increase of temperature from 175 to 400 °C at 25 MPa.

2. **Cellobiose.** The kinetics of cellobiose decomposition in HCW was studied in batch and continuous reactors with a wide range of initial concentrations (0.01–24.4 g/L) at different temperatures (180–400 °C) and pressures (10–40 MPa).[91, 95, 96, 98, 123, 124] Sasaki et al. demonstrated that the reaction rate constants of cellobiose decomposition in HCW decrease with the increase of pressure from 25 to 40 MPa at the same temperature. The study further suggested that the reaction rate constants are correlated to the density of water.[95] Moreover, familiar to that on glucose, the reaction rate constants of cellobiose decreases with the increase of initial concentration in HCW at 200–275 °C and 10 MPa.[100] In addition, the study by Matsumara et al. suggested that the increase of temperature (from 300 to 350 °C) at the same pressure (25 MPa) strongly enhances the reaction rate constants of retro-aldol reaction.[96] The influence of reaction conditions on the reaction pathways will be further discussed on following sections.

3. **Cellulose.** The decomposition of microcrystalline cellulose requires a minimal ~240 °C (reaction rate constant at 0.0015 s^{-1}) as demonstrated by Mochidzuki et al.[66] Moreover, the kinetics of cellulose decomposition in HCW has drastic differences between supercritical and subcritical conditions. Sasaki et al. demonstrated that the reaction rate constants of cellulose jumps from 1 to 10 s^{-1} at the critical point (~375 °C and 25 MPa) with the increase of temperature under the same pressure, suggesting that supercritical water is more suitable for the decomposition of cellulose for sugar recovery.[89] In contrast, Rogalinski et al. proposed a two-stage (260 and 200 °C) method for the decomposition of cellulose under subcritical conditions. After pretreatment under 260 °C, the decomposition of cellulose was achieved at 200 °C, which is likely because of the changes in the crystalline form of cellulose after pretreatment.[42]

Table 2.2: Kinetics of glucose, cellulose, and cellobiose decomposition in water with different reaction parameters

Feedstock	Reactor type	Initial concentration	Temperature (°C)	Pressure (MPa)	Residence time	Activation energy (kJ/mol)	Frequency factor (s^{-1})	Reference
Glucose	Continuous	1.2 g/L	300–400	25–40	0.02–2s	96	N.A.	B. Kabyemela, et al.[111]
Glucose	Continuous	3.6–21.6 g/L	175–400	25	Up to 350s	121	1.33×10^{10}	Y. Matsumara, et al[122]
Glucose	Continuous	15 g/L	300–460	25	Up to 60s	95.5	6.9×10^{7}	C. Promdej, et al[123]
Glucose	Batch	10.8 g/L	180–220	10	Up to 180 min	118.8	1.4×10^{11}	Q. Jing, et al[124]
Glucose	Continuous	0.00001–1g/L	175–275	10	1–56s	90–109	$(2-10) \times 10^{8}$	Y. Yun, et al[80]
Glucose	Batch	0.73–162 g/L	250–350	N.A.	10s to 10 days	114	7.7×10^{8}	D. Knezevic, et al[125]
Cellobiose	Batch	10 g/L	180–249	N.A.	Up to 14 min	136	N.A.	O. Bobleter, et al[98]
Cellobiose	Continuous	0.824 g/L	300–400	25	0.04–2s	96.4	N.A.	B. Kabyemela, et al[96]
Cellobiose	Continuous	10 g/L	320–420	25–40	Up to 3s	51	N.A.	J. H. Park, et al[126]
Cellobiose	Continuous	9.8–24.4 g/L	325–400	25–40	0.01–0.54s	111.2	$1 \times 10^{9.4}$	M. Sasaki, et al.[95]
Cellobiose	Continuous	0.01-1.0 g/L	200–275	10	1–250s	73–131	N.A.	Y. Yun, et al.[91]
Cellulose	Continuous	100 g/L	290–400	25	0.02–13.1s	548/149 (super/sub critical)	$10^{44.6}/10^{11.9}$(super/sub critical)	M. Sasaki, et al.[90]
Cellulose	Semi-Continuous	10 g/L	240–310	20–25	Up to 200s	163.9	7.7×10^{13}	T. Rogalinski, et al[63]
Cellulose	Batch	100 g/L	250–300	10	8–18 min	230	1.6×10^{19}	Y. Mochidzuki, et al.[66]

Based on the above discussion, several findings can be concluded as follows. First, the changes in temperature strongly influence the kinetics. For instance, the reaction rate constants of feedstocks were drastically increased with the increase of reaction temperatures in previous studies.[80, 100, 126] Second, pressure is related to (or cooperated with) temperature as the physiochemical properties varies with the change of pressure and temperature[127], especially, drastic difference in kinetics of the decomposition of various model molecules between subcritical and supercritical water were reported.[89, 111, 118] For example, the frequency factor of cellulose decomposition decreases drastically from ~ 1×10^{45} s^{-1} in subcritical water to ~1×10^{12} s^{-1} in supercritical water. Third, the activation energies were also concluded. The results indicate that the activation energies of glucose, cellobiose, and cellulose are different under different conditions. For glucose decomposition, the activation energies are in the range from 90–121 kJ/mol, and that for cellobiose and cellulose is 51–136 kJ/mol and 149–548 kJ/mol, respectively.

2.5   Factors Influencing the Reaction Pathways of Model Compounds

As mentioned on Section 2.3, there are various reaction pathways of glucose, cellobiose and cellulose in HCW, and the control of these reaction pathways is significant for the production of desirable products. To alter the reaction pathways, it is necessary to have a comprehensive understanding on the factors (e.g., catalysts, temperature, pressure, solvents) responsible for the reaction pathways under hydrothermal conditions. The following sections review the studies on the decomposition of glucose, cellobiose, and cellulose to provide a comprehensive understanding on the major factors that influence the reaction pathways.

2.5.1   Reaction Parameters

Previous studies indicated that the reaction parameters including temperatures, pressures, initial concentrations, and reactor types are responsible for the changes in

reaction pathways.[80, 82, 89, 100, 112, 128, 129] The influences of each factor on the reaction mechanisms were concluded in Table 2.3. The effect of each reaction parameter is discussed as follows.

1. **Temperature.** As discussed on above, changes in temperature cause significant differences to the kinetics of glucose, cellobiose, and cellulose decomposition. In addition, the effect of reaction temperature on the reaction pathways is discussed, because the rate constants of reactions are correlated to the reaction pathways according to the Arrhenius equation [$k = Ae^{-Ea/(RT)}$]. For example, Zhang et al. studied that an increase of temperature from 150 to 180°C enhanced the rate constant of retro-aldol reaction from 0.028 to 0.162 s^{-1}.[128] In addition, the maximal concentration of glycolaldehyde was increased from ~3 to ~7%, indicating that the retro-aldol reaction was enhanced by the increase of temperature.[128] Moreover, a recent study on cellobiose estimated the primary selectivities of each products and demonstrated that the increase of temperature from 200 to 275 °C were preferred for the hydrolysis and dehydration reactions of cellobiose, while the dehydration reaction was suppressed.[100] Furthermore, the changes in temperatures may influence the reaction by altering the properties of HCW. For example, Sasaki studied that the increase of temperature to above critical point drastically enhanced the hydrolysis of cellulose, however, it was because that the dissolution of cellulose in supercritical water is higher than that in subcritical water.[89, 130]

2. **Initial Concentration.** The initial concentration of feedstock can significantly affect the reaction mechanism of sugar decomposition. Yu et al. demonstrated that the increase in primary concentrations of glucose enhanced the selectivity of dehydration reactions and suppressed the selectivity of isomerization at 175–275 °C and 10 MPa.[80] For example, with the increase of glucose concentration from 1 to 1000 mg/L, the selectivity of 5-HMF was increased from ~1 to ~20 wt% at the same glucose conversion (~80%); while the selectivity of fructose was decreased from ~16 to ~8 wt%.[80] The same group also demonstrate that an increase in initial concentrations enhanced the hydrolysis and suppressed the isomerization during

cellobiose hydrothermal decomposition.[100] Moreover, as discussed on Section 2.4, the initial concentrations of feedstocks (e.g., glucose and cellobiose) cause drastic differences to the reaction kinetics.

Table 2.3: Effects of reaction parameters on the mechanisms of glucose, cellobiose, and cellulose ("+" for "enhanced", "–" for "suppressed", and "N.A." for "not available")

Feedstock	Factor	Effect on Mechanism						Reference
		Retro-aldol	Isomerization	Epimerization	Dehydration	Hydrolysis	Reversion	
glucose	Temperature (↑)	+						J. Zhang, et al[128]
glucose	concentration (↑)						+	H. M. Pilath, et al[112]
glucose	concentration (↑)		−		+			Y. Yu, et al[80]
cellobiose	Temperature (↑)	.		+	−	+		Z. M. Shafie, et al[100]
cellobiose	concentration (↑)		−	−		+		
cellulose	semi-continuous compared with batch					+		Y. Yu, et al[82]
cellulose	Continuous compared with batch				−	+		K. Ehara, et al[129]
cellulose	Temperature (↑)					+		M. Sasaki, et al[89]

2.5.2 Catalysts

Catalysts are widely used in biomass processing for optimizing the selectivity to target products, enhancing the reaction rate and lowering down the requirement for experimental parameters such as temperature and pressure. The catalysts used for biomass refinery are generally classified into two types, i.e., homogeneous catalysts and heterogeneous catalysts.[12, 35] For the treatment of cellulose, various homogeneous catalysts are used including brønsted acids[131-133], organic acids[134-136], Lewis acids[60, 137-139] and bases[140]. Compared with homogeneous catalysts, heterogeneous ones are generally in solid phase. The solid form of heterogeneous catalysts is preferred because the catalysts in solid phase can be easily separated from liquid products in industrial application and can be sustainably used as cost effective catalysts for biomass refinery. Thus, solid supported catalysts are widely researched for cellulose or glucose oligomers treatment.[141-144]

Another reason for the use of catalysts in biomass processing is that catalysts are effective to tune the reaction pathways to generate ideal products. Herein, the effect of catalysts on the reaction mechanisms of model molecules including glucose, cellobiose and cellulose in water under hydrothermal conditions is reviewed. The effect of various catalysts to the mechanisms of glucose, cellobiose and cellulose are shown in Table 2.4, Table 2.5, and Table 2.6, respectively. The effect of catalysts onto the reaction mechanisms of corresponding model compounds are concluded as follows.

1. **<u>Catalytic Decomposition of Glucose.</u>** To the decomposition of glucose, brønsted acids (e.g., sulfuric acid) are preferred to enhance the reversion reactions of glucose at 150–200 °C.[112] Under the familiar temperatures and pressures, bases (both homogeneous and heterogeneous ones) and Lewis acids enhance the isomerization and epimerization reactions. For example, Sn-Beta, or zeolite supported Sn were studied to enhance the isomerization and epimerization of glucose under mild reaction conditions (< 200 °C).[110, 145] There were other base catalysts (e.g., anatase

TiO$_2$) studied to have increase the retro-aldol and dehydration reactions at 200 °C.[140]

2. **Catalytic Decomposition of Cellobiose.** To the decomposition of cellobiose (shown in Table 2.5), the previous studies mainly investigated the effect of catalyst on the isomerization and hydrolysis reactions. [60, 99, 146-150] For instance, brønsted acids were studied to enhance the hydrolysis reactions of cellobiose in HCW (<300 °C).[146, 147] In contrast, Lewis acids suppress the hydrolysis and enhance the isomerization reactions at similar temperatures.[60] As aforementioned, there are various reaction pathways of cellobiose decompositions in HCW. Catalysts effect on the other reactions such retro-aldol reaction and dehydration reactions needs to be further understood.

3. **Catalytic Decomposition of Cellulose.** To the decomposition of cellulose (present in Table 2.6), major interests were on the hydrolysis of cellulose, because saccharification is one of the key purposes of biomass hydrothermal processing and cellulose is the most abundant component in lignocellulosic biomass. For example, the previous studies have tried different acids (e.g., sulfuric acids, organic acids, solid supported brønsted acids) to enhance the decrystallization and hydrolysis reactions to increase the recovery of sugars from cellulose decomposition (<300 °C).[46, 151, 152] Moreover, there are also other catalysts used for other purposes. For example, carbon-supported tungsten has been studied to enhance the splitting (or retro-aldol reactions) of cellulose under familiar conditions (~250 °C and ~6 MPa).[153]

Table 2.4: Various catalysts used for glucose decomposition under hydrothermal conditions and the effect on the mechanism. (("+" for "enhanced", "–" for "suppressed", and "N.A." for "not available")

Feedstock	Catalyst	Effect on Mechanism					Reference
		Retro-aldol	Isomerization	Epimerization	Dehydration	Reversion	
Glucose	0.2–1.2 wt% H_2SO_4					+	H. M. Pilath, et al[112]
Glucose	Organic base (PET)		+				Q. Yang, et al[154]
Glucose	organic base (PS)		+				Q. Yang, et al[29]
Glucose	Lewis Acid (Sn-Beta)		+	+			R. B. Deval, et al[110]
Glucose	Lewis Acid (Sn-Beta)		+				Y. R. Leshkov, et al[155]
Glucose	Ammonium Metatungstate	+					J. Zhang, et al[128]
Glucose	Anatase TiO_2		+		+		M. Watanabe, et al[140]
Glucose	Amino Acids		+				Q. Yang, et al[156]
Glucose	Solid acid				+		M. Ohara, et al[157]
Glucose	metallosilicate solid		+				S. Lima, et al[158]
Glucose	Carbonic acid		+				S. Jing, et al[131]
Glucose	silica-supported copper			+			M. Makkee, et al[159]
Glucose	Sn-Beta zeolites			+(with salt)			W. R. Gunther, et al[145]
Glucose	Acids (modeling results)					+	D. Liu, et al[160]
Glucose	Carbon-supported Ru, Pt, etc.	+					G. Zhao, et al[161]
Glucose	Carbon Dioxide		+		+		T. Miyazawa, et al[162]

Table 2.5: Various catalysts used for cellobiose decomposition under hydrothermal conditions and the effect on the mechanism. ("+" for "enhanced", "–" for "suppressed", and "N.A." for "not available")

Feedstock	Catalyst	Effect on Mechanism					Reference
		Retro-aldol	Isomerization	Epimerization	Dehydration	Hydrolysis	
cellobiose	H_2SO_4 (pH at 4-7)		–	–		+	Z. M. Shafie, et al[146]
cellobiose	organic acids					+	J. A. Bootsma, et al[147]
Cellobiose	NaCl					–	S. Tsubaki, et al[99]
Cellobiose	H_2SO_4					+	O. Bobleter, et al[148]
Cellobiose	AAEM chlorides	+	+	+		–	Y. Yu, et al[60]
Cellobiose	sulfates and H_2SO_4	–				+	I. C. Kim, et al[149]
Cellobiose	NaOH					–	G. Bonn, et al[150]

Table 2.6: Various catalysts used for cellulose decomposition under hydrothermal conditions and the effect on the mechanism. ("+" for "enhanced", "–" for "suppressed", and "N.A." for "not available")

Feedstock	Catalyst	Effect on Mechanism					Reference
		Retro-aldol	Isomerization	Epimerization	Hydrolysis	Decrystallization	
microcrystalline cellulose	carbon-supported tungsten	+					N. Ji, et al[153]
cotton cellulose	formic acid				+		A. Yuki, et al[46]
corn fiber	carboxylic acids				+		N. S. Mosier, et al[135]
microcrystalline cellulose	sulfonated chloromethyl polystyrene				+		S. Li[163]
pine sawdust	H$_2$SO$_4$					+	P. Sannigrahi[151]
microcrystalline cellulose	alkali-acrylonitrile					+	A. Hirai, et al[164]
microcrystalline cellulose	sulfonated activated-carbon				+		A. Onda[152]

2.5.3 **Solvent System**

Currently, various solvents have been used for biomass processing. Generally, the solvents can be classified into aprotic solvents (THF, GVL, Acetone, etc.), protic solvents (water, ethanol, methanol, etc.) and ionic liquids.[17-26] The use of solvents in biorefinery can be classified into two categories, i.e., pure solvents for biomass liquefaction and co-solvents or aqueous organic solvents for biomass hydrothermal processing. The liquefaction of biomass in various organic solvents has been studied as an alternative way for biomass pyrolysis.[13, 22, 26, 92, 165, 166] The main reaction pathways under liquefaction conditions are dehydration that can generate various dehydration products.[70] Moreover, aqueous organic solvents have been widely studied (present in Table 2.8) for various purposes.

1. **Aprotic solvents/water.** The presence of aprotic solvents is shown to have significant effect for the dehydration of glucose with acids as catalyst. For instance, the production of 5-HMF from glucose can be enhanced in GVL/water (9:1), THF/water (9:1) and γ-hexalactone (GHL)/water (9:1) to more than 90% under catalytic conditions at moderate conditions (< 200 °C).[167] For cellobiose, the hydrolysis to glucose is promoted in GVL/water compared with that in water with the same amount of sulfuric acid (0.05 mM) as catalyst(< 200 °C).[33] Moreover, the use of aqueous aprotic solvents (e.g., THF/water) was studied to enhance the hydrolysis of cellulose and increase the sugar yields from cellulose decomposition. Compared with other solvents, aprotic solvents are easier to be separated from water, for example, GVL could be easily separated from water by adding sodium chloride into GVL/water systems.[30]

2. **Protic solvents/water.** Protic solvents such as methanol and ethanol were also studied for biomass processing. Recent studies indicated that the use of aqueous protic solvents enhanced the isomerization of glucose with the use of zeolite or acids as catalysts (< 200 °C).[168] However, the effect of protic solvents on the reaction pathways of cellobiose and cellulose is not well studied. It should be noted

that the etherification reaction between alcohols and glucose or glucose oligomers also happens with the increase of methanol concentrations to methanol-rich conditions[169], which has enhanced the difficulty of products analysis.

3. **Ionic liquids/water.** Recent studies used ionic liquids on glucose transformation under acidic conditions. The dehydration reactions of glucose were shown to be significantly enhanced in ionic liquid/water/acids. Unlike that for glucose, the main purpose of using ionic liquids for cellulose decomposition is to enhance the decrystallization and hydrolysis of cellulose under moderate temperatures (< 200 °C) to achieve high sugar yields[42, 44]; while the decomposition temperature of crystalline cellulose in HCW was at ~250 °C.[82] However, the separation of liquid products from ionic liquids and the reuse of ionic liquids are the key challenges for the application of ionic liquid in biorefinery.[6]

4. **Other Solvents.** There are also other solvents that have been used for biomass processing, for instance, bio-oil derived from biomass liquefaction was recently studied to be applicable for cyclic biomass processing, which was recommended as a sustainable way for biomass refinery.[17, 170] Organic Electrolyte Solutions, mixtures with ionic liquid and polar organic solvents, were proposed as effective alternatives for biomass treatment[171]. Moreover, physical or physiochemical treatments were also studied previously to be effective for biomass processing. For instance, steam treatment was used for the fractionation of biomass and enhances the enzymatic treatment of cellulose.[172, 173] Ball milling could effectively decrystalize and depolymerize crystalline cellulose, and the effect could be promoted with the presence of acids and other catalysts.[43, 174-176] Electron beam irradiation was also studied to be applicable for the degradation of cellulose.[177]

The studies on glucose, cellobiose, and cellulose decomposition in aqueous solvents are present in Table 2.8. Several findings can be concluded as follows. First, organic solvents (aprotic, protic and ionic liquids) are applicable for biomass processing that can control the reaction pathways of model compounds. Second, the use of organic

solvents is always combined with catalysts (heterogeneous or homogeneous), where the role of solvents are located to the effect of solvents on the performance of catalysts. Third, the effect of solvents on the reaction mechanisms is unclear without comprehensive analysis of all possible reaction pathways. For instance, the studies on glucose are mainly on the dehydration reactions; while those on cellobiose and cellulose are mainly on the hydrolysis reactions. Moreover, the use of solvents on biomass processing has thrown technical challenges to instruments for products. For example, in the previous studies[42, 82], total organic carbon (TOC) was detected as a key and precise value to quantify the conversion of cellulose. However, with the presence of organic solvents, the previous method would not be applicable. Other techniques such as high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC–PAD), which is previously applied as a key instrument for the detection of isomers and epimers of glucose and glucose oligomers[91], may also be affected because of the possible interference of organic solvents.

2.6   GVL and Its Application on Biomass Hydrothermal Processing

GVL is a polar aprotic solvent with low melting point (i.e., −31 °C), high boiling point (i.e., 207 °C), and high open cup flash point (i.e., 96 °C) and low toxicity as shown in Table 2.7 that is presented in a previous study[178]. Unlike that for the other aprotic solvents, GVL can be generated from biorefinery with high yields (e.g., yields at ~75% was achieved with levulinic acid as feedstock).[31] A detailed introduction of GVL is present as follows. In general, as a biomass derived platform chemical for petroleum engineering, GVL has attracted wide interests from different areas to study GVL as a fuel purpose and as a (co-)solvent.

2.6.1   GVL as a Fuel

GVL is recommended as a promising fossil fuel substitute for several reasons through comparing with other recommended fossil fuel substitutes as present in Table 2.7. First, the physical properties of GVL are more suitable as a liquid fuel than other chemicals. For instance, GVL is more applicable than methyl t-butyl ether (MTBE) as the toxicity of GVL is lower than MTBE.[178] Second, compared with ethyl t-butyl ether (ETBE), another recommended fossil fuel substitute, GVL is sustainable as a biomass derived chemical.[31, 178] Third, compared with methanol and ethanol, which can also be derived from biomass[179, 180], GVL has higher heating value with higher carbon and lower oxygen contents that are preferred in fuel industry. And also, used as a platform chemical, GVL can be further converted into various alkenes via petroleum engineering approaches.[181] Thus, producing GVL via hydrothermal processing of biomass is recommended as a sustainable and promising approach to produce fossil fuel substitutes.

Table 2.7: Selected physicochemical properties of GVL with comparison with other fossil fuel substitutes.[178]

	Methanol	Ethanol	MTBE	ETBE	GVL	THF
molar weight(g/mol)	32.04	46.07	88.15	102.17	100.12	86.13
Carbon (w%)	37.5	52.2	66.1	70.53	60	69.7
Hydrogen (w%)	12.6	13.1	13.7	13.81	8	11.6
Oxygen (w%)	49.9	34.7	18.2	15.66	32	18.7
Boiling point	65	78	55	72–73	207–208	78
Melting point (°C)	−98	−114	−109	−94	−31	−136
Density (°C)	0.79	0.80	0.74	0.74	1.05	0.86
Open cup flash point (°C)	16.1	14	−33	−19	96	−11
LD_{50}, oral for rat (mg/kg)	5628	7060	4800	5000	8800	N/A

Table 2.8: Effect of solvents on the mechanisms of glucose, cellobiose, and cellulose.

Feedstock	solvents	Effect on Mechanism				Reference
		decrystalllization	Isomerization	Dehydration	Hydrolysis	
glucose	ionic Liquid/metal chlorides			+		H. Zhao, et al[182]
	DMSO/water/acid			+		M. A. Mellmer, et al[34]
	THF/water/acid			+		
	dioxane/water/acid			+		
	MeCN/water/acid			+		
	methanol/water/zeolite		+			S. Saravanamurugan, et al[168]
	ionic solvent/lewis acid		+			E. A. Pidko, et al[183]
	DMSO/water			+		V. Vasudevan, et al[116]
	TMF/water			+		
	DMF/water			+		
	ionic liquid/lanthanide			+		T. Stahlberg, et al[184]
	DMSO/water/acid			+		X. Qian, et al[185]
cellobiose	ethanol/water		+			N. Soisangwan, et al[186]
	GVL/water/sulfuric acid				+	M. A. Mellmer, et al[33]
	THF/water/sulfuric acid				+	
	dioxane/water/sulfuric acid				+	
cellulose	ethanol/water	+		+		P. Sannigrahi, et al[151]
	THF/water/salt	+			+	Z. Jiang, et al[79]
	ionic liquid/acid	+			+	K. Kuroda, et al[19]
	ionic liquid/water	+				Q. Zhang, et al[44]
	THF/water	+			+	B. Mostofian, et al[187]

2.6.2 GVL as a Solvent

Despite that GVL is a promising fuel substitute, GVL can also be used as a solvent for various chemical processes of biorefinery including pretreatment, further processing of hemicellulose, cellulose, and biomass derived platform compounds (e.g., 5-HMF, LGA, Furfural, Glucose, and Fructose). As shown in the schematic (Figure 2.16), GVL is produced from catalytic transformation of levulinic acid, which is originated from biomass via different catalytic routes from cellulose and hemicellulose. Interestingly, as an aprotic solvent, the dash lines in Figure 2.16 also indicate that GVL can participate into the multiple steps from biomass to GVL as reaction medium.[188] The advantages of using GVL as a solvent for biorefinery are concluded as follows.
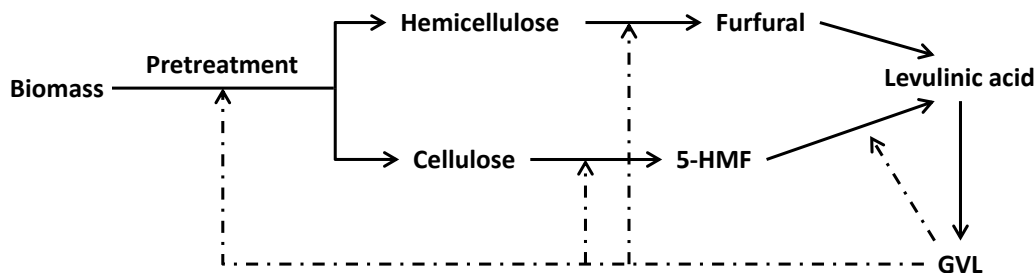
Figure 2.16: Schematic of GVL production from biomass with GVL as solvent and co-solvent participating the process.[188]

First, GVL can be used for biomass pretreatment that can fractionate biomass into separated parts (i.e. lignin-reach part and sugar-reach parts) by mixing with water as a GVL/water binary system, or hot-compressed GVL/water (HCGW).[189] With the used of HCGW, lignin was fractionated from cellulose and hemicellulose under moderate conditions (~170 °C).[189] After separating the GVL/water mixtures to two phases, the major part of lignin is dissolved in GVL rich fraction, while most of the biomass derived sugars are dissolved in water rich fraction.[61, 190]

Second, GVL strongly promotes the performance of acids for the degradation of cellulose or cellulose derived oligomers under hydrothermal conditions. It is demonstrated in the previous study that only 0.005 mol/L of sulfuric acid is needed in HCGW with GVL at 80% on a volume basis compared with that at 0.1 mol/L in HCW.[30] This process (shown in Figure 2.17) has several advantages over acids catalyzed biomass decomposition. First, the reaction temperatures (160–220 °C) for this process are lower compared with that for biomass decomposition in HCW (~250 °C). Second, by saving the use of sulfuric acid from 0.1 to 0.005 mol/L, less corrosion to equipment are caused, which reduces the process costs. Moreover, GVL can be easily separated from water by adding salt or supercritical CO_2 extraction. And also, after extraction, lignin is mainly in GVL-rich phase, and sugars are mainly in water-rich phase, which character is preferred for the recycle use of GVL, making the process sustainable.[189]
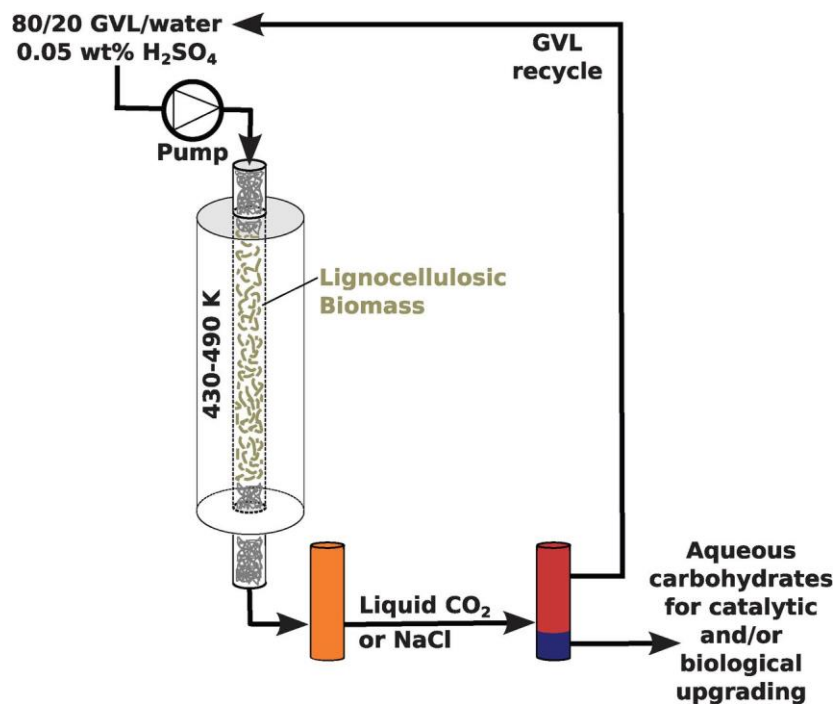
Figure 2.17: conceptual graph for biomass processing with GVL/water binary solvent.[30]

Third, used as a single solvent, GVL is studied as a reaction medium for the decomposition of biomass derived platform chemicals such as glucose, fructose, levogluocan, 5-HMF, and furfural.[191-195] For example, with pure GVL as reaction medium, the direct liquefaction of cellulose can be achieved to produce platform chemicals including LGA, 5-HMF, and furfural .[26] Moreover, compared with water (maximal 5-HMF yield at ~50%), GVL enhanced the 5-HMF from glucose, fructose, and sucrose to different extend (~80% or higher).[113, 195] And also, 5-HMF was demonstrated as a feedstock for GVL production with GVL as reaction medium.[191]

As shown in Table 2.7, the boiling point of GVL is at 207–208 °C, higher than all the other widely used organic solvents in biomass processing (e.g. acetone, 1,4-Dioxane, methanol, ethanol, THF), and GVL has the lowest vapor pressure. As the reaction condition for biomass hydrothermal processing in aqueous organic solvents ranges from about 100–500 °C, using GVL is safer compared with other solvents. Overall, GVL has been proved as an ideal biomass derived solvent for biomass treatment. However, only a few studies were conducted to study the fundamental effect of GVL on the hydrothermal processing of biomass.[32, 33] Alonso et al. demonstrated that the Gibbs free energy for the conversion from R to P was reduced in HCGW compared with that in HCW with both strong and weak acids as catalysts (shown in Figure 2.18), indicating that the presence of GVL strengthened the performance of acids.[32] Moreover, a further study with cellobiose as model compounds demonstrated that the HCGW drastically enhanced the rate constants of cellobiose hydrolysis compared with HCW under acidic conditions (8.9 times in HCGW with 80% of GVL compared with that at 0.6 in HCW).[33] More recently, HCGW was demonstrated to be applicable to optimize the rate and selectivity of the dehydration process from biomass derived monomer (e.g., fructose) to 5-HMF under acidic conditions.[34] However, to the best knowledge of the author, the solvent effect of GVL to the decomposition of biomass under catalyst-free conditions was not studied, which is the primary motivation of this PhD project.
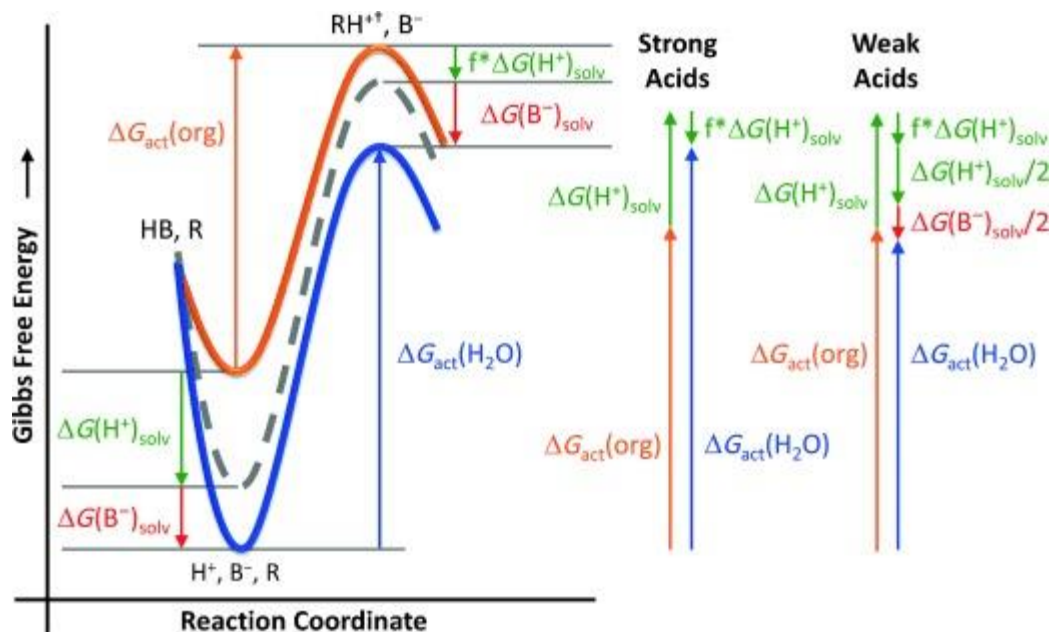
Figure 2.18: Gibbs free energy surface in H_2O and polar aprotic organic solvents of the conversion of reactant R into product P catalyzed by acids.[32]

2.7 Conclusion and Research Gap

Based on the above sections, following conclusions can be drawn:

- Biorefinery is one of the promising approaches to produce sustainable and carbon-balanced substitutes for fossil fuels with integrated technologies from different disciplines.
- Hydrothermal processing is one of the key technologies for biorefinery that can be used in various steps from biomass as feedstock to the production of target chemicals.
- The reaction mechanisms of biomass decomposition in HCW have been widely studies using glucose, cellobiose and cellulose as model compounds.
- There are various factors influencing the performance of biomass hydrothermal processing such as the reaction temperatures, pressures, catalysts and solvent systems. In other words, the reaction pathways of biomass processing can be optimized or tuned, given an in-depth understanding on the effect of different factors.

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- Solvent treatment of biomass and biomass derived compounds is being widely studied to provide accessible approaches for biorefinery. Various organic solvents including aprotic solvents, protic solvents and ionic liquid solvents have been tried onto biomass for hydrothermal processing.

- As a biomass derived sustainable chemical, GVL is being widely studied as a solvent or co-solvent for the treatment of biomass or biomass derived chemicals.

- In all the previous studies applying GVL/water onto biomass processing, different acids are used as catalysts. And it is proved that GVL promotes the catalytic performances of various acids for biomass hydrothermal processing.

Unfortunately, as a biomass-derived solvent that can be used in various steps of biorefinery and has achieved predominant contributions to biomass processing, the reasons behind the use of GVL as a solvent for biorefinery is not well understood. The research gaps of the current studies on GVL related biorefinery technologies are listed out as follows based on the current research status:

- The detailed reaction pathway of different components (lignin, hemicellulose, cellulose) in GVL/water is not clearly studied.

- The solvent effect of GVL on the processing of biomass derived monomers under catalyst-free conditions is unclear.

- The solvent effect of GVL on the mechanism and kinetics of cellobiose and cellulose decomposition is unclear under catalyst-free conditions.

- The solvent effect of GVL on the hydrothermal processing of biomass under catalyst-free conditions is unclear.

- The difference between GVL and other previously used organic solvents on biomass processing under catalyst free conditions has not been studied.

2.8   Research Objectives of the Present Study

From the literature review carried out in this study, a number of research gaps in the field had been identified. However, it is impossible to address all the research gaps identified in a PhD study. Therefore, the scope of current study is limited to the solvent effect of GVL on the reaction mechanisms of fructose, glucose, cellobiose and cellulose under acid free conditions, with a case study of GVL/water on mallee wood processing. The main objectives of current study are:

- To investigate the solvent effect of GVL on the reaction mechanisms and kinetics of glucose in HCGW under catalyst-free conditions at various GVL concentrations, in comparison to those under hot-compressed water (HCW) conditions;
- To understand the solvent effect of GVL on the reaction mechanisms and kinetics of cellobiose in HCGW under catalyst-free conditions;
- To further investigate sugar recovery from cellulose and lignocellulosic biomass via hydrothermal processing in HCGW under catalyst-free conditions;
- To compare the solvent effect of GVL with other organic solvents during hydrothermal processing of fructose and glucose under catalyst-free conditions. The following work has been completed to achieve these objectives.

Chapter 3: Research Methodology and Analytical Techniques

3.1   Introduction

This chapter will provide the research methodology employed to achieve the objectives outlined in Section 2.8. The experimental setups and analytical techniques used will be described in detailed in this chapter.

3.2   Methodology

To achieve the main research objectives outlined in Section 2.8, a series of experiments had been carried out. These include:

- Hydrothermal processing of glucose in hot-compressed water (HCW) and various gamma-valerolactone/water (GVL/water) mixtures. The experiments were carried out in a batch reactor heated in a sand-bath.

- Hydrothermal processing of cellobiose in water and various GVL/water mixtures. The experiments were also carried out in the same batch reactor system.

- Hydrothermal processing of cellulose and lignocellulosic biomass in water and various GVL/water mixtures. The experiments were carried out in a semi-continuous reactor system.

- Hydrothermal decomposition of glucose and fructose in water and various aqueous organic co-solvents. The experiments were also carried out in a batch reactor system.

The overall methodology to achieve the objectives of this study is illustrated in Figure 3.1.
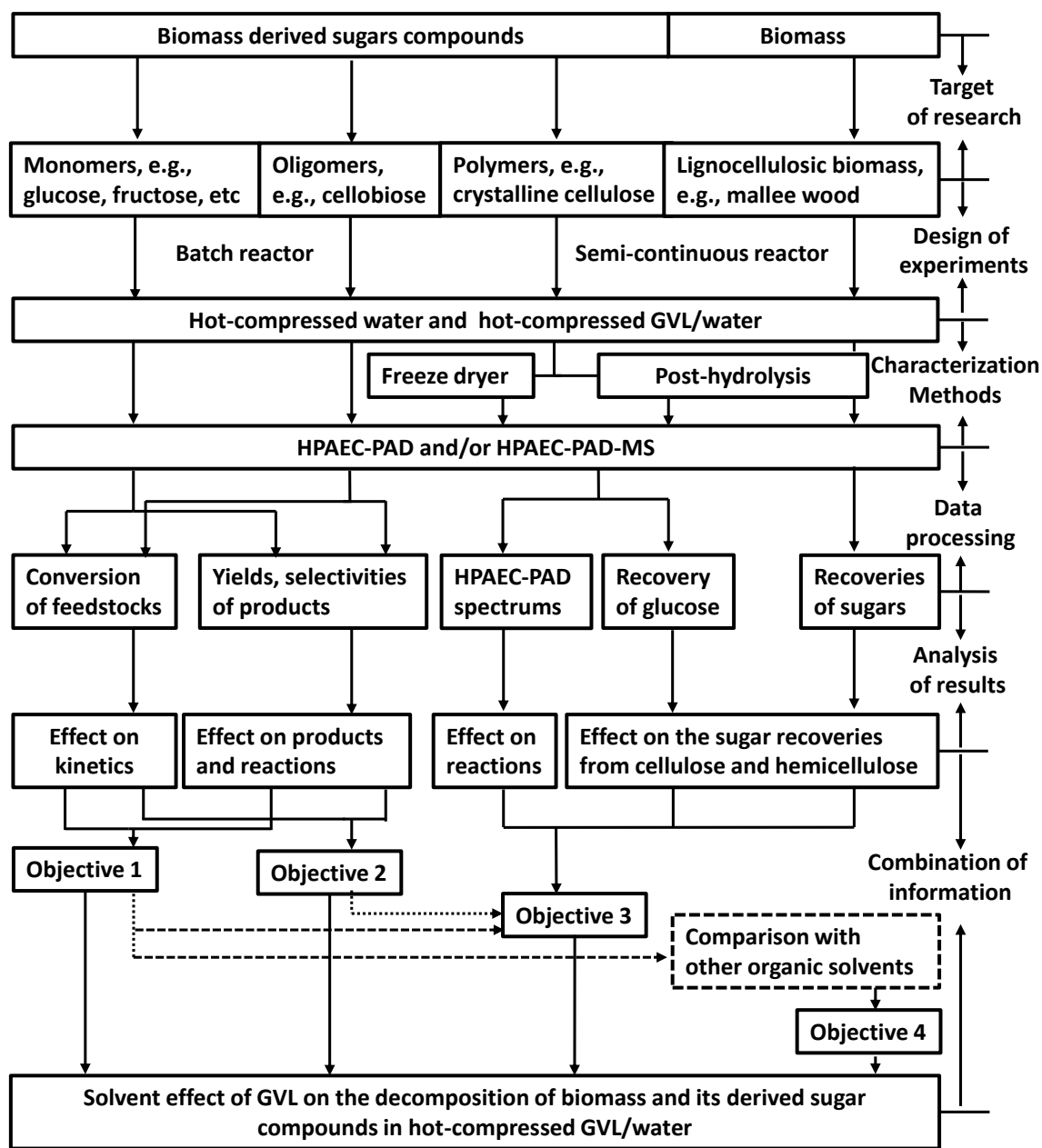
Figure 3.1: Research methodology and the linkages to the research objectives (in Section 2.8) to be achieved in this PhD study.

3.2.1 Glucose and Cellobiose Decomposition in HCGW

To achieve the objectives of these researches, a series of experiments were performed under different temperatures in HCW and hot-compressed GVL/water (HCGW) with a wide range of GVL concentrations (on volume basis). After the reaction, all samples

were characterized by high performance anion exchange chromatography with pulsed amperometric detection (HPAEC–PAD) and high performance anion exchange chromatography with pulsed amperometric detection and mass spectrometry (HPAEC–PAD–MS). The details on the experimental setup and procedure are given in Section 3.3. The data were processed to calculate the conversion of the feedstocks (i.e. glucose and cellobiose), the yields and selectivity of products, and the reaction rates of feedstocks.

Based on the experiments, the reaction pathways of glucose and cellobiose in water and different binary solvents were analysed and discussed in details as shown in Section 4 and Section 5.

3.2.2 **Decomposition of Cellulose and Biomass in HCGW**

To investigate the decomposition behaviour of cellulose and biomass in GVL/water as the third objective aforementioned, cellulose and mallee wood were prepared and processed under hydrothermal conditions with a semi-continuous reactor under different temperatures. After hydrothermal treatment, the liquid samples were further processed via post-hydrolysis with sulfuric acids as catalysts to quantify the monomers. The samples were characterized with a HPAEC–PAD system with different columns and programs, according to the different purposes. The solvent effect of GVL on the decomposition behaviour of cellulose and biomass were discussed as shown in Section 6.

3.2.3 **Decomposition of Glucose and Fructose in Organic-Water Co-Solvents**

To have a comprehensive understanding on the solvent effect of GVL on biomass processing, hydrothermal experiments were organised with GVL and other organic solvents as co-solvent for glucose decomposition under the same conditions as introduced in Section 3.3. The products were quantified by a HPAEC–PAD system with a same program used for glucose in GVL/water. The reaction pathways of

glucose in different solvent systems were verified based on the experimental results. The differences between different solvents on the decomposition of glucose were discussed in details in Section 7.

3.3   Experimental

3.3.1   Raw Materials and Chemicals

Feedstocks including D-(+)-cellobiose (99%), D-(+)-glucose (99%) and avicel cellulose (PH-101) were purchased from Sigma-Aldrich. The biomass samples used in this study is mallee wood separated from mallee (*Eucalyptus loxophleba, subspecies Lissophoia*) tree harvested in Western Australia. The mallee wood was dried then cut using a cutting mill before it was sieved to a size fraction of 150–250 μm. The samples were stored in freezer prior to experiment. Standard chemicals used for peak identification and quantification including fructose (99%), mannose (99%), erythrose (75%), glycolaldehyde dimer (98%), 5-HMF (99%), and 1,6-anhydro-β-D-Glucose (99%) were also obtained from Sigma-Aldrich. Other standards including 1,6-anhydro-β-D-Cellobiose (98%), cellobiulose (glucosyl-fructose, GF; 95%), and glucosyl-mannose (GM; 95%) were synthesized by Synthose Inc. (formally known as LG Scientific Inc., Canada). The high-performance liquid chromatography (HPLC) grade methanol, ethanol, GVL, acetone and 1,4-dioxane were also purchased from Sigma-Aldrich.

3.3.2   Reactor Systems

The hydrothermal treatment experiments were carried out in 2 types of reactor systems, (1) batch reactor system and (2) semi-continuous reactor system. The batch reactor system was used for the hydrothermal processing of glucose, cellobiose in water, GVL/water, or other solvents. The semi-continuous reactor was used for hydrothermal processing of solid feedstocks (i.e. cellulose and mallee wood biomass).

Batch Reactor and Sand-Bath System

A schematic of the batch reactor system which includes a batch reaction and the sand-bath is shown in Figure 3.2. The batch reactor consists of a needle valve and stainless-steel tube with a volume of ~10 mL. To heat the batch reactor to reaction temperature, the batch reactor was submerged in a fluidising sand-bath (Techne, model SBL-2). The sand in the sand-bath is electrically heated and fluidised by the compressed air supplied externally.

Batch Reactor   **Sand Bath**
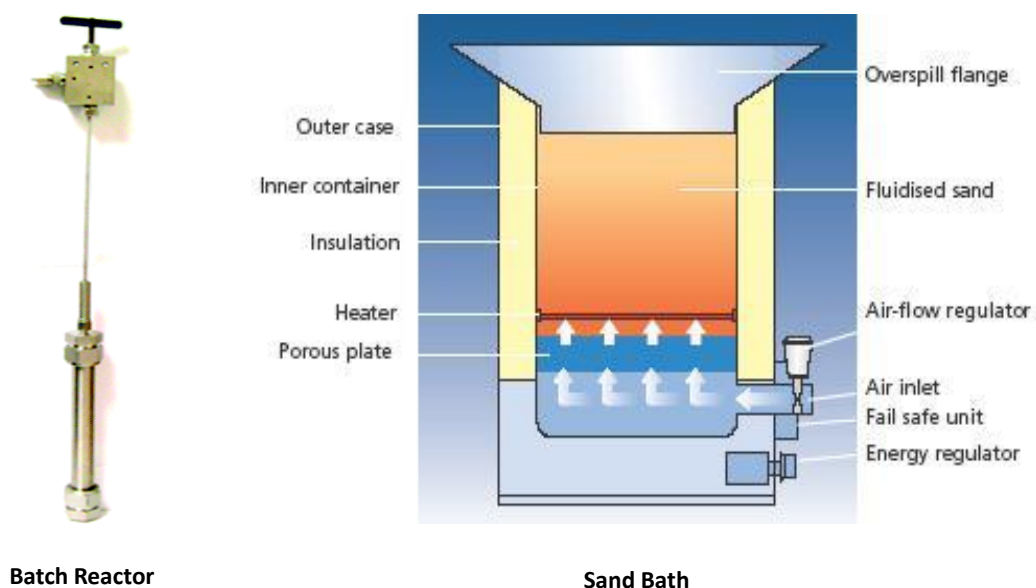
Figure 3.2: Schematic of the batch reactor system used for hydrothermal processing of glucose and cellobiose. The reactor system consists of a batch reactor and a sand bath.[64]

Semi-continuous Reactor System

The hydrothermal processing of cellulose and mallee wood was carried out in the same semi-continuous reactor system primarily used in a previous study.[49] The schematic of the system used is shown in Figure 3.2.
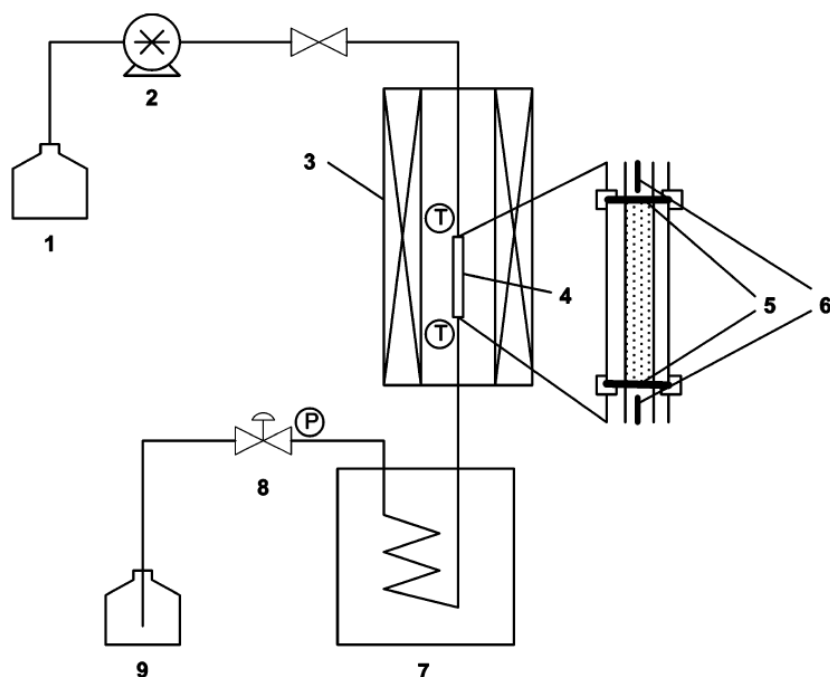
Figure 3.3: Schematic diagram of the semi-continuous reactor system used for hydrothermal processing of cellulose and biomass. The reactor system consists of: (1) water reservoir; (2) HPLC pump; (3) infrared image furnace; (4) sample chamber; (5) sintered stainless steel filter; (6) thermocouple; (7) ice water bath ; (8) pressure regulator; (9) liquid product collector.[49]

The reactor system mainly consisted of a HPLC pump, an infrared gold image furnace, an ice water bath and a pressure regulator. The HPLC pump (Alltech 627 HPLC pump) is used to deliver a constant flow (e.g. 20 mL/min) of water to the system. The water was preheated to the hydrolysis temperature in the furnace before entering to the sample chamber. The sample chamber used was a SUS316 stainless steel tubular reactor celled with silver-plated stainless-steel gasket filters placed at the front and end of the tubular reactor to retain the cellulose and biomass samples in the reactor. The effluent from the reactor was rapidly quenched to 0 °C by using a stainless-steel tube coil submerged in an ice water bath. The back-pressure regulator located right after the cooling unit was used to regulate the pressure of the HCW (e.g., 10 MPa). The liquid product was sampled at the outlet.

3.3.3 **Sample Preparation**

Objective 1 and 2 (hydrothermal decomposition of glucose and cellobiose).

The solutions were prepared at a concentration of 1 g/L in water and various GVL/water mixtures (at a wide range of GVL concentration of 0.03–75% on a volume basis). In each experiment, ~10 ml of glucose or cellobiose solution was loaded into the reactor, and the loaded solution was estimated to occupy 95% of the reactor volume. After purging with helium to remove the air in the reactor, the reactor was submerged vertically into a fluidized sand bath (model: Techne SBL-2) to preheat the reactor to desired reaction temperatures in 3 minutes. After holding at the reaction temperature for a desired reaction time (i.e. 5–120 min), the reactor was lifted from the sand bath and placed in an ice water bath to rapidly cool the reactor to room temperature.

Objective 3 (hydrothermal decompostion of cellulose of biomass).

The cellulose was first sieved for a size fraction at 75-106μm. The hydrothermal treatment of cellulose was performed using a semi-continuous reactor system as used in our previous studies with detailed descriptions and procedures for operation elsewhere.[42, 81, 82] Based on the previous study on the primary liquid products from cellulose hydrothermal treatment[82], an optimal reaction condition (temperature at 250 °C, flow rate at 20 mL/min, sample loading at 15 mg, pressure at 10 MPa) with minimized secondary products was chosen to understand the solvent effect of GVL on cellulose decomposition. The binary GVL/water solvents were prepared with GVL concentrations range from 0.5% to 20% based on volume. For each experiment, ~15 mg of cellulose (or ~50 mg of mallee wood) was weighted and charged into the reactor cell. Prior to hydrothermal processing in HCW, the sample was leached with water at room temperature with 10 mL/min of ultrapure water (resistivity >18.2 MΩ-cm) delivered by a HPLC pump for 30 min to remove water-soluble AAEM species. Then, the reactor was pressurised to 10 MPa. The hydrolysis began by heating reactor and water rapidly (in 2 mins) to hydrolysis temperatures (150–250 °C) and the temperature was held constant for a certain period of time. The reactor effluent was immediately quenched with an ice water bath to minimise any subsequent secondary

reaction of the liquid product. The liquid product was sampled at designated time intervals (2.5–10 mins). The TOC, and saccharides of the liquid product were analysed swiftly after each experiment. The TOC content was analysed by a TOC analyser. The total saccharide in the liquid sample was analysed via HPAEC–PAD system following post-hydrolysis. The details of the instrument and analytical techniques used are given in Section 3.3.4. Experiments with various flow rates (i.e. 5–20 ml/min) were also performed for further understanding on the solvent effect at various reaction times. After each experiment, the liquid samples were prepared for post-hydrolysis and freeze-drying separately. The post-hydrolysis experiments were conducted to determine the glucose recovery, following a NREL method.[196] The freeze drying of liquid samples were performed by a freeze dryer (Alpha 2-4 L Dplus, Martin Christ) with 48 hours for main drying at 65 °C and 24 hours for final drying at 55 °C to remove the solvents including GVL and water. The dried samples were then dissolved with deionized water for characterization. Experiments for biomass hydrothermal treatment were also performed with the same semi-continuous reactor system with water and GVL/water (GVL concentration at 0.5% and 5% on a volume basis) as solvents. The contents of arabinan, galactan, glucan, xylan and mannan of the mallee wood biomass were also determined by the NREL method.

Objective 4 (hydrothermal processing of glucose and fructose in multiple aqueous organic co-solvents).

Glucose and fructose solutions were prepared at a concentration of 1 g/L with various aqueous organic solvents prepared by mixing the chosen solvents with deionized water at 10% on a volume basis, respectively. The experiments were performed at 175–225 °C with reaction time at 10–120 min for glucose samples and 150–200 °C at 10–120 min for fructose in a familiar stainless steel batch reactor as used in previous studies[64, 197].

3.3.4 Sample Characterization

The glucose derived products (e.g. fructose, mannose, 5-HMF, glycoaldehyde, levoglucosan LGA) and monosaccharides (arabinan, galactan, glucan, xylan, mannan) from hydrothermal processing of biomass were analysed using a HPAEC–PAD system using a method described in an earlier study[59] after post-hydrolysis. The HPAEC-PAD system is essentially a Dionex ICS-3000 ion chromatography system equipped with pulsed electrochemical detection (PAD with Au electrode and Ag/AgCl reference). In order to achieve an adequate separation of arabinose, galactose, glucose, xylose and mannose with CarbonPac PA20 analytical and guard columns, a gradient program listed in **Error! Reference source not found.** was used. The total flow rate of the eluent was maintained at 0.5 mL/min. To ensure sufficient linearity of the detector respond, post-column base addition was required. 0.4 mL/min of 300 mM NaOH was added to analytical column effluent by using a PEEK flow path HPLC pump, For protecting the analytical column and adequate peak resolutions, the post-hydrolysis samples were diluted at least 5 times with ultrapure water prior to sample injection to reduce the concentration of sulphuric acid down in the sample to < 0.8 wt%.

The cellobiose derived products (e.g. cellobiose, glucosyl-fructose (GF), glucosyl-mannose (GM), glucose) were also analysed using another HPAEC–PAD system with a method introduced elsewhere.[91] The HPAEC–PAD is essentially a Dionex ICS–5000 ion chromatography system equipped with pulsed electrochemical detection (PAD with Au electrode and Ag/AgCl reference). In order to achieve an adequate separation of the isomer and epimer of cellobiose with CarbonPac PA20 analytical column, a gradient program listed in Table 3.2 was used. The total flow rate of the eluent was maintained at 0.5 mL/min.

Table 3.1: HPAEC–PAD gradient program used for separation of monosaccharides and glucose derived products

Time	Eluent		
	A (%) 0.3M NaAc in 0.1M NaOH	B (%) 0.3 M NaOH	C (%) Water
0.0	0	0	100
30.0	0	0	100
30.5	100	0	0
33.5	100	0	0
34.0	0	100	0
40.0	0	100	0
40.5	0	0	100
55.0	0	0	100

Table 3.2: HPAEC–PAD gradient program used for separation of cellobiose and cellobiose derived chemicals

Time	Eluent	
	A (%) Water	B (%) 0.1 M NaOH
0.0	95	5
15.0	95	5
15.5	100	5
45.0	100	60
45.5	10	90
65.0	10	90
65.5	95	5
95.0	95	5

The cellulose derived glucose oligomers were analysed with the same Dionex ICS-5000 ion chromatography system equipped with pulsed electrochemical detection (PAD) and mass spectrometry (MS). A schematic of the system is illustrated in Figure 3.4. It should be noted that the samples were separated by Dionex CarbonPac PA20 and PA200 columns separately with programs listed in

Table 3.3 and Table 3.4, respectively, in order to achieve a better separation of isomers and epimers of different oligomers. The methods were introduced as follows. After separating the sample by the column (PA20 or PA200) with corresponding eluent program, the flow was split into two streams for PAD and MS analyses separately. It should be noted that a suppressor was used for the stream to MS as an in-line desalter to reduce the pH of the eluent as high eluent pH (10 or higher) are not

compatible with MS. After desalting, 0.05mL/min of 0.5 mM of LiCl solution was added into the stream to assist in ionization of the sugars in mass spectrometer.
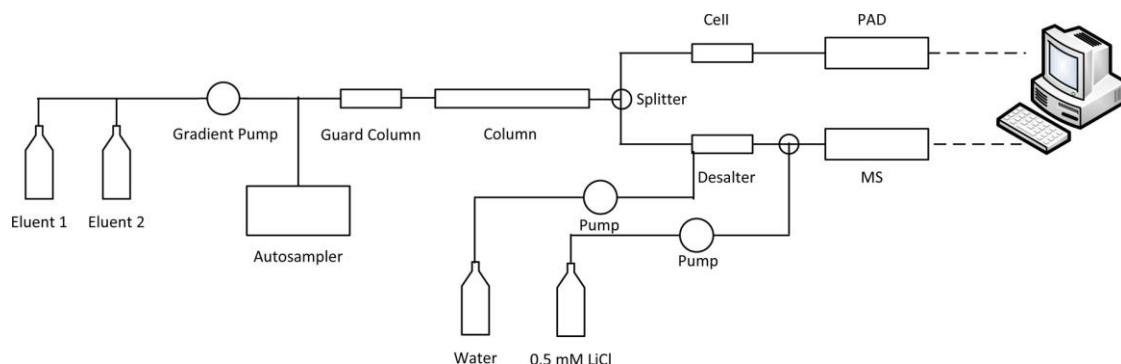
Figure 3.4: Schematic diagram of the HPAEC–PAD–MS system.

Table 3.3: HPAEC–PAD gradient program used for separation of oligomers at lower DPs (DP1–DP4)

Time	Eluent	
	A (%) Water	B (%) 0.1 M NaOH
0.0	0	5
10.0	0	5
10.5	100	5
40.0	100	60
120.0	0	100
120.5	0	5
135.0	0	5

Table 3.4: HPAEC–PAD gradient program used for separation of oligomers at higher DPs (DP >5)

Time	Eluent	
	A (%) 0.5M NaAc in 0.1M NaOH	B (%) 0.1 M NaOH
0.0	4	96
30.0	45	55
35.0	45	55
35.5	4	96
45.0	4	96

Figure 3.5 shows a sample chromatogram from the analysis of a liquid sample from decomposition of cellulose in HCW at 270 °C separated using Dionex CarboPAc

PA200. From the chromatogram, the extracted MS peaks suggested that the shoulder peaks of oligomers from DP5–DP8 have the same molecular weight with the corresponding main peaks, indicating that these peaks were well separated. However, this PA200 column failed to separate the isomer peaks of glucose oligomers with DP1–DP4. To achieve a better separation of the DP1–DP4 and their isomers, Dionex CarboPac PA20 column was used and the corresponded chromatogram is present in Figure 3.6. Overall, a method for the separation and characterization of the isomers of glucose oligomers at different DPs (DP1–DP8) using the HPAEC–PAD–MS system was developed.
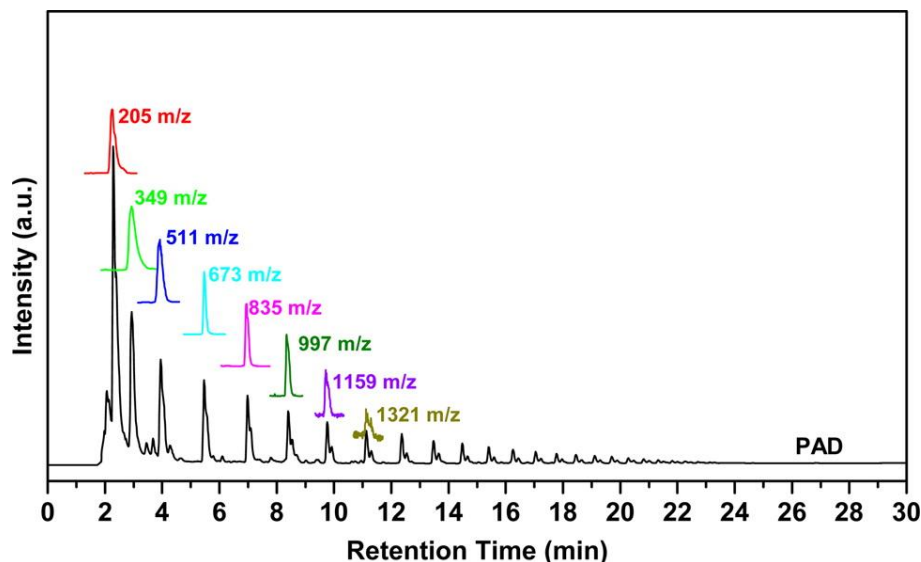
Figure 3.5: HPAEC–PAD–MS analysis of a liquid sample from cellulose decomposition in HCW at 270 °C. Column, Dionex CarboPac PA200 analytic column; eluents, 20–225 mM sodium acetate and 100 mM NaOH over 30 min at a flow rate of 0.5 mL min^{-1}; suppressor, Dionex AERS 500 (4 mm); suppressor current, 186 mA; MS detection mode, ESI positive; probe temperature, 450 °C; cone voltage, 75 V; and needle voltage, 3.5 kV.
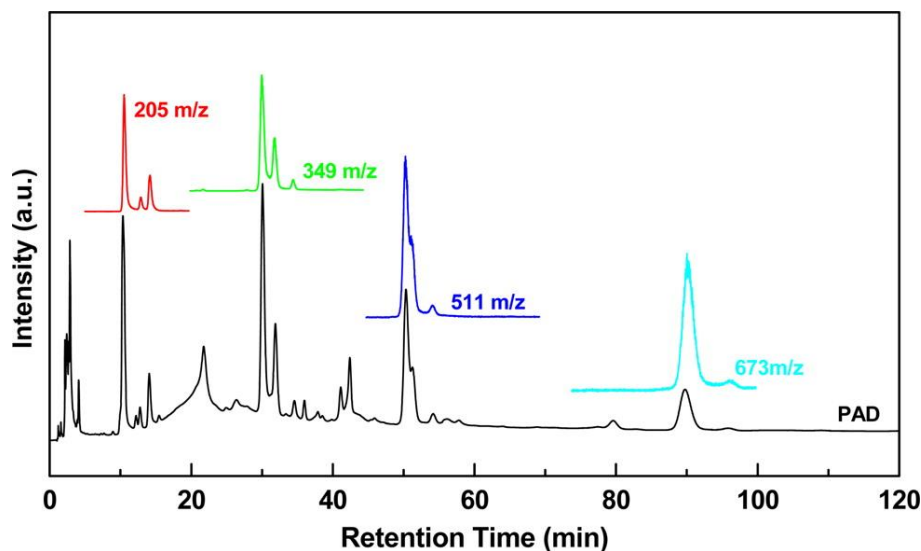
Figure 3.6: HPAEC–PAD–MS analysis of a liquid sample from cellulose decomposition in HCW at 270 °C. Column, Dionex CarboPac PA20 analytic column; eluents, 5 mM NaOH for the first 10 min, 5–60 mM NaOH over the following 30 min, and 60–100 mM NaOH over the following 80 min at a flow rate of 0.5 mL min^{-1}; suppressor, Dionex AERS 500 (4 mm); suppressor current, 186 mA; MS detection mode, ESI positive; probe temperature, 450 °C; cone voltage, 75 V; and needle voltage, 3.5 kV.

Moreover, the total organic carbon (TOC) of liquid samples from cellulose decomposition with water as solvent was characterized by a carbon analyser (Shimadzu Model TOC-V$_{CPH}$).

3.4   Data Acquisition and Processing

3.4.1   Conversion, Yield and Selectivity

After quantification of glucose, cellobiose and decomposition products using HPAEC-PAD and HPAEC-PAD/MS, the conversion (X), the yield (Y_i) and the selectivity (S_i) of a compound i at a reaction time of t were calculated based on the following equations:

$$X = \frac{C_0 - C_i}{C_0} \tag{3.1}$$

$$Y_i = \frac{C_i * a_i}{C_0 * a_0} \tag{3.2}$$

$$S_i = \frac{Y_i}{X} = \frac{C_i * a_i}{(C_0 - C_i) * a_0} \tag{3.3}$$

where C_i is the concentration of a compound i in the liquid sample after reaction; C_0 and is the concentrations of the feedstock before reaction and after reaction; a_i is the carbon content for a compound i; and a_0 is the carbon content of feedstock.

To ensure the repeatability of the results obtained from this research, all experiments were carried out at least in duplicates. The average value along with the error bar (standard error) of the data is reported.

3.4.2 **Kinetics**

Assuming the glucose and cellobiose decomposition follows the first-order kinetics, the reaction rate k (s^{-1}) of glucose and cellobiose decomposition was determined by equation (4):

$$-ln\frac{C(t)}{C(0)} = k\tau \tag{3.4}$$

where τ (s) is the reaction time.

According to the delplot method,[198] the reaction rate (k_i) for a certain reaction was further determined using the following equations:

$$\frac{k_i}{k} = \lim_{n \to 0} S_i = \lim_{n \to 0} \frac{Y_i}{X} \tag{3.5}$$

3.5 **Summary**

Model compounds including glucose, cellobiose and cellulose were hydrothermally treated in water and the mixture with GVL at different concentrations under acid free conditions, in order to understand the solvent effect of GVL on the hydrothermal processing of biomass derived sugars. Furthermore, GVL/water mixtures were used on mallee wood biomass to understand the solvent effect of GVL on biomass processing. The products were characterized by HPAEC–PAD and HPAEC–PAD–MS systems.

The yield and selectivity of each product was calculated and discussed based on the experimental results. The reaction mechanisms of model compounds were further understood based on the contributions of primary reactions. Thus, the solvent effect of GVL on the transformation of model compounds was studied. Furthermore, the effect of GVL on the kinetics of each model compound was also insight based on the first-order kinetics. The effect of GVL on the hydrothermal treatment of biomass was further understood based on the yields of each monosaccharide.

Chapter 4: Mechanisms and Kinetics of Glucose Conversion in Hot-Compressed Gamma-Valerolactone/Water

4.1   Introduction

As introduced in Chapter 2, biomass refinery is of great significance as a sustainable technology to partially solve the energy-deficit problem, and ease the environmental pressure that caused by the over emission of CO_2 due to the burning of fossil fuels. One of the key technologies for biorefinery is hydrothermal processing. For hydrothermal processing, the employment of solvents as an optimal reaction medium benefits the production of ideal products, reduces environmental pollution, and lowers down the requirement in reaction conditions (e.g. equipment, temperature, pressure, catalysts, etc.). Recently, various solvents (e.g., acetone, methanol, gamma-valerolactone) have been studied for biomass hydrothermal processing [17-26], among which gamma-valerolactone (GVL) has its advantages on several aspects. First, GVL is harmless and renewable as a biomass derived chemical. Second, GVL is stable with low melting point and low vapour pressure[178] that can stand with hydrothermal conditions. Third, GVL is miscible with water and can be easily separated from GVL-water mixtures. Thus, GVL is recommended as a promising solvent for biomass processing.

Previous studies have provided insight into the effects of GVL on the performance of acids for biomass decomposition[33] and proposed different methods to apply hot-compressed GVL/water (HCGW) on biomass processing including the pretreatment or fractionation, and the hydrothermal treatment of biomass derived platform chemicals[33, 189, 199, 200]. However, the effect of GVL on the chemistry of other sugars including various monomers and biomass derived glucose polymers under acid free hydrothermal conditions remains unclear.

As the most abundant monomer from lignocellulosic biomass decomposition, glucose plays an important role for the multi-application of biomass, the reaction pathways of which under hydrothermal conditions have been widely researched including splitting (or retro-aldol condensation), dehydration, isomerization, epimerization, and reversion reactions.[29, 112, 114, 156, 157, 201, 202] One of the key value-added chemicals from glucose transformation is 5-HMF. The production of 5-HMF from glucose processing is influenced by various factors including catalysts, reaction equipment, primary concentrations, pressure and temperature, as well as the reaction solvents [29, 80, 156, 203, 204]. A previous study indicated that glucose processing in aqueous polar aprotic solvents including THF, GVL and DMSO could enhance 5-HMF yield in a cost effective way with sulfuric acid as catalyst.[205] However, to the best of my knowledge, the reaction mechanism and kinetics of glucose decomposition in GVL/water are not well studied.

Hence, this chapter is carried out to understand the conversion of glucose in HCGW under catalyst-free hydrothermal conditions.

4.2   Yields of Various Products during Glucose Decomposition in HCGW

In absence of GVL, glucose decomposition in hot-compressed water (HCW) mainly proceeds with isomerization reaction to produce fructose and mannose, dehydration reactions to produce 5-HMF and levoglucosan (LGA), and retro-aldol condensation reactions to glyceraldehyde, glycolaldehyde and fructose.[80, 118] The selectivities of those reactions largely depend on reaction parameters such as temperature, pressure and initial concentration. In this study, similar products were identified from glucose decomposition in HCGW, such as 5-HMF, fructose, mannose, and levoglucosan (LGA). The yields of glucose and its main decomposition products in GVL/water mixtures at different GVL concentrations (0–75%) are shown in Figure 4.1 and only some typical results (0, 5 and 50%) are presented in Figure 4.2. It can be found that GVL addition suppresses the glucose conversion in HCGW. For example, glucose conversion at 175 °C and 120 mins reduces from ~37% in water, to ~30% in 5%

GVL/water, further to ~25% in 50% GVL/water. At 225 °C, almost all glucose is converted after 50 mins in water, compared to only ~80% of glucose conversion in 50% GVL/water under the same condition.

Among the identified products, 5-HMF has the highest yield, ranging from ~45% in water to ~58% in 5% GVL/water. Further observation on the yields of 5-HMF shows that the yields of 5-HMF increases from 1% GVL/water (maximal yield at ~50% after 20 min at 225 °C) to 5% GVL/water (maximal yield at ~58% after 40 min at 225 °C), followed by slight decreases to 75% GVL/water (maximal yield at ~50% after 50 min at 225 °C). The yield of LGA is also enhanced with GVL addition. As shown in Further observation on the yields of 5-HMF shows that the yields of 5-HMF increases from 1% GVL/water (maximal yield at ~50% after 20 min at 225 °C) to 5% GVL/water (maximal yield at ~58% after 40 min at 225 °C), followed by slight decreases to 75% GVL/water (maximal yield at ~50% after 50 min at 225 °C).

The yields of decomposition products are strongly dependent on the reaction conditions. At 175 °C, the yields of all products increase with reaction time under the current conditions. When the temperature increases to 200 °C, only the 5-HMF yield increases with reaction time while the yields of other products decrease with reaction time. At 225 °C, the yield of 5-HMF first increases with reaction time until a maximal value is achieved, followed by a reduction with a further increase in reaction time. The maximal 5-HMF yield increases from 45% in water to 58% in 5% GVL/water, followed by a slight reduction to 51% in 50% GVL/water. GVL addition seems to increase the yield of LGA but decrease the yield of fructose.
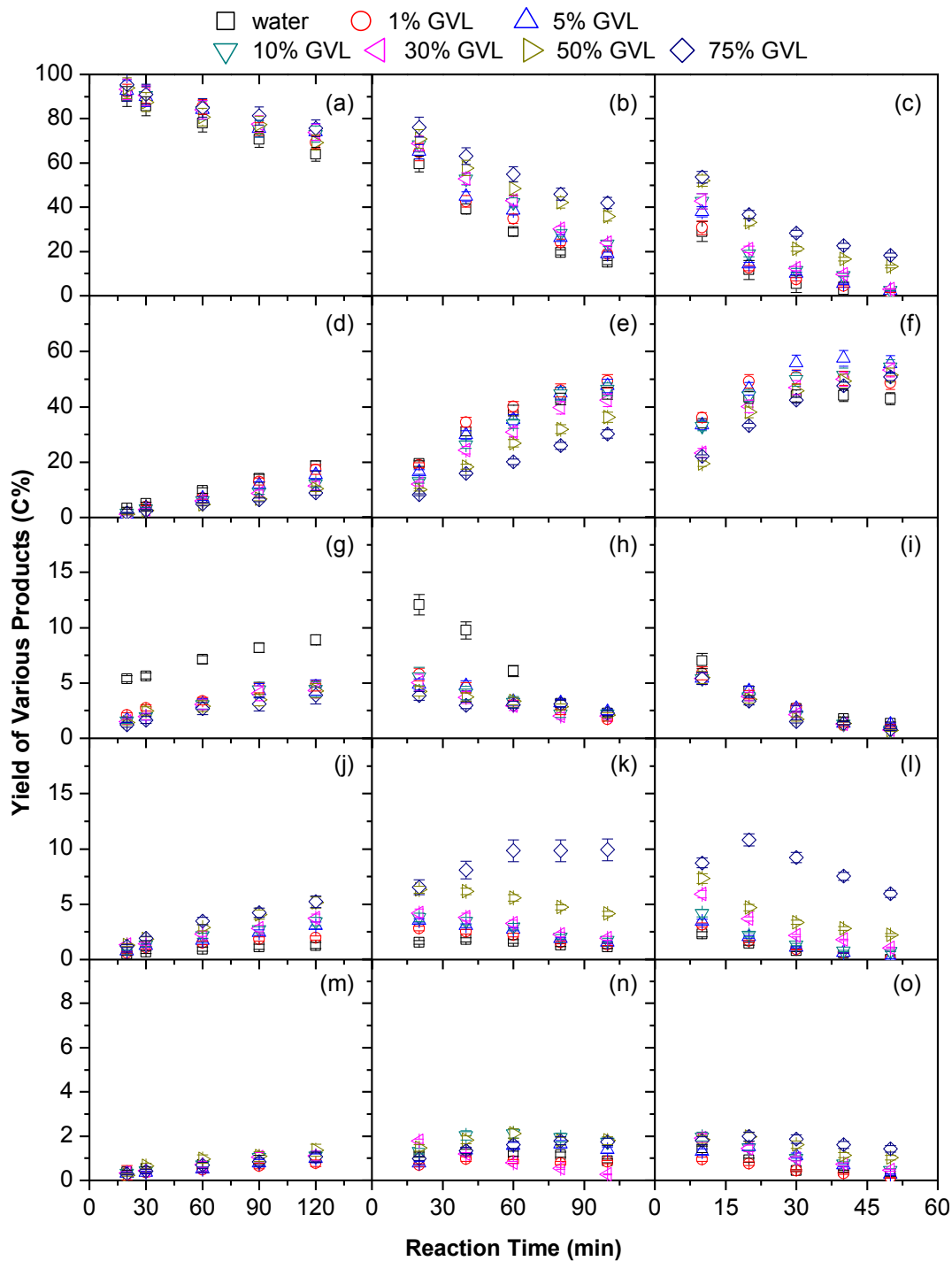
Figure 4.1: Yield of detectable products from glucose decomposition at various temperatures and GVL-water binary mixtures present by various reaction temperatures. a-c glucose at 175-225 ℃; d-f 5-HMF at 175- 225 ℃; g-i fructose at 175-225 ℃; j-l levoglucosan at 175-225 ℃; m-o mannose at 175-225 ℃.
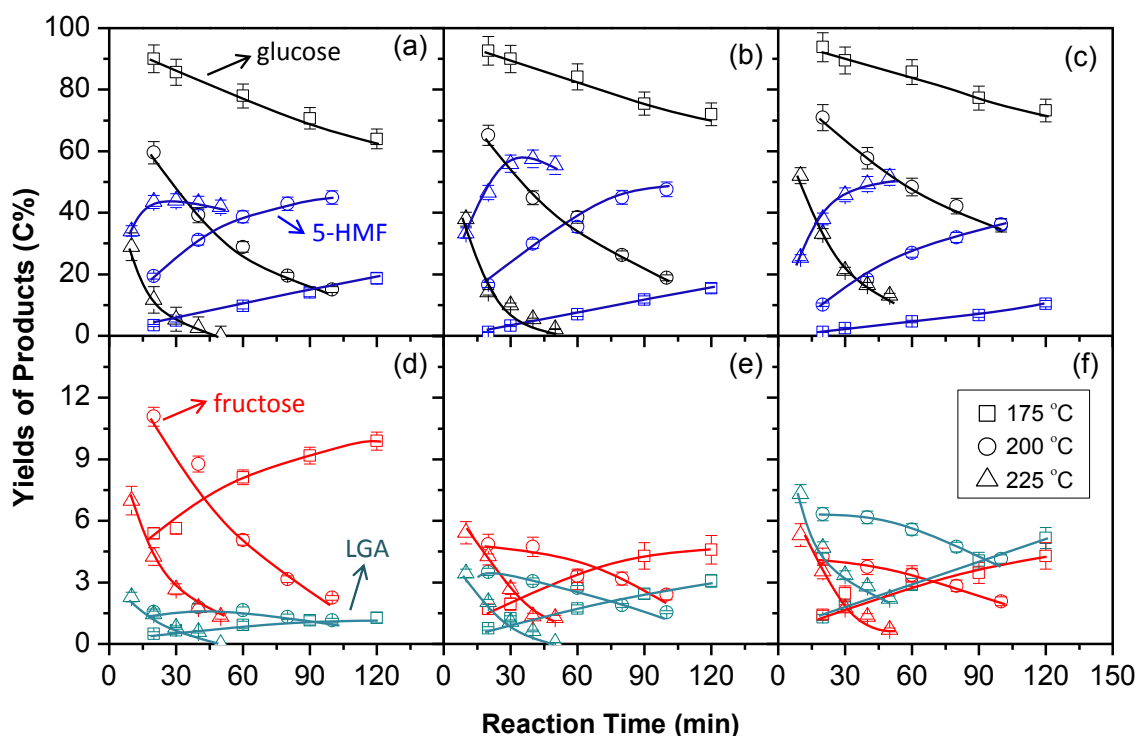
Figure 4.2: Yield of glucose, 5-HMF, fructose and LGA at various temperatures and GVL-water binary mixtures. (a) glucose and 5-HMF in water; (b) glucose and 5-HMF in GVL/water (5/95); (c) glucose and 5-HMF in GVL/water (50/50); (d) fructose and LGA in water; (e) fructose and LGA in GVL/water (5/95); (f) fructose and LGA in GVL/water (50/50).

4.3   Selectivities of Products during Glucose Decomposition in HCGW

Based on the concentrations of various products in the liquid sample, the selectivities of major products were calculated on a carbon basis and plotted as a function of glucose conversion in Figure 4.3 and Figure 4.4. As shown in Figure 4.3, the selectivities of 5-HMF in water and 1–30% GVL/water increase continuously from the beginning (glucose conversion at ~5%) to the maximum (glucose conversion at ~60%), followed by decreases till the end of glucose conversion. However, the selectivities for 50–75% GVL/water increase continuously during the whole process of glucose conversion (~5–80%). The selectivity of LGA decreases continuously till the minimum with the progress of reaction likely via hydrolysis to glucose or further

dehydration to levoglucosenone (LGO), which is an isomer of 5-HMF verified in the previous study.[205] The selectivities of fructose and mannose also decrease continuously under all conditions with the progress of glucose conversion, and the selectivity of fructose at the same glucose conversion decreases with the increase of GVL concentration. For example, at glucose conversion at ~5%, the selectivity of fructose continuously decreases from ~63% in water to at ~20% in 75% GVL/water.
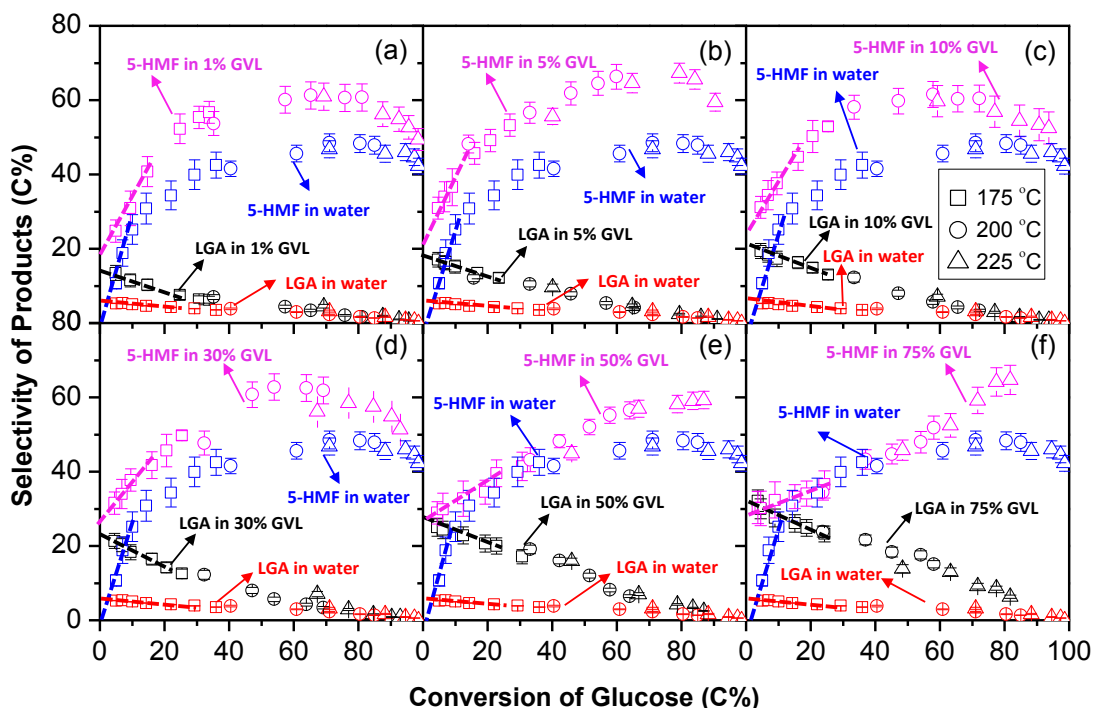
Figure 4.3: Selectivity of 5-HMF (1) and LGA (3) in GVL as a function of glucose conversion compared with that in water (2 and 4). (a) water and GVL/water (1/99); (b) water and GVL/water (5/95); (c) water and GVL/water (10/90); (d) water and GVL/water (30/70); (e) water and GVL/water (50/50); (f) water and GVL/water (75/25).

The contributions of various primary reactions can be further estimated via a delplot method.[91, 198, 206] Since glucose decomposition is fast at high temperatures, this study only estimated the contribution of various reactions at 175 °C, and the results are shown in Figure 4.5. As expected, the isomerization reaction to produce fructose is the dominant primary reaction of glucose decomposition in water, with dehydration and

epimerization as two minor primary reactions to produce LGA and mannose, respectively. It should be noted that, dehydration reaction to produce 5-HMF, which is not a primary reaction of glucose decomposition in water, becomes an important primary reaction of glucose decomposition in GVL/water.
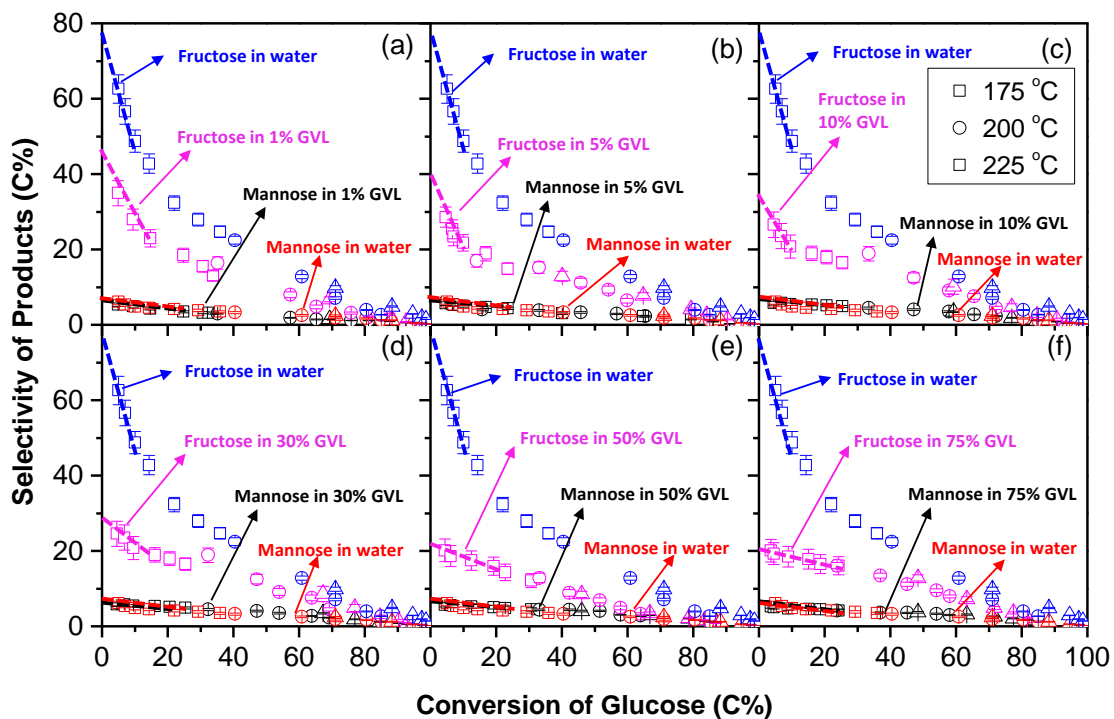
Figure 4.4: Selectivity of fructose (1) and mannose (3) in GVL as a function of glucose conversion compared with that in water (2 and 4). (a) water and GVL/water (1/99); (b) water and GVL/water (5/95); (c) water and GVL/water (10/90); (d) water and GVL/water (30/70); (e) water and GVL/water (50/50); (f) water and GVL/water (75/25).

The contribution of isomerization reaction reduces as the GVL concentration increases, i.e., from ~78% in water to ~40% in 5% GVL/water, final to ~20% in 75% GVL/water. In contrast, the dehydration reactions to produce LGA and 5-HMF increase with GVL concentration. For example, the contributions of dehydration reactions to produce LGA and 5-HMF increase from ~5 and 0% in water to ~12 and ~22% in 5% GVL/water, and finally to ~30 and 32% in 75% GVL/water, respectively. Compared to other primary reactions, the contribution of epimerization reaction to mannose maintains at ~6% for all conditions with negligible changes.
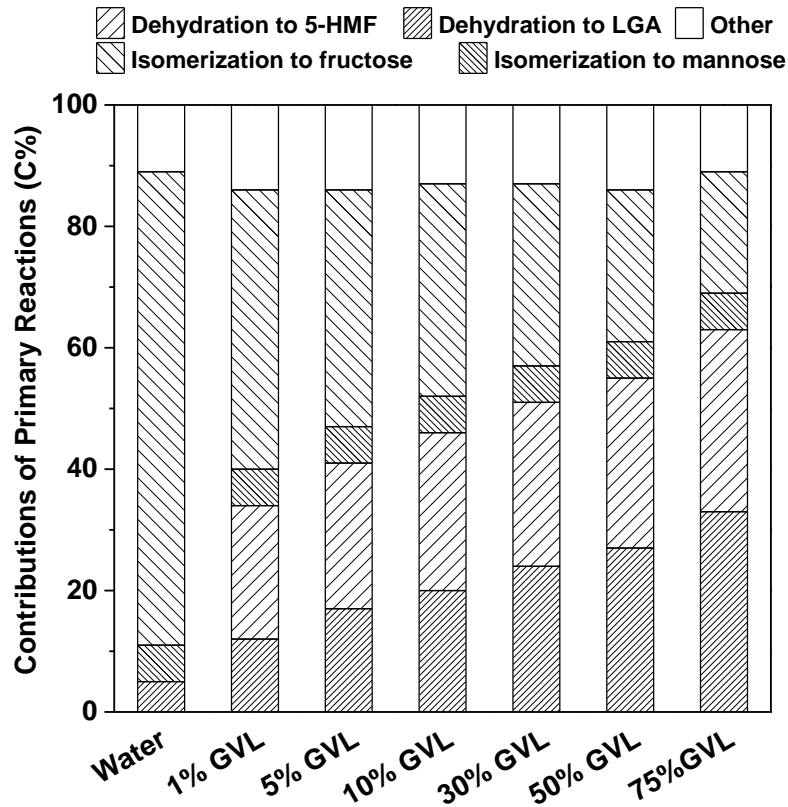
Figure 4.5: Contribution of primary reactions in water and various GVL/water mixtures.

Overall, these four primary reactions account for 85−90% of reaction during glucose decomposition in HCGW. Other primary reactions may exist, such as retro-aldol condensation reaction to produce glyceraldehyde and erythrose.[80, 111, 118] However, no other primary products were detected in this study, possibly due to the extensive dilution (i.e., 200−500 times dilution depending on GVL concentration) required for sample analysis in this study.

4.4 Kinetics of Glucose Decomposition in HCGW

The above results show significant changes in kinetics of glucose decomposition in HCGW. In this study, further efforts are taken to analyze the kinetics of glucose decomposition in various GVL/water mixtures. As shown in Figure 4.6, linear relationships between $-\ln[C(t)/C(0)]$ and reaction time t at all conditions can be easily

seen, indicating that glucose decomposition in HCGW follows first-order reaction kinetics, and the reaction rate constants were further calculated and the results are present in Table 4.1. As shown, the reaction rate constant of glucose decomposition increases with the enhancement of reaction temperature of HCW and HCGW. For example, the reaction rate constant is 0.0034 in HCW at 175 °C, which is increased to 0.0181 at 200 °C and 0.0794 at 225 °C. It can also be found that GVL addition reduces the reaction rate constant of glucose decomposition in HCGW at all temperatures. For example, the reaction rate constant at 175 °C reduces from 0.0034 min^{-1} in water to 0.0025 min^{-1} in 5% GVL/water, finally to 0.0020 min^{-1} in 75% GVL/water.

According to the contribution of each primary reaction in above section, the reaction rate constant of each primary reaction during glucose decomposition in HCGW at 175 °C can be obtained. The correlation between the reaction rate constant at 175 °C and the GVL concentration were further evaluated to show the effect of GVL on the kinetics of each primary reaction. As shown in Figure 4.8, fairly good correlations can be found between the reaction rate constants and GVL concentrations. The reaction rate constants of isomerization reactions linearly decrease with the increase of GVL concentraion; while those of dehydration reactions increases with the increase of GVL concentration.This clearly indicates that isomerization and epimerization reactions are more favored in water, while the dehydration reactions are more preferred in GVL.

The kinetic parameters were further estimated based on the reaction rate constants at different temperatures (the Arrhenius plot is present in Figure 4.7), and the results are also presented in Table 4.1. It is interesting to see that both activation energy and pre-exponential factor decrease with an increase in GVL concentration. For example, the activation energy reduces from ~117 kJ/mol in water to ~96 kJ/mol in 75% GVL/water. Considering the increasing contribution of dehydration reactions as GVL concentration increases, it is suggested that the activation energy of dehydration reaction is reduced at higher GVL concentrations.
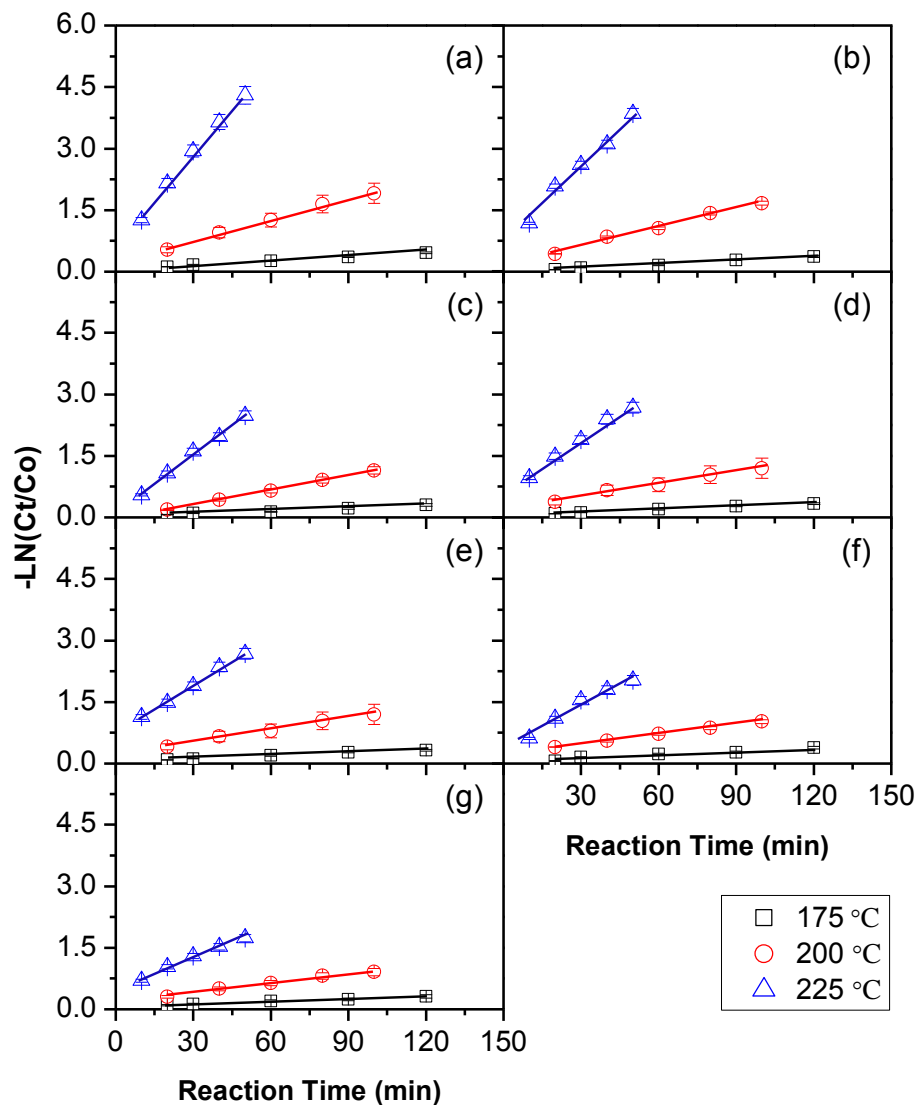
Figure 4.6: Correlation between –Ln[C(t)/C(0)] and reaction time for glucose decomposition in water and GVL-water binary mixtures, where C(0) and C(t) represent the concentration of glucose at the reactant and product after a reaction time t. (a) water; (b) 1% GVL; (c) 5% GVL; (d) 30% GVL; (e) 50% GVL; (f) 75% GVL.
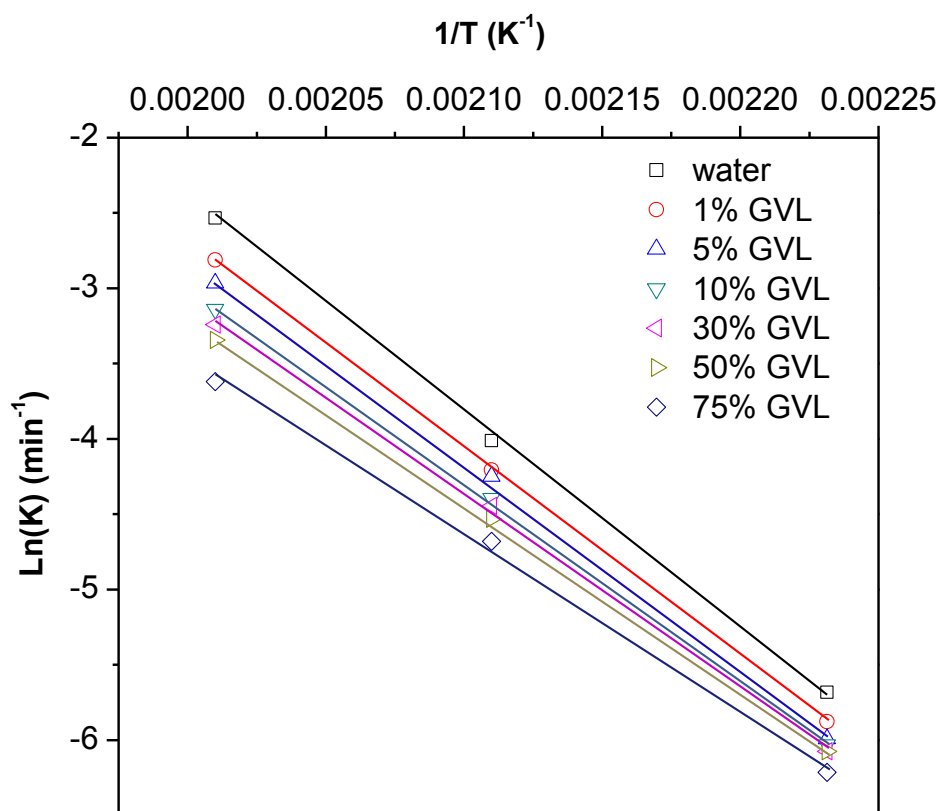
Figure 4.7: Arrhenius plots of glucose decomposition in water and GVL/water mixtures at various GVL concentrations.

Table 4.1: Reaction rate constant and activation energy at various conditions

	reaction rate constant (min^{-1})			activation energy ($kJ\ mol^{-1}$)	pre-exponential factor (min^{-1})
	175 °C	200 °C	225 °C		
water	0.0034	0.0181	0.0794	117	1.5×10^{11}
1% GVL	0.0028	0.0152	0.0600	114	5.4×10^{10}
5% GVL	0.0025	0.0117	0.0515	112	2.9×10^{10}
10% GVL	0.0024	0.0101	0.0433	107	7.4×10^{9}
30% GVL	0.0023	0.0096	0.0391	105	4.0×10^{9}
50% GVL	0.0023	0.0088	0.0353	101	1.4×10^{9}
75% GVL	0.0020	0.0076	0.0268	96	3.3×10^{8}
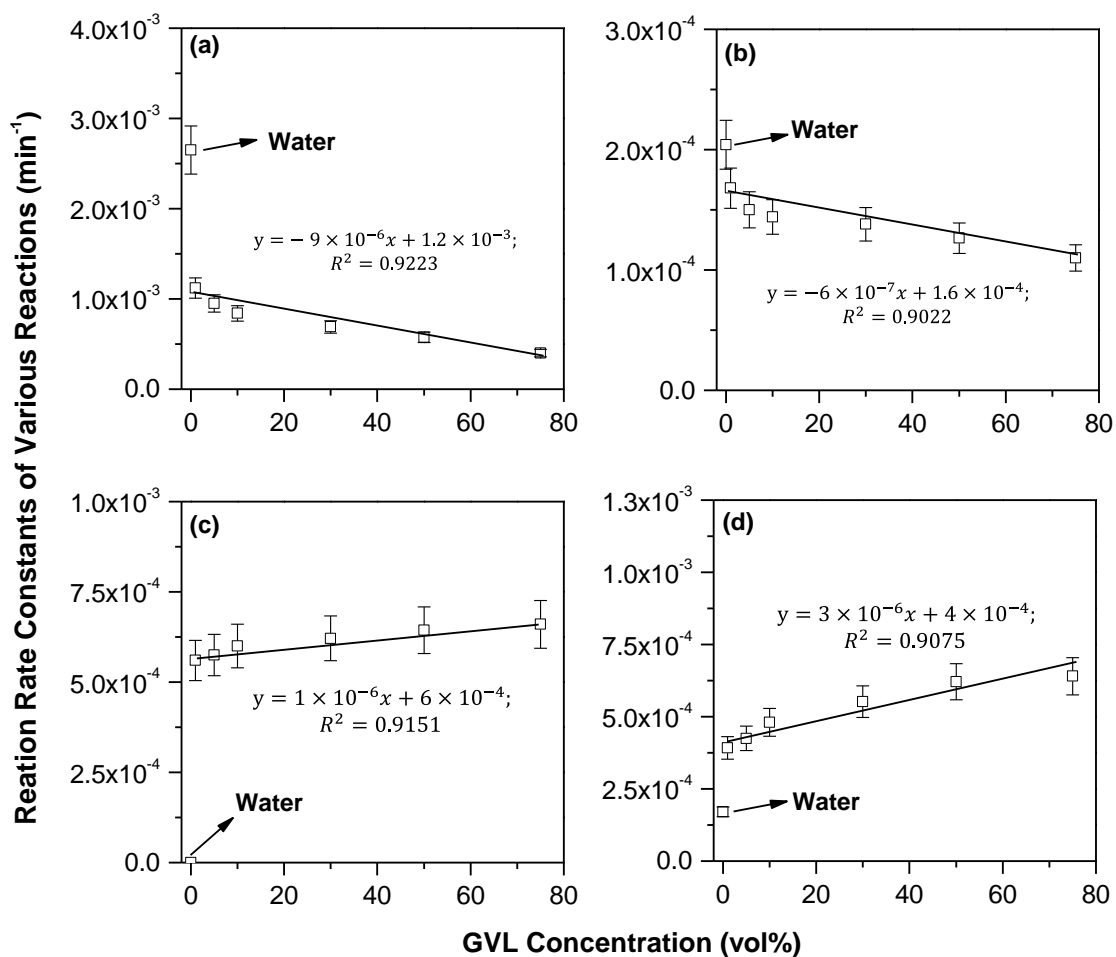
Figure 4.8: Correlation between the GVL concentration of GVL/water mixtures and the reaction rate constants of various reactions. (a) isomerization; (b) epimerization; (c) dehydration to 5-HMF; (d) dehydration to LGA.

4.5   Reaction Mechanism of Glucose Decomposition in HCGW

The above results clearly show that the reaction mechanism of glucose decomposition in HCGW is significantly different from that in HCW. According to the results in this study, the reaction pathways of glucose decomposition in HCW and HCGW are summarized in Figure 4.10. Apart from those reactions (i.e., isomerization reaction to fructose, epimerization reaction to mannose, dehydration to LGA) reported for glucose decomposition in HCW, a new reaction pathway, which is the direct dehydration of glucose to 5-HMF, is confirmed to be the primary reaction of glucose decomposition

in HCGW. Particularly, it seems that the reaction rate constants of dehydration reactions linearly increase with GVL concentration, while the reaction rate constants of isomerization and epimerization reactions linearly decrease with GVL concentration. This clearly indicates the important solvent effect of GVL in changing the reaction pathways of glucose decomposition.

Further discussion on the solvent effect of GVL is given as follows. As shown, the dominant primary reaction of glucose in HCW is isomerization to fructose, which is suppressed in HCGW. In contrast, the dehydration reaction from glucose to LGA is enhanced in HCGW. Moreover, the dehydration of glucose to 5-HMF is shown to be a primary reaction in HCGW. Interestingly, the reaction from glucose to fructose and that from glucose to 5-HMF have the same intermediate (i.e., HMF intermediate in the cyclic mechanism, or 1,2-enediol in the open chain mechanism), which is initiated by the protonation of the C2-OH of glucose.[207, 208] After the generation of the intermediate, following transformation happens either through the hydride transfer from C2 to C1 to produce fructose or through the proton-catalysed C2-O2 bond breaking and C2-O5 bond forming to produce 5-HMF (Figure 4.9).
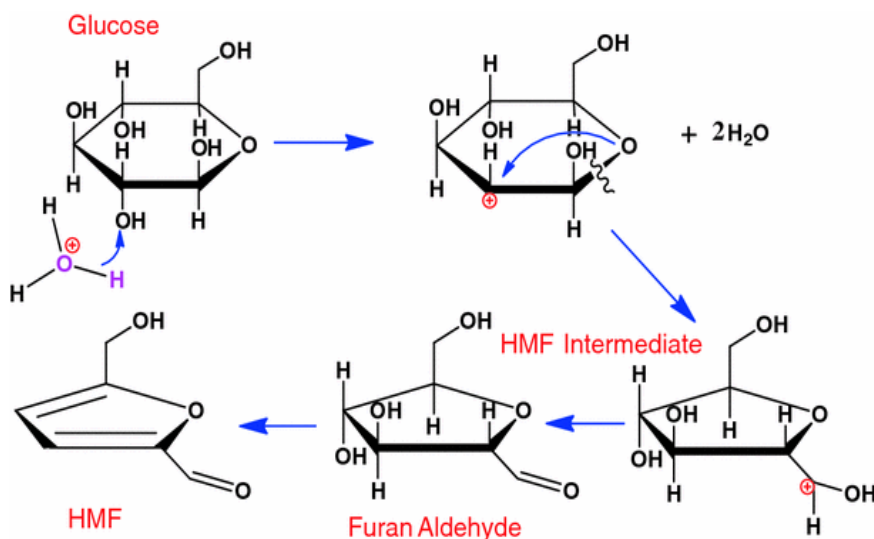
Figure 4.9: Proposed reaction pathways of glucose decomposition in hot-compressed water[209]

First, GVL addition appears to influence the protonation of glucose during its decomposition. Simulation studies[16, 210] have demonstrated that both dehydration of

glucose to 5-HMF and isomerization of glucose to fructose have the same reaction intermediate (i.e., HMF intermediate in the cyclic mechanism, or 1,2-enediol in the open chain mechanism), which is initiated by the protonation of the C2-OH of glucose. After the generation of the intermediate, it can be transformed into either fructose via the hydride transfer from C2 to C1 or 5-HMF via the proton-catalysed C2-O2 bond breaking and C2-O5 bond forming. The hydride transfer is preferred in HCW because the energy barrier for C2-C1 hydride transfer is lower than that of C2-O2 bond breaking in water.[209] Thus, the isomerization to fructose is the dominant primary reaction of glucose decomposition in HCW, while the dehydration of glucose to 5-HMF is suppressed. However, the protonation of glucose intermediates is greatly influenced by the solvent system. Moreover, the presence of aprotic solvents such as DMSO, THF, and DMF has been studied to suppress the hydride transfer and enhance the C2-O2 breaking. Thus, it is plausible that the presence of GVL, another aprotic solvent, also causes the same effect onto the transformation of glucose intermediate. Nevertheless, the presence of aprotic solvents also reduces the distribution of water on the surface of glucose molecules[211], which can enhance the dehydration of glucose to LGA via direct dehydration between C1 and C6 hydride groups, because the dehydration of glucose to LGA is preferred under unwatered conditions[212].

Second, GVL addition likely influences the conformation of glucose, which can change the reaction pathways of glucose decomposition in HCGW. In fact, a previous study has shown that the major conformation for glucose is β-D-glucopyranose, which is preferred for the isomerization to fructose; while β-D-glucofuranose for the dehydration to 5-HMF is suppressed in HCW by in situ NMR analysis[213]. An *in situ* study on fructose decomposition in different solvents (i.e., water, methanol, DMSO) has also demonstrated that the β-D-fructopyronose is the dominant conformation in water, which is preferred for the isomerization from fructose to glucose; but in DMSO, β-D-fructopyronose is suppressed and β-D-fructofuranose is enhanced, which is preferred for the dehydration to 5-HMF[214]. Therefore, our results indicate that the presence of GVL changes the glucose conformation in HCGW, which is preferred for dehydration reactions.

The results in this study also have important implications for the production of value-added products (i.e., 5-HMF) from glucose. It is known that 5-HMF cannot be directly produced from glucose in HCW, leading to a low 5-HMF yield and selectivity. However, the presence of GVL can change the reaction pathways, making 5-HMF directly produced from glucose dehydration in HCGW as a primary product. Other major primary products from glucose decomposition in HCGW, such as fructose and LGA, can also be easily converted into 5-HMF via secondary reactions [205, 215, 216], resulting in an improved 5-HMF yield (i.e., 58% in 5% GVL) in HCGW, compared to that of 45% in HCW. This clearly demonstrates that GVL/water co-solvent is more suitable than water for 5-HMF production from glucose. Future optimization of solvent systems and process parameters may further improve the 5-HMF yield from glucose.
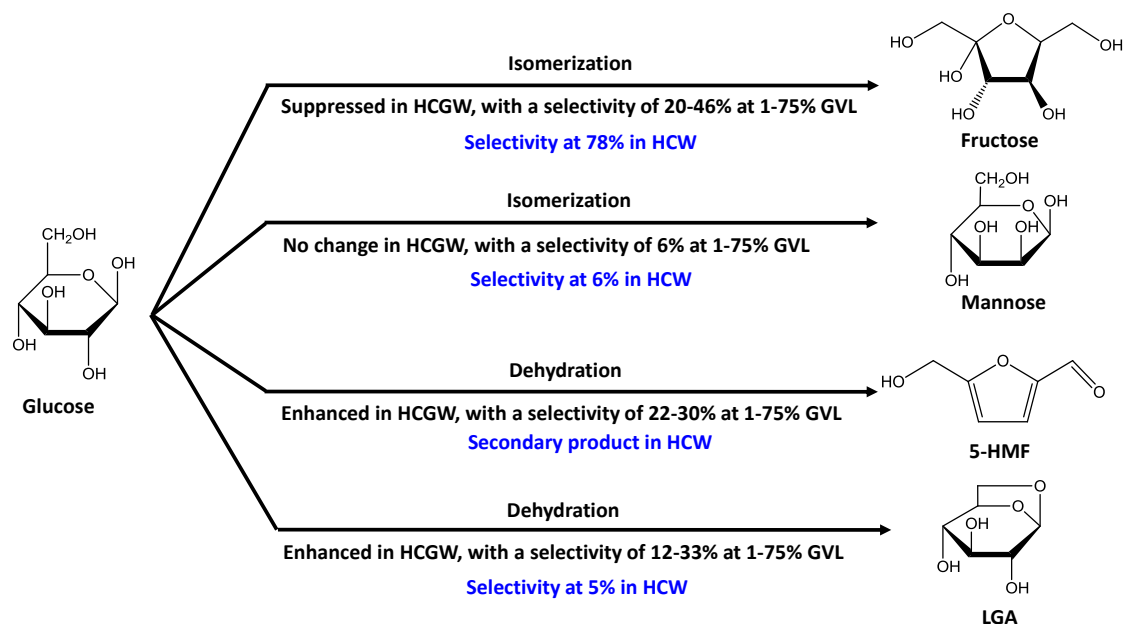
Figure 4.10: Proposed reaction pathways of glucose decomposition in hot-compressed water (HCW) and hot compressed GVL/water (HCGW).

4.6   Conclusion

This study investigates the mechanism and kinetics of glucose decomposition in HCGW at various GVL concentrations of 0−75 vol% and temperatures of 175−225 °C.

Our results show that primary reaction pathways of glucose decomposition are greatly affected by GVL addition, shifting from isomerization to dehydration reactions as the GVL concentration increases. Particularly, direct dehydration of glucose to 5-HMF is found to take place during glucose decomposition in HCGW, contributing to 20–30% of primary reactions at 175 °C depending on the GVL concentration. The contribution of dehydration to LGA is also enhanced, i.e., from 12 to 33% as the GVL concentration increases from 1 to 75 %. In contrast, isomerization reaction to fructose is largely suppressed in HCGW, only contributing to 20–46% of primary reactions at 175 °C. Moreover, the reaction rate constants of various primary reactions is found to correlate well with the GVL concentrations, with the reaction rate constants of isomerization reactions decreasing almost linearly with the GVL concentration while those of dehydration reactions increasing almost linearly with the GVL concentration. This study clearly demonstrates that GVL/water co-solvent is more suitable than water to produce biofuels and value-added biochemicals (i.e., 5-HMF) from glucose, due to the enhanced dehydration reactions.

Chapter 5: Mechanisms and Kinetics of Cellobiose Decomposition in Hot-Compressed Gamma-Valerolactone/Water

5.1   Introduction

As concluded in Chapter 2, GVL is a promising biomass derived organic solvent for biomass hydrothermal treatment. While GVL has been widely used for biomass hydrothermal processing,[31, 33, 195] the underlying reaction mechanism during biomass hydrothermal processing in GVL/water system is not well studied. Under acidic conditions, GVL can increase the hydrolysis reaction rate and reduce the activation energy for biomass hydrolysis.[33] However, little has been reported on the effect of GVL during biomass hydrothermal processing under acid-free conditions. In Chapter 3 of this thesis, the solvent effect of GVL onto the conversion of glucose was investigated. Hot-compressed GVL/water (HCGW) was proved to change the reaction pathways and kinetics of glucose conversion. However, the has been no study on the solvent effect of GVL onto the decomposition of biomass derived oligomers. In this regard, this study employs cellobiose, a biomass derived oligomer, to investigate the fundamental reaction mechanisms of cellobiose decomposition in HCGW under acid-free conditions.

5.2   Yields of Primary Products during Cellobiose Decomposition

At temperatures below 300 °C, cellobiose decomposition in hot-compressed water (HCW) proceeds via four primary reactions, including the isomerization to produce cellobiulose (glucosyl-fructose, GF) at selectivity of 63-81% and glucosyl-mannose (GM) at selectivity of 8-12%, the hydrolysis reaction to produce glucose at a selectivity of 6−27%, and the retro-aldol reaction to glucosyl-erythrose (GE) and glycolaldehyde at a selectivity of <5%.[100] It should be noted that this study only presents the data for GF and glucose, which account for 80–88% of the primary

products during cellobiose decomposition in HCGW, depending on the reaction conditions. Other primary products (i.e., GM, GE, and glycolaldehyde) could be present in the sample but could not be detected because of the low concentration of these products and the high dilution (200–1000 times) required for the GVL/water samples to eliminate the inference of GVL during HPAEC–PAD analysis.

Figure 5.1 presents the yields of cellobiose, glucose and GF at 150–200 °C in HCW and HCGW. It can be seen that the effect of GVL addition on cellobiose conversion is negligible at GVL concentrations <1%. However, GVL addition increases cellobiose conversion as GVL concentration increases from 1% to 25%. Further increasing the GVL concentration to 75% actually suppresses cellobiose conversion. For example, after 60 min reaction time at 175 °C, cellobiose conversion reduces from ~80% at 25% GVL concentration, to ~74% at 50% GVL concentration, then dramatically to ~46% at 75% GVL concentration. The results show that the presence of GVL only enhances cellobiose conversion at GVL concentrations <25% and excessive GVL in the GVL/water mixture inhibits cellobiose decomposition reactions.

It is interesting to note that while the addition of GVL in water at concentrations <1% has little effect on cellobiose conversion, a significant reduction in GF yield can be clearly seen, with its maximal yield decreasing from ~20% in water to ~5% at 1% GVL concentration. The results demonstrate that the addition of GVL substantially suppresses the isomerization reactions during cellobiose decomposition. It is also interesting to see that the GF yield continues to decrease as the GVL concentration increases from 1% to 10%. At GVL concentrations >25%, GF almost completely disappears in the products.

On the contrary, the addition of GVL greatly enhances the production of glucose but only at GVL concentrations up to 25%. At 150 and 175 °C, the glucose yield increases continuously with reaction time under the current reaction conditions. However, as temperature further increases to 200 °C, glucose decomposition becomes important so that the glucose yield first increases with reaction time to a maximum, followed by a

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reduction as the reaction time further increases. It is noted that in comparison to merely ~30% for cellobiose decomposition in water, the maximal glucose yield increases to ~66% at 25% GVL concentration. However, a further increase in GVL concentration to 75% leads no further increase in the glucose yield.
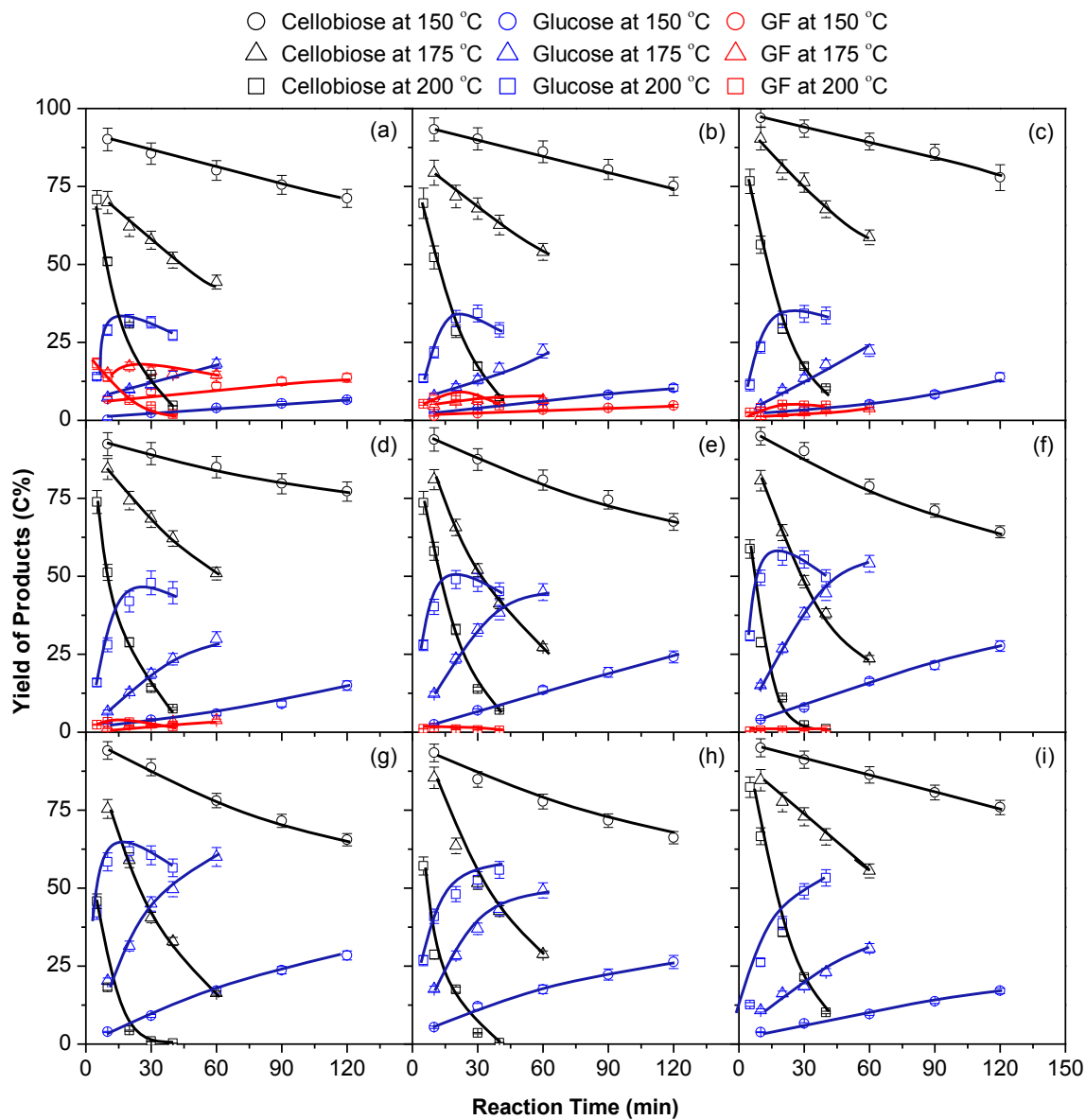
Figure 5.1: Yields of cellobiose, glucose and glucosyl-fructose (GF) at 150–200 °C in HCW and HCGW. (a) water; (b) 0.03% GVL; (c) 0.3% GVL; (d) 1% GVL; (e) 5% GVL; (f) 10% GVL; (g) 25% GVL; (h) 50% GVL; (i) 75% GVL.

5.3   Selectivities of Primary Products during Cellobiose Decomposition

Figure 5.2 and Figure 5.3 further present the selectivities of glucose and GF as a function of cellobiose conversion in HCW and HCGW, respectively. There are significant differences in the selectivity of glucose during cellobiose decomposition in water and GVL/water mixtures. As shown in Figure 5.2a, the glucose selectivity during cellobiose decomposition in water is initially low but continuously increases until a high cellobiose conversion, followed by a reduction as cellobiose conversion further increases. For example, the glucose selectivity in water increases from ~9% at ~5% cellobiose conversion to a maximum of ~33% at ~90% cellobiose conversion.

In HCGW, the trends of glucose selectivity vs cellobiose conversion are totally different (see Figure 5.2b-i). Only at very low GVL concentrations (i.e., 0.03%), the glucose selectivity first increases to a maximum with the conversion of cellobiose, followed by a reduction as cellobiose conversion further increases. Another interesting finding is that the initial glucose selectivity increases greatly even at very low GVL concentrations. For example, at 0.03% GVL concentration, the glucose selectivity increases from ~37% at ~7% cellobiose conversion to a maximum of ~51% at a ~46% cellobiose conversion, and then reduces gradually at increased cellobiose conversions. At higher GVL concentrations (>0.3%), there are negligible changes in glucose selectivity at early conversions (<25%), but it starts to decrease at mid conversions. Moreover, the initial glucose selectivity seems to increase with GVL concentration, i.e., from ~57% (at ~3% conversion) for 0.3% GVL concentration to ~81% (at ~5% conversion) for 10% GVL concentration. A further increase in GVL concentration doesn't leads to an increase in the initial glucose selectivity.

The GF selectivity also changes significantly in HCGW, as show in Figure 5.3. Although the GF selectivity continuously decreases as cellobiose conversion increases, the initial GF selectivity reduces dramatically when the GVL concentration increases. Even at very low GVL concentrations (e.g., 0.03%), the GF selectivity at 150 °C reduces by over half, from ~69% (at ~10% conversion) for water to ~34% (at ~7%

conversion) at 0.03% GVL concentration. As the GVL concentration further increases, the GF selectivity rapidly decreases to close to zero at 10% GVL concentration. At higher GVL concentrations (>10%), GF cannot be detected under all conditions in this study, clearly indicating the elimination of isomerization reactions in GVL/water mixtures. Therefore, the results clearly show that the isomerization reactions during cellobiose decomposition can be suppressed (or even eliminated) in GVL/water mixtures, depending on the GVL concentration.

To obtain further information on the contribution of primary reactions during cellobiose decomposition in HCGW, the delplot method[198] was used to estimate the rate constant ratio of each primary reaction (i.e., hydrolysis and isomerization) to overall cellobiose decomposition, based on the intercept of the selectivity of primary products (i.e., glucose and GF) at cellobiose conversion approaching zero. It should be noted that only the selectivity of primary products at early conversions (i.e., <25%) can be used to estimate the rate constant ratio of primary reactions. Thus, the results in this study only allow us to estimate the rate constant ratios of hydrolysis and isomerization reactions at 150 °C. As shown in Figure 5.4, the contribution of hydrolysis reaction to cellobiose decomposition continuously increases with increasing GVL concentration, from ~8% for water, to ~35% for only 0.03% GVL concentration, then to ~65% for 1% GVL concentration. The contribution of hydrolysis reaction stabilizes at ~80% when the GVL concentration increases to 10%, and a further increase in GVL concentration leads to negligible changes in the contribution of hydrolysis reaction to overall cellobiose decomposition. In contrast, the contribution of isomerization reaction to produce GF reduces drastically from ~80% in water to ~47% in GVL/water mixture at a GVL concentration of 0.03%. No isomerization reaction to produce GF even takes place at GVL concentrations >10%.
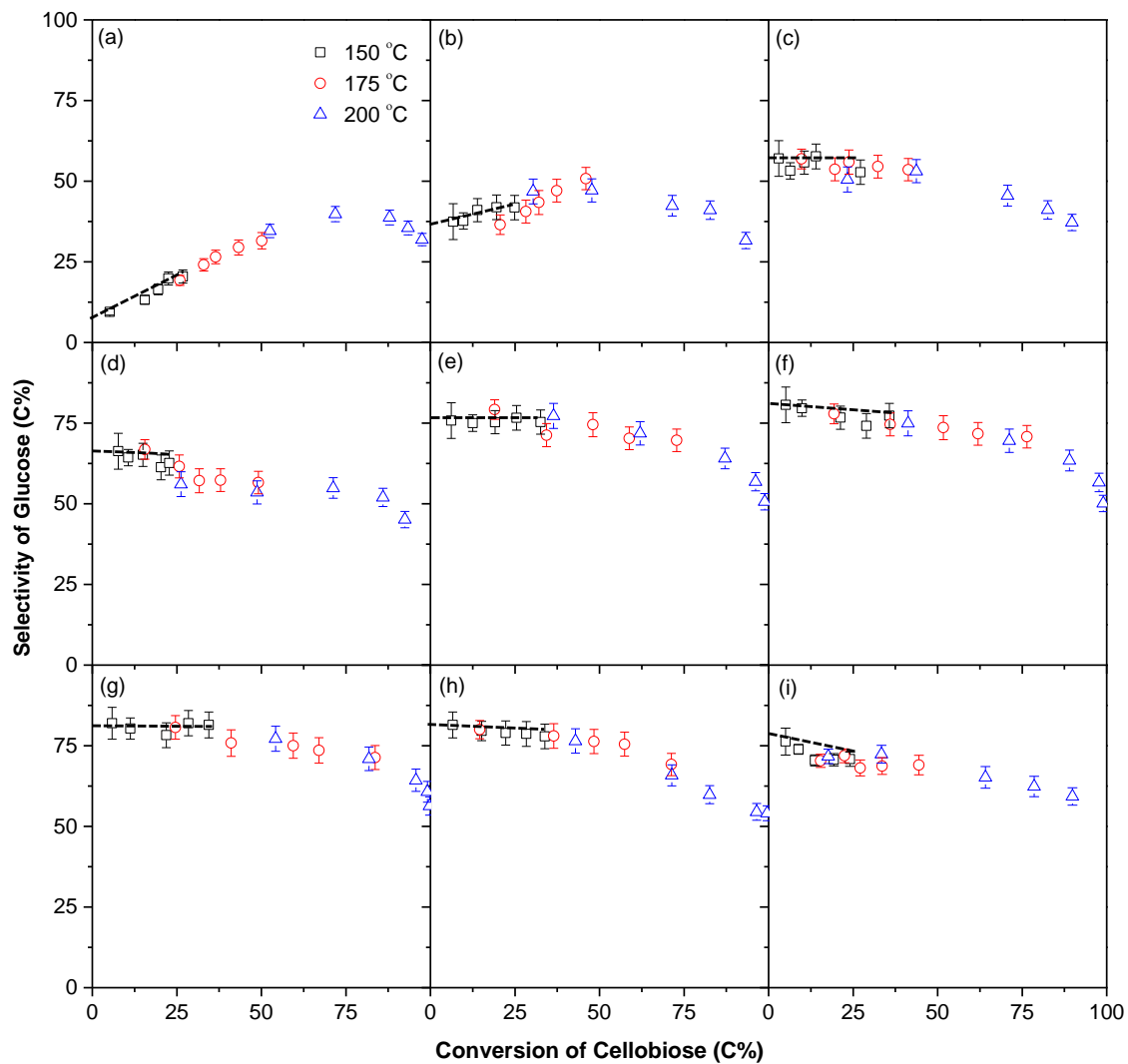
Figure 5.2: Selectivity of glucose as a function of cellobiose conversion at 150−200 °C in HCW and HCGW. (a) water; (b) 0.03% GVL ; (c) 0.3% GVL; (d) 1% GVL; (e) 5% GVL; (f) 10% GVL; (g) 25% GVL; (h) 50% GVL; (i) 75% GVL.
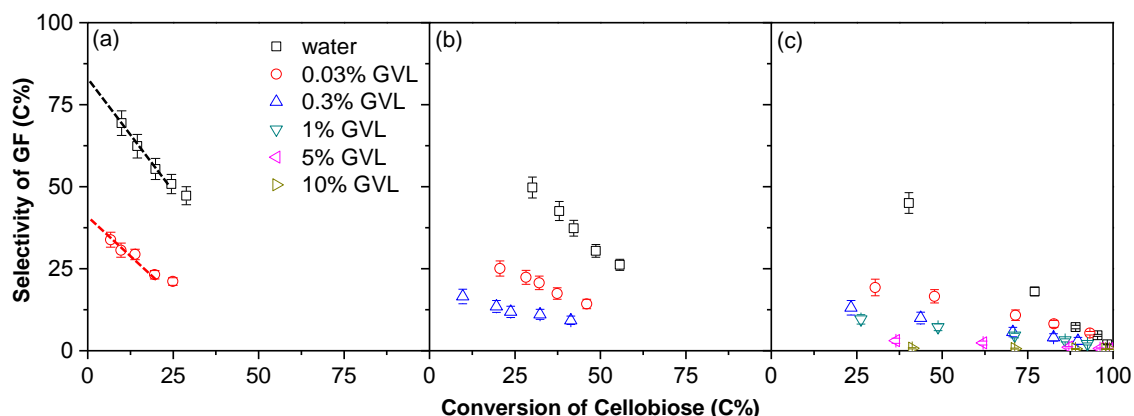
Figure 5.3: Selectivity of GF as a function of cellobiose conversion at 150−200 °C in HCW and HCGW. (a) 150 °C; (b) 175 °C; (c) 200 °C.
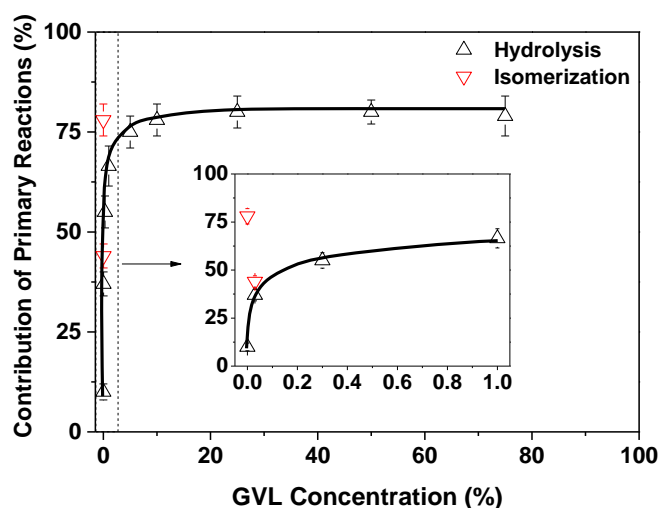
Figure 5.4: Contribution of hydrolysis and isomerization reactions at various GVL concentrations during cellobiose decomposition in HCGW at 150 °C.

5.4 Kinetics of Cellobiose Decomposition in HCW and HCGW

Further analyses were made to investigate the kinetics of cellobiose decomposition in water and GVL/water mixture. As shown in Figure 5.5, cellobiose decomposition in GVL/water mixtures indeed follows the first-order reaction kinetics. This is evident by the linear relationship between $-ln[C(t)/C(0)]$ and reaction time t for all reaction conditions. The reaction rate constant was then calculated and the results are presented

in Table 5.1. There is negligible difference in the reaction rate constants of cellobiose decomposition in water and low GVL (<1%) concentrations, but the reaction rate constant starts to increase at 1% GVL concentration and are almost doubled at 5% GVL concentration. The reaction rate constant further increases when the GVL concentration increases to 25%, followed by a reduction with a further increase in GVL concentration to 75%. It is also noted that the reaction rate constants for 75% GVL concentration are similar to those for water.
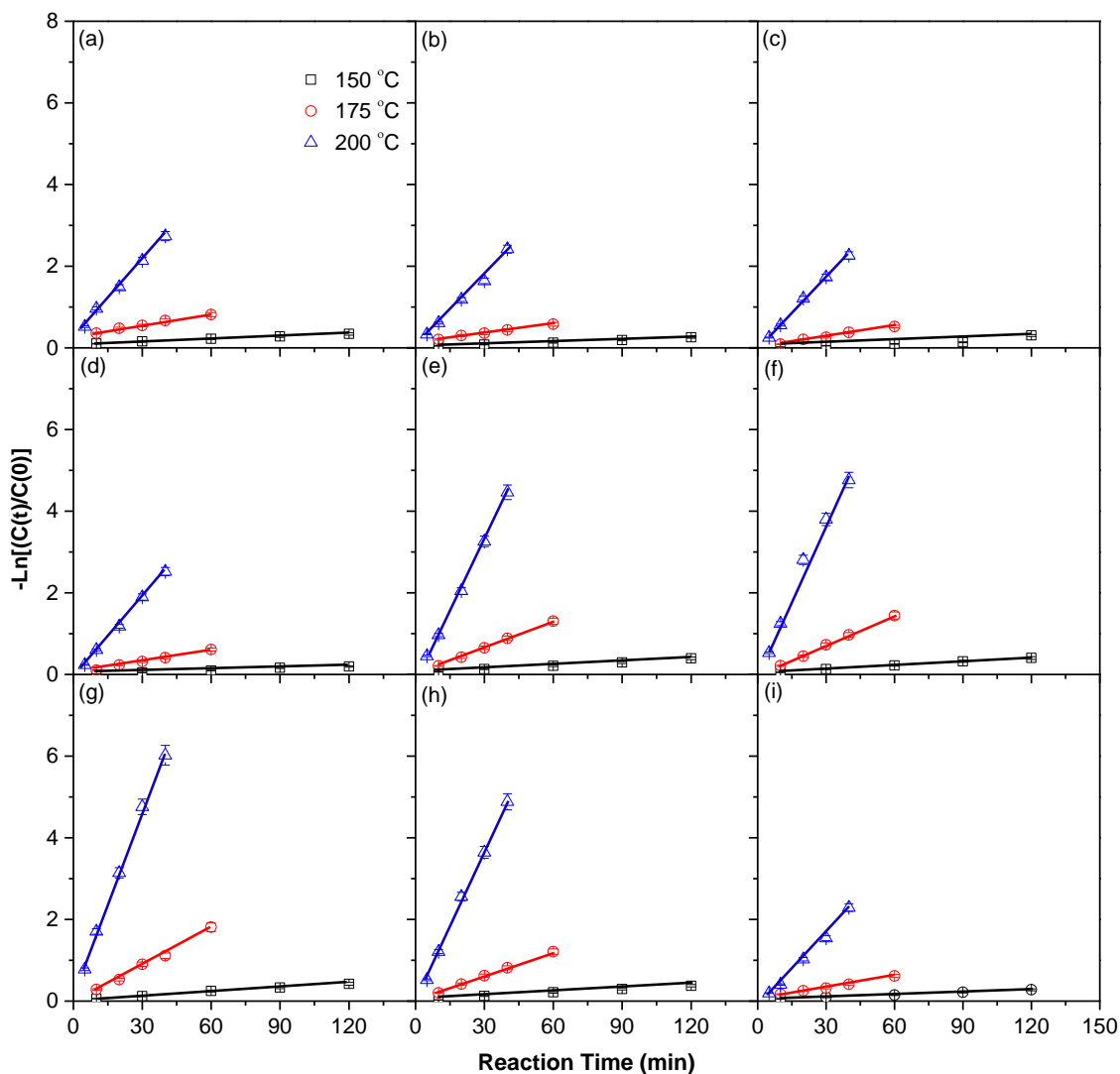
Figure 5.5: Correlations between $-\mathrm{Ln}[C(t)/C(0)]$ and reaction time for cellobiose decomposition in water and GVL/water mixtures.

Based on the reaction rate constants at various temperatures, the activation energy and pre-exponential factor can be determined. As shown in Table 5.1, the activation energy of cellobiose decomposition slightly increases from ~119 to ~125 kJ mol^{-1} as the GVL concentration increases to 10%, and almost remains unchanged as the GVL concentration further increases to 25%, followed by a slight decrease to ~120 kJ mol^{-1} as the GVL concentration increases to 75%. However, the pre-exponential factor increases by one order with an increase in the GVL concentration from 0% to 25%, and then starts to decrease with a further increase in the GVL concentration to 75%. The slight increase in the activation energy during cellobiose decomposition at higher GVL concentrations is likely due to the increased contribution of hydrolysis reaction, which requires a higher activation energy to take place.[100]

Table 5.1: Reaction rates constant and kinetic parameters for cellobiose decomposition in water and GVL/water mixtures.

| | reaction rate constant (min^{-1}) | | | kinetic parameters | |
	150 °C	175 °C	200 °C	activation energy (kJ mol^{-1})	pre-exponential factor (min^{-1})
water	0.0017	0.0093	0.0566	119	6.7×10^{11}
0.03% GVL	0.0017	0.0094	0.0570	119	7.2×10^{11}
0.3% GVL	0.0019	0.0096	0.0576	119	8.0×10^{11}
1% GVL	0.0021	0.0099	0.0651	121	8.8×10^{11}
5% GVL	0.0029	0.0220	0.1187	124	5.4×10^{12}
10% GVL	0.0031	0.0237	0.1303	125	7.5×10^{12}
25% GVL	0.0036	0.0283	0.1503	125	8.3×10^{12}
50% GVL	0.0033	0.0236	0.1310	123	4.5×10^{12}
75% GVL	0.0017	0.0097	0.0583	120	3.0×10^{11}

5.5   Discussions on Cellobiose Decomposition Mechanism

The above results have clearly shown that cellobiose decomposition mechanism changes significantly in HCGW. The primary reactions of cellobiose decomposition in GVL/water mixture have been summarized in Figure 5.6. Several important findings can be observed by comparing the cellobiose decomposition mechanism in HCW and HCGW.

First, the isomerization reaction which dominates the cellobiose decomposition in HCW is suppressed or even eliminated in HCGW, depending on the GVL concentration. The domination of isomerization reaction during cellobiose decomposition in water is an important reason leading to a low glucose yield in water. The suppression of isomerization reactions in HCGW can greatly enhance the glucose selectivity under hydrothermal conditions, and such an effect is obviously due to the solvent effects of GVL. Solvent plays an important role in the selective conversion of sugar molecules (i.e., glucose) in solvent/water mixture by changing the local arrangement of solvents around the sugar molecules. The solvent competes strongly with water to coordinate with sugar molecules, leading to fewer water molecules in the first solvent shell of sugar molecules. According to a recent molecular simulation study on glucose isomerization,[217] intramolecular hydride transfer is considered as the rate limiting step of glucose isomerization reaction. The free energy barrier of intramolecular hydride transfer was calculated to be lower in water, due to the improved solvation of the transition state and the product state by water.[218] Therefore, it seems that the addition of GVL reduces the coordination of water with cellobiose and increase the free energy barrier of intramolecular hydride transfer, thus suppressing or eliminating isomerization reactions during cellobiose decomposition in GVL/water mixture.

Second, GVL addition significantly promotes the hydrolysis reaction. The increase of GVL concentration increases not only the selectivity of hydrolysis reaction but also the rate constant of hydrolysis reaction. At a GVL concentration of >10%, the

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contribution of hydrolysis reaction stabilized at ~80%. Considering that the overall rate constant of cellobiose decomposition is more than doubled at 10% GVL concentration, the increase in the rate constant of hydrolysis reaction is more significant (i.e., a factor of 17 at 150 °C). A previous work has reported that GVL can increase the reaction rate constant of acid-catalysed cellobiose hydrolysis by reducing the activation energy, due to the change in the acidic proton stabilization relative to the protonated transition state in aprotic organic solvents. However, the activation energy under acid-free condition in this study doesn't reduce in HCGW. In fact, the pre-exponential factor increases significantly when GVL concentration increases, indicating the presence of more active sites during cellobiose decomposition in HCGW. A previous simulation has indicated that during cellobiose hydrolysis the conformation of the non-reducing ring undergoes a significant modification before breaking the glycosidic bond.[97, 219] It is likely that GVL can facilitate the conformation change of cellobiose thus promoting hydrolysis reaction.

Third, similar to cellobiose decomposition in hot-compressed water,[91] some other reactions (e.g., retro-aldol reaction) could also be possible during cellobiose decomposition in HCGW. Unfortunately, those products could not be detected due to the interference of GVL during sample analysis. Nevertheless, based on the results of this study, the total contribution of the primary products produced from those other possible primary reactions accounts for <20% of the primary products from cellobiose decomposition in HCGW. Certainly, the presence of those undesired reactions leads to difficulties to further enhance the glucose selectivity during cellobiose decomposition under acid-free conditions. Overall, the results reported in this study have demonstrated that the HCGW is a promising solvent for achieving a high glucose recovery from cellobiose. The maximal glucose yield achieved in HCGW is ~66% (at 25% GVL concentration and 200 °C), much higher than that of ~32% in water. It should be noted that this is the highest glucose yield reported so far from cellobiose hydrothermal decomposition under acid-free conditions.
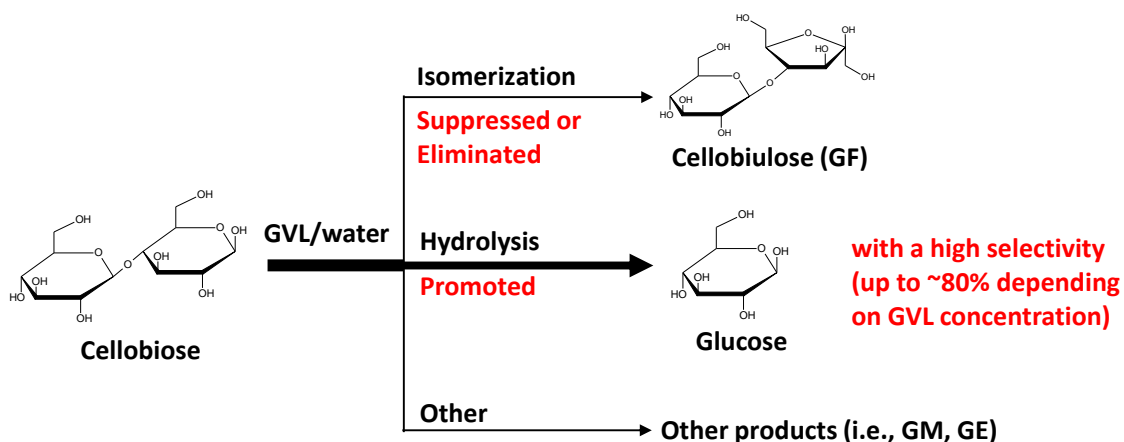
Figure 5.6: Primary reaction pathways during cellobiose decomposition in HCGW.

5.6   Conclusion

This study reports the formation of primary products from cellobiose decomposition in HCGW at a wide range of GVL concentration of 0.03–75%. As the dominant primary reaction of cellobiose decomposition in water, the isomerization reaction to produce GF is largely suppressed or even eliminated in HCGW, depending on GVL concentration. More importantly, GVL addition significantly promotes the hydrolysis reaction to produce glucose. The selectivity of hydrolysis reaction increases with GVL concentration, and stabilizes at ~80% when the GVL concentration increases to >10%. As a result, a high glucose yield of ~66% can be obtained from cellobiose at 25% GVL concentration and 200 °C. To the best of my knowledge, this is the highest glucose yield reported so far from cellobiose hydrothermal decomposition under acid-free condition.

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Chapter 6: Solvent Effect of GVL on Cellulose and biomass hydrolysis in Hot-Compressed GVL/water

6.1 Introduction

As accentuated in previous chapters, biomass refinery is being widely studied as a sustainable technology to partially solve the energy crisis that the world is facing with and ease the environmental pressure that caused by the over emission of CO_2 because of the burning of fossil fuels.[1-4] There are various biomass feedstocks including woods, sewages, algae, and other complexes, among which lignocellulosic biomass is one of the most abundant and valuable resources for the production of biomass derived sugars and sugar based valued added chemicals.[220] Especially, the major fractions of lignocellulosic biomass are cellulose (40-60 wt%) and hemicellulose (20-40 wt%).[5, 221] The fractionation and processing of cellulose and hemicellulose are of great significance as a key procedure of bio-refinery for the production of various value-added chemicals such as fuel type molecules (e.g. branched C_{10} and C_{11} hydrocarbons) and commodify chemicals (e.g. 5-Hydroxymethylfurfural).[222, 223]

Hydrothermal processing is one of the key technologies and has been studied for decades for the treatment of lignocellulosic biomass.[11, 13, 14] For example, the pre-treatment of biomass via hydrothermal approaches are significant for the fractionation of biomass to produce biomass derived sugar oligomers and lignin for further processing.[224, 225] Moreover, hydrothermal treatment is also an important approach for the production of biomass-derived value-added chemicals such as 5-hydroxymethylfurfural (5-HMF), levoglucosenone (LGO), furfural and levulinic acid as reported in previous studies.[157, 226-230] However, there are also challenges for the hydrothermal treatment of biomass. For instance, the hydrothermal treatment of biomass in hot-compressed water (HCW) without catalyst results in high sugar loss at approximately 20% evn under the conditions with minimized secondary products.[59] To

overcome this challenge, various catalysts (e.g. acids) or/and co-solvents (e.g. ionic liquids) are employed to promote the sugar recovery.[224, 231, 232] Nevertheless, the use of catalysts or co-solvents always leads to higher progress expenditure because of the usage and recycling of solvents or/and catalysts.[1]

Various solvents have been employed to enhance the sugar recovery at moderate temperatures.[48, 233, 234] Recently, gamma-valerolactone (GVL) has been reported as a cost-effective solvent for sugar recovery from biomass.[30] A high sugar recovery (~90%) can be achieved from biomass hydrolysis in hot compressed GVL/water (HCGW) under acidic conditions, with the sugar production cost economically competitive with the traditional sugar production processes.[30] Moreover, GVL is a green solvent that can be produced from biomass-derived products,[31, 235, 236] making this process more sustainable. However, the solvent effect of GVL on biomass hydrolysis in HCGW remains unclear, especially under acid-free conditions. Our previous work (Chapter 5) using cellobiose as a model compound indicates that GVL addition strongly suppresses the isomerization reaction and enhances the hydrolysis reaction of cellobiose. Under acids conditions, it was reported that GVL addition can reduce the activation energy of cellobiose hydrolysis.[32, 33] So far, there has been no systematic study to understand the reaction mechanism of cellulose or biomass hydrolysis in HCGW, especially under acid-free conditions. Our previous study has clearly shown that cellulose hydrolysis in HCW produces glucose and its oligomers of a wide range of oligomers as primary products.[82] To provide new insights into the solvent effect of GVL on cellulose hydrolysis in HCGW, it is important to understand the primary products of cellulose hydrolysis in HCGW.

Therefore, this study employs a semi-continuous reactor system to investigate the primary liquid products from cellulose hydrolysis in HCGW at 250 °C, providing new understandings into the solvent effect of GVL on cellulose hydrolysis mechanism in HCGW. Moreover, biomass experiments are performed at 150 and 250 °C to understand the solvent effect of GVL on the recovery of various sugars from biomass hydrolysis in HCGW.

6.2 Glucose Recovery during Cellulose Hydrolysis in HCGW

It is known that cellulose hydrolysis in HCW converts long cellulose chains to produce glucose oligomers with different DPs.[82] However, those high-DP oligomers are not soluble in HCW until its DP reduces to a low level (i.e., 25 at 250 °C[82]). Therefore, the high-DP glucose oligomers are still retained in the solid phase, experiencing further decomposition reactions (i.e., hydrolysis, isomerization, retro-aldol reactions) until the decomposed products can be dissolved in HCW as primary liquid products.[25,28,31-33] During cellulose hydrolysis in HCW, cellulose conversion on a carbon basis can be easily quantified by analysing the carbon content of liquid sample (see the dash line in Figure 6.1). However, this is not suitable for the samples from cellulose hydrolysis in HCGW due to the present of GVL. Therefore, this study only compares the glucose recovery in the primary liquid product (on a carbon basis via post-hydrolysis) as a function of reaction time during cellulose hydrolysis in HCGW with different GVL concentrations at 250 °C, and the results are shown in Figure 6.1. It can be seen that glucose recovery achieves a final glucose recovery of ~80% after complete conversion in ~2 h. This is consistent with our previous study,[82] because some parallel decomposition reactions (i.e., isomerization and retro-aldol reactions) in the solid phase lead to the formation of non-sugar products.[81]

The addition of GVL greatly improves glucose recovery in the primary liquid products from cellulose hydrolysis in HCGW at least in two different ways. First, cellulose hydrolysis reaction rate is largely enhanced in HCGW. For example, the glucose recovery at a reaction time of 20 min increases from ~40% in water to ~58% even in 0.5% GVL/water, and further to ~80% in 10% GVL/water. As a result, the reaction time required to achieve complete conversion reduces from ~2 h in water to ~40 min in 10% GVL/water. A further increase of the GVL concentration to 20% does not lead to an increase in the cellulose hydrolysis reaction rate. Second, the final glucose recovery is increased in HCGW. Even at a low GVL concentration of 1%, the final glucose recovery increases to ~84%. As the GVL concentration increases to 10%, the glucose recovery increases to ~91%. Similarly, there is no significant increase in the

final glucose recovery when the GVL concentration increases to 20%. Therefore, GVL addition not only improves the hydrolysis reaction rate but also enhances the final glucose recovery during cellulose hydrolysis in HCGW. Moreover, our results also indicate cellulose conversion is enhanced during hydrolysis in HCGW, which can be indirectly analysed by the glucose carbon. For example, the glucose carbon during cellulose hydrolysis in 0.5% GVL/water at 20 min is ~58%, higher than the total carbon (i.e., ~50%) during cellulose hydrolysis in HCW. With the increase of GVL concentration to 10%, the glucose carbon is further increased to ~88%, showing a significant increase in cellulose conversion. The above results indicates that hydrolysis reactions in the solid phase to produce sugars are greatly promoted, while other parallel decomposition reactions leading to the formation of non-sugar products are suppressed during cellulose hydrolysis in HCGW.
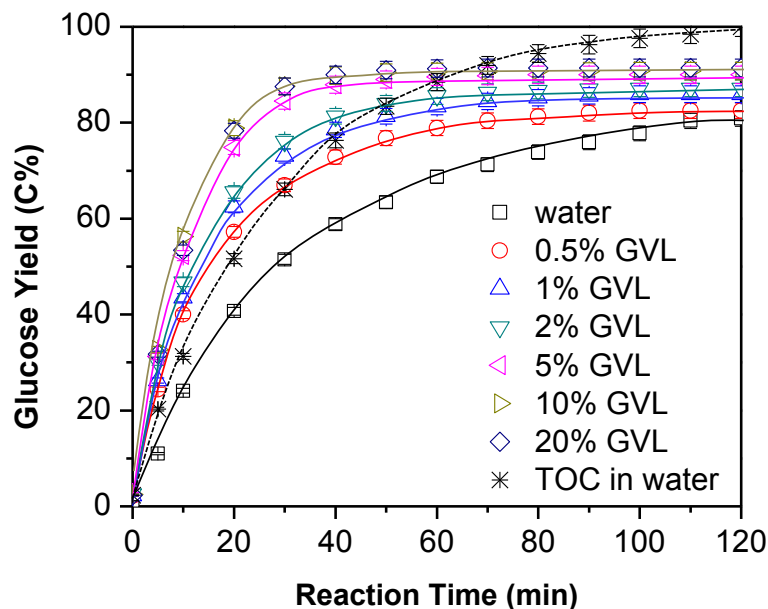
Figure 6.1: Glucose yields (based on carbon) after post-hydrolysis from the hydrothermal processing of cellulose in HCW and HCGW. Dash line represents the total organic carbon (TOC) in water.

6.3   Distribution of Sugars from Cellulose Hydrolysis in HCGW
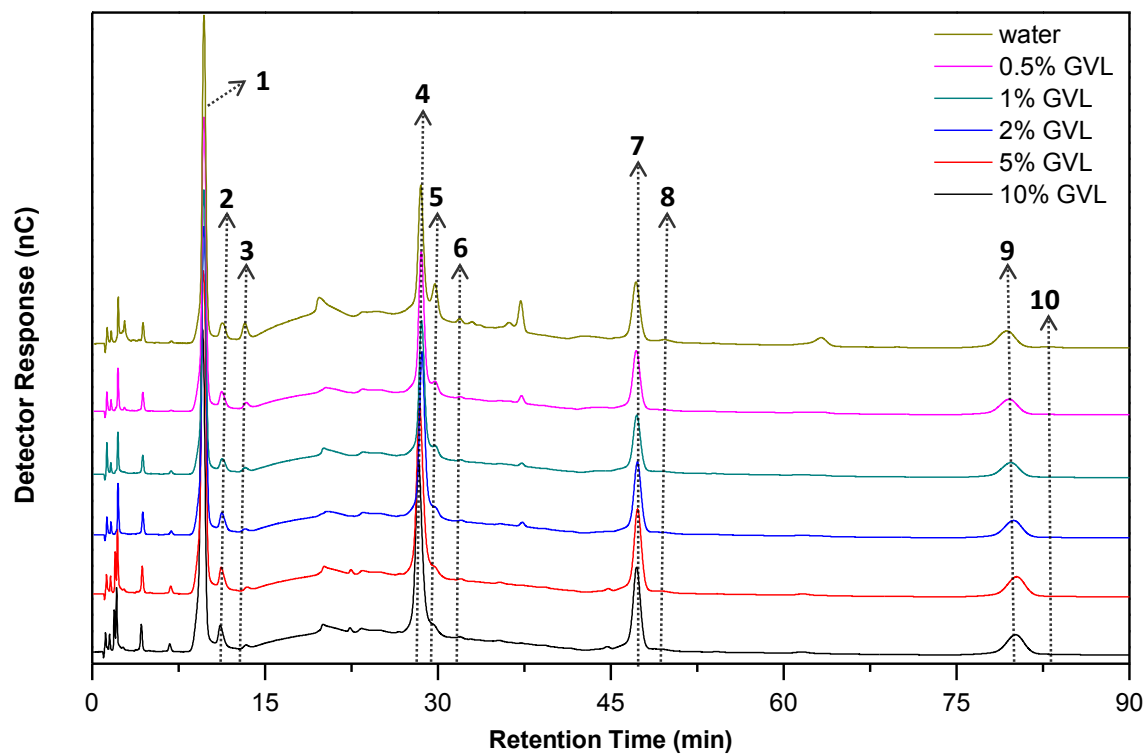
Figure 6.2: HPAEC–PAD chromatograms of the primary liquid products of cellulose hydrolysis in HCW and HCGW, obtained under condition: 10 MPa, 250 °C, flow rate of water and GVL/water mixtures at 20ml/min. 1. glucose; 2.mannose (epimer of glucose); 3. fructose (isomer of glucose); 4. cellobiose; 5. glucosyl-fructose (isomer of cellobiose); 6. glucosyl-mannose (epimer of cellobiose); 7. cellotriose; 8. isomer/epimer of cellotriose; 9. cellotetraose; 10. isomer/epimer of cellotetraose.

To understand the solvent effect of GVL on cellulose hydrolysis reactions in HCGW, it is important to analyse the primary liquid products from cellulose hydrolysis in HCGW. Due to the interference of GVL on sugar analysis by HPAEC–PAD, the GVL in the liquid sample needs to be removed before analysis. It is known that primary products of cellulose hydrolysis in HCW contain glucose oligomers with a wide range of DP up to 25 at 250 °C,[82] and the high-DP (>5) glucose oligomers cannot be completely dissolved in room temperature water due to their low solubilities.[49] Our previous study[49] also demonstrated that the low-DP (<6) glucose oligomers have high

solubilities in room temperature water thus those oligomers can be successfully quantified by re-dissolving the dried sample in water for HPAEC–PAD analysis.

The HPAEC–PAD chromatograms of the liquid samples (after GVL removal) at different GVL concentrations are shown in Figure 6.2, with major peaks identified with standards. During cellulose hydrolysis in HCW, the results confirm that the isomers (i.e., with reducing end as fructose and mannose) of glucose oligomers are present in the primary liquid products, apart from those glucose oligomers with different DPs. However, those isomer peaks are largely reduced as the GVL concentration increases, clearly showing the inhibition of isomerization reactions during cellulose hydrolysis in HCGW.
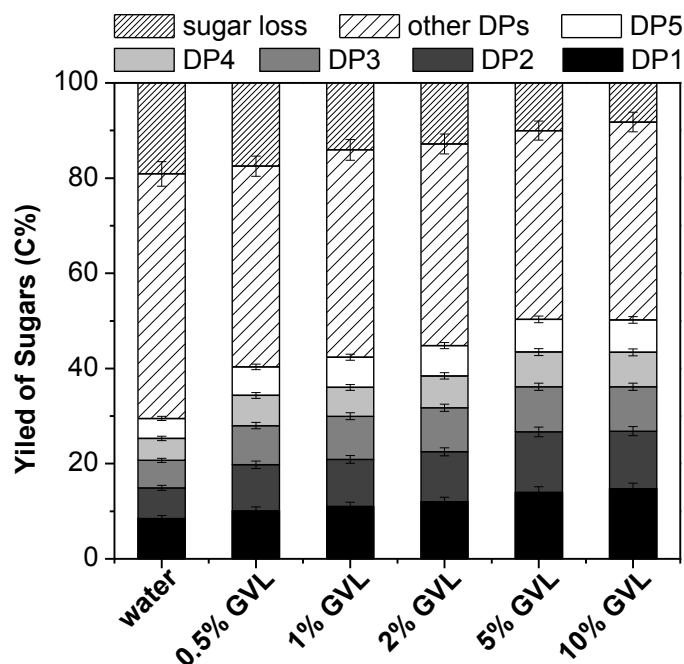
Figure 6.3: Yields of sugars from cellulose decomposition in HCW and HCGW.

The glucose oligomers with DP of 1−5 are then quantified with standards, and the distribution of those low-DP sugar oligomers in the primary liquid products of cellulose hydrolysis in HCGW after complete conversion are compared in Figure 6.3. It can be seen that GVL addition largely affects the distribution of sugars in the primary products of cellulose hydrolysis in HCGW. Particularly, the yields of low-DP

glucose oligomers are increased. For example, the glucose yield increases from ~8% in water to ~10% in 0.5% GVL/water, further to ~14% in 10% GVL/water. The total yield of glucose oligomers with DPs of 1−5 increases from ~30% in water to ~40% in 0.5% GVL/water, further to ~50% in 10% GVL/water. The results suggest that GVL addition indeed promote the hydrolysis reactions in the solid phase, leading to more formation of low-DP glucose oligomers in the primary liquid product during cellulose hydrolysis in HCGW.

To further understand the solvent effect of GVL on the secondary reactions of primary liquid products in the liquid phase during cellulose hydrolysis in HCGW, more experiments were performed at lower flow rates of 5 and 10 ml/min to increase the residence time, thus enhancing the secondary reactions of primary liquid products. The distributions of sugar products in the liquid products of cellulose hydrolysis in water and 5% GVL/water at different flow rates are shown in Figure 6.4. At least two important findings can be observed. First, although there is no significant effect when reducing the flow rate from 20 to 10 ml/min, a further reduction of the flow rate to 5 ml/min shows a considerable reduction in the sugar recovery in water, i.e., from ~80% at 20 ml/min to ~74% at 5 ml/min. In contrast, almost no reduction in sugar recovery can be found for the sugar recovery of cellulose hydrolysis in 5% GVL/water when the flow rate reduces from 20 to 5 ml/min. This clearly demonstrates that GVL addition also suppresses the parallel reactions (i.e., isomerization) in the liquid phase to produce non-sugar products. Second, with the flow rate reducing from 20 to 5 ml/min, the total yield of glucose oligomers with DP of 1−5 shows a substantial increase in 5% GVL/water. For example, the total yield of those low-DP glucose oligomers increases from ~50 to ~63% in 5% GVL/water, compared to only a small increase from ~30 to ~35% in water. This clearly shows that the hydrolysis reactions in the liquid phase are promoted in GVL/water to produce more low-DP glucose oligomers. Therefore, the presence of GVL also dramatically influences the secondary reactions of primary liquid products in the liquid phase during cellulose hydrolysis in HCGW, i.e., enhancing the hydrolysis of high-DP to low-DP glucose oligomers and suppressing the parallel reactions to produce non-sugar products.
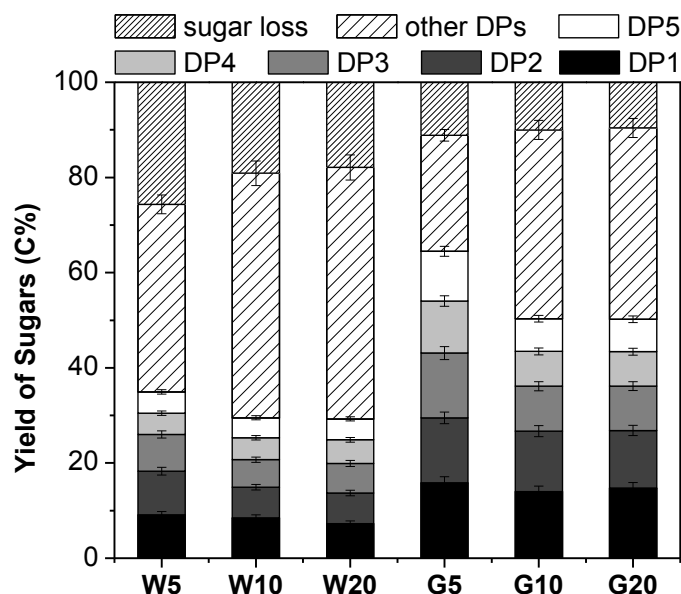
Figure 6.4: Yields of sugars from cellulose decomposition at various solvent flow rates in HCW and HCGW with 5% of GVL. W5, W10 and W20 represent water flow rate at 5 ml/min, 10 ml/min and 20 ml/min. G5, G10 and G20 represent GVL/water flow rate at 5ml/min, 10 ml/min, and 20 ml/min.

6.4   Effect of GVL on Cellulose Hydrolysis Mechanism in HCGW

The above results have clearly shown that GVL addition strongly affects the primary hydrolysis reactions in the solid phase during cellulose hydrolysis in HCGW, leading to a high sugar recovery (i.e., ~91%) as well as a high yield (i.e., ~50%) of glucose oligomers with DP of 1−5 in the primary liquid product. The solvent effect of GVL on the reaction pathways of cellulose hydrolysis in HCGW are summarized in Figure 6.5. As mentioned before, cellulose primary hydrolysis in HCW converts long cellulose chains into glucose oligomers of different DPs. However, those high-DP oligomers (i.e., >25 at 250 °C) are not soluble in HCW so those oligomers will experience further secondary reactions in the solid phase, until the products can be dissolved in HCW as primary liquid products. The primary reactions of cellulose hydrolysis may also produce some low-DP oligomers (i.e., <25 at 250 °C) which can be dissolved in HCW as primary liquid products. Therefore, the primary liquid products in the semi-

continuous reactor system consist of not only the soluble glucose oligomers directly from cellulose primary hydrolysis but also the soluble products from the secondary reactions of insoluble glucose oligomers in the solid phase.

Our results have shown that GVL addition affects the cellulose hydrolysis reactions in both solid and liquid phases. First, the GVL addition enhances the cellulose hydrolysis reactions in the solid phase, leading to an increased hydrolysis reaction rate. The detailed mechanism for the solvent effect of GVL on solid phase hydrolysis reaction is not clearly understood yet. However, some recent studies[187, 237] employed molecular dynamics simulations to provide new insights into the interactions between organosolv-water co-solvents and cellulose for various solvents (i.e., THF, GVL, acetone, ethanol). It was reported that co-solvent mixtures like GVL/water have local phase separation on the cellulose surfaces due to its chemical heterogeneity with both hydrophobic and hydrophilic regions.[187, 237] Organic solvent molecules preferentially bind to the hydrophobic surfaces, while water molecules preferably form hydrogen bonds with the hydrophilic surfaces.[187] As a result, the presence of organic solvent like GVL changes the water structure on cellulose surfaces, resulting in stronger hydrogen bonds within the glycosidic bond oxygens, which may facilitate the hydrolysis reactions.[187] Second, isomerization reactions of insoluble glucose oligomers in the solid phase are strongly suppressed in HCGW. Previous studies[217] using model compounds have indicated that intramolecular hydride transfer is the rate-limiting step for isomerization reaction, while the free energy barrier of intramolecular hydride transfer is much higher in organosolv-water co-solvents due to the change of local solvent arrangement around the sugar molecules.[211] Third, GVL also affects the secondary reactions of soluble glucose oligomers in the liquid phase, i.e., enhancing hydrolysis reactions and inhibiting the isomerization reactions. This has been demonstrated in Chapter 4 on cellobiose hydrolysis in HCGW. Therefore, GVL addition enhances hydrolysis reactions and suppresses isomerization reactions in both solid and liquid phases, leading to increased sugar recovery during cellulose hydrolysis in HCGW.
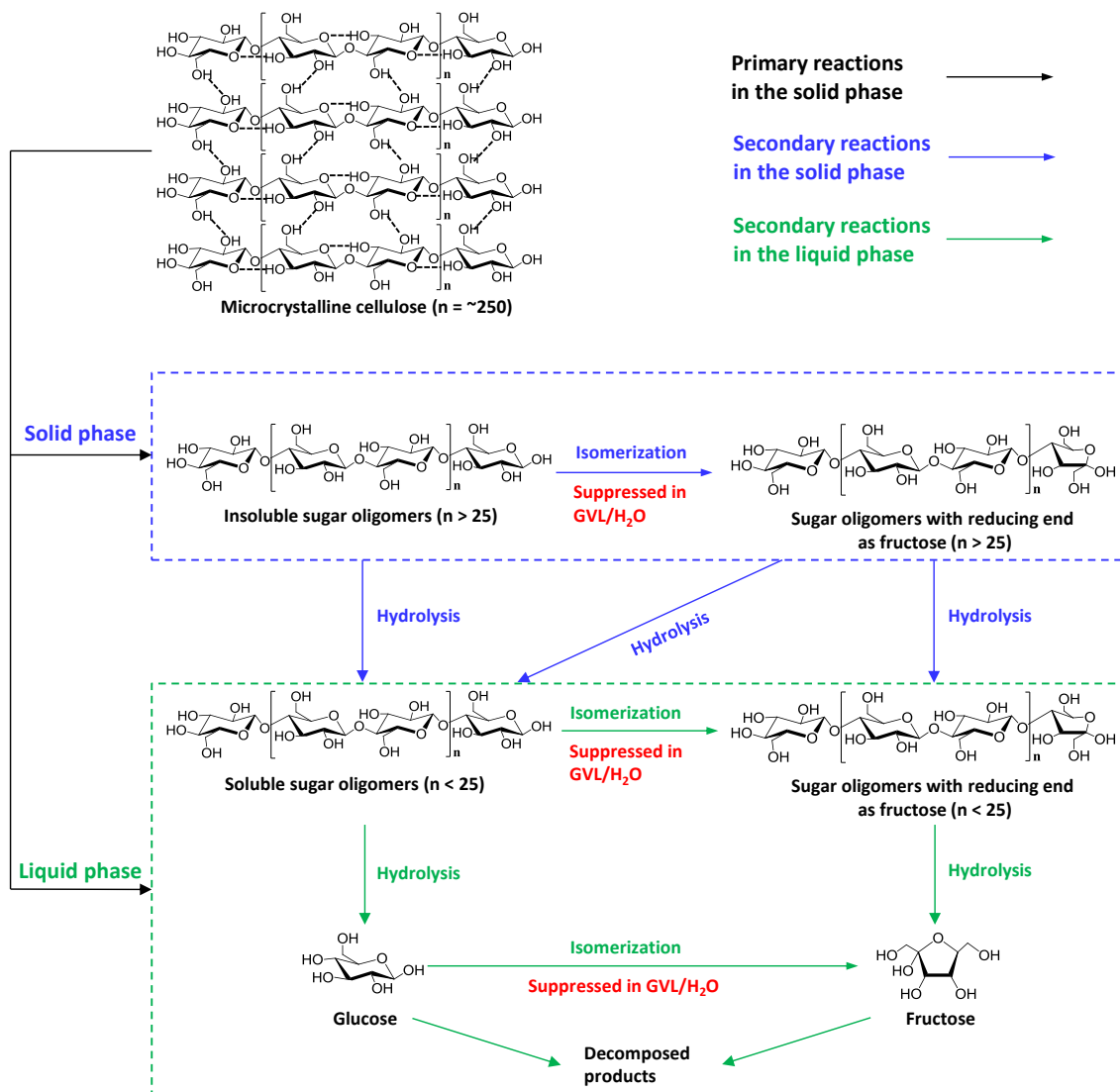
Figure 6.5: A schematic diagram on the solvent effect of GVL on cellulose hydrolysis in HCGW under the reaction conditions in this study.

6.5 Application of Biomass Hydrolysis in HCGW

Further experiments were performed to investigate the sugar recovery during biomass hydrolysis in HCGW. Figure 6.6 presents the recovery of various sugar monomers (i.e., arabinose, galactose, glucose, xylose, and mannose, the composition of mallee wood is present in

Table 6.1 during biomass hydrolysis in HCGW at different GVL concentrations at 150 and 250 °C. It should be mentioned that different reaction temperatures were selected to investigate the solvent effect of GVL on sugar recovery from hemicellulose and cellulose. As expected, the GVL addition largely enhances the sugar recovery from hemicellulose at 150 °C. For example, the xylose recovery after 70 min increases from ~54% in water to ~60% in 0.5% GVL/water, further to ~82% in 5% GVL/water. As a result, the overall sugar recovery at 150 °C is increased from ~18% in water to ~30% in 5% GVL/water.
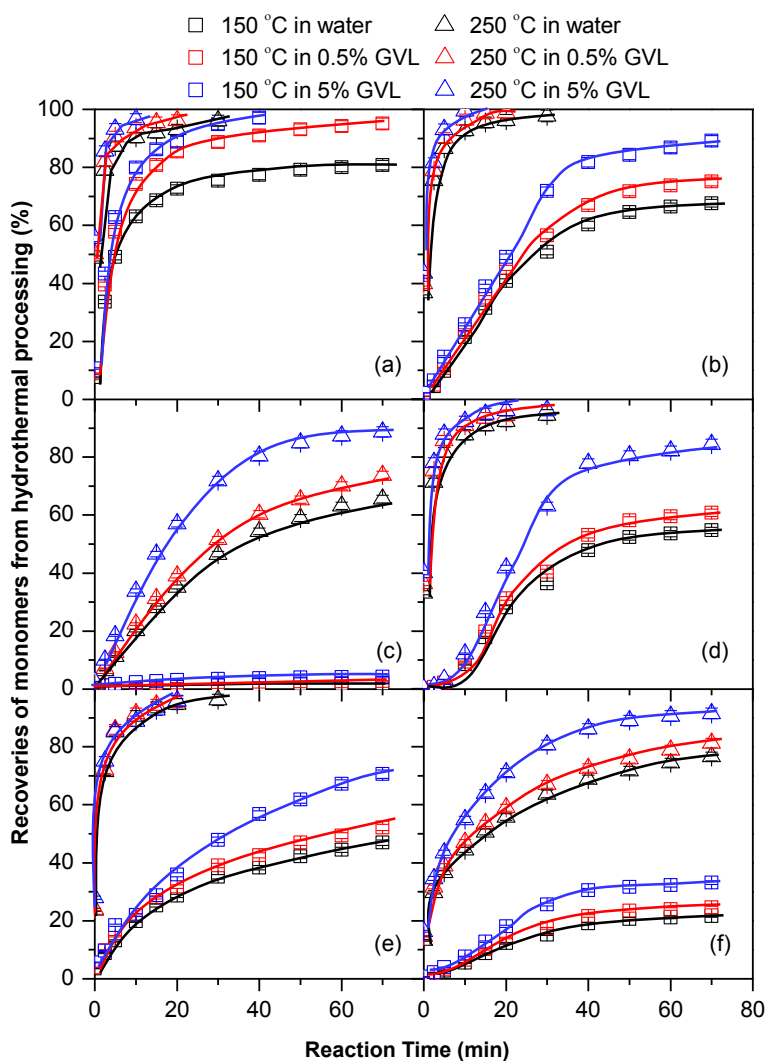
Figure 6.6: Recoveries of various monomers from mallee wood hydrothermal processing in HCW and HCGW with GVL at 0.5% and 5%, respectively. (a) arabinose; (b) galactose; (c) glucose; (d) xylose; (e) mannose; (f) total.

Table 6.1: Saccharides and inorganic species content (wt% in dry basis) of mallee wood used in this study.

Saccharides content (wt%, db)				
Arabinan	Galactan	Glucan	Xylan	Manan
1.06	2.21	40.66	17.95	0.38

At 250 °C, almost all the arabinose, galactose, xylose and mannose are recovered in HCGW within 30 mins. Although GVL addition does not influence the final recovery of these hemicellulose-derived sugars, the reaction time required to achieve complete conversion is reduced. For example, nearly all xylose (i.e. ~96%) is recovered in water after ~30 min, while the reaction time is reduced to ~20 and in 5% GVL/water. In contrast, a drastic increase in glucose recovery is achieved in HCGW. The glucose recovery at 250 °C and 70 min is increased from ~60% in water to ~90% in 5% GVL/water, in consistent with the results from cellulose hydrolysis. This leads to the overall sugar recovery increasing from ~74% in water to ~93% in 5% GVL/water. Thus, the results clearly demonstrate that GVL/water co-solvent even at a low GVL concentration (i.e., 5%) can achieve a near-complete sugar recovery during lignocellulosic biomass hydrolysis in HCGW under acid-free conditions.

6.6   Conclusion

This chapter provides some new insights into the solvent effect of GVL during cellulose hydrolysis in HCGW via characterising the primary liquid products produced from a semi-continuous reactor system. Compared to water, GVL/water co-solvent is found to be more effective to hydrolyse cellulose with faster hydrolysis reaction rate and higher sugar recovery. Analyses of the primary liquid products from cellulose hydrolysis in HCGW by HPAEC-PAD indicate that GVL addition enhances hydrolysis reactions and suppresses isomerization reactions in the solid phase during cellulose hydrolysis in HCGW, leading to an increased sugar recovery (i.e., ~91%)

and a higher yield of low-DP glucose oligomers (i.e., ~50% in 10% GVL/water for DPs up to 5) in the primary liquid products. Further hydrolysis experiments at reduced flow rates show that the presence of GVL also promotes hydrolysis reactions and inhibits isomerization reactions in the liquid phase, producing more low-DP glucose oligomers (i.e., ~63% in 5% GVL/water for DPs up to 5) without reduction in total sugar recovery. Finally, a near-compete sugar recovery of ~93% can be achieved from biomass hydrolysis at 250 ℃ in HCGW even at a low GVL concentration of 5%, demonstrating excellent performance of GVL/water co-solvent for biomass hydrolysis under acid-free conditions.

Chapter 7: Solvent Effect of Aprotic and Protic Solvents on the Hydrothermal Decomposition of Glucose and Fructose

7.1   Introduction

Despite that GVL is being widely studied for biomass hydrothermal processing, recent researches have also shown strong interests in biorefinery with multiple organic solvents.[238] Especially, more and more biomass derived organic solvents have been used for biomass hydrothermal processing to achieve high yields and selectivity of value-added chemicals from biomass and biomass derived compounds.[167, 182, 239] For example, aprotic solvents including gamma-valerolactone (GVL), tetrahydrofuran (THF), and gamma-hexalactone (GHL) have been used as co-solvent for glucose hydrothermal processing and have achieved high 5-hydroxymethyl-furfural (5-HMF) yields at ~90%.[167] Other aprotic solvents such as acetone, 1,4-dioxane and acetonitrile have been used for cellulose liquefaction to increase the yields of value added chemicals including 5-HMF and furfural.[26, 240, 241] Moreover, multiple protic solvents including methanol, ethanol, ethylene glycol have also been studied for cellulose and biomass processing and have achieved better yields of corresponding target products compared with using water.[23, 78, 239, 242] With the wide application of organic solvents in biorefinery, in-depth understandings to identify the effect of different solvents are significant to guide the use of solvents for biomass processing.

To help understand the effect of solvents, our previous chapters have chosen GVL, a biomass derived aprotic solvents, as research target to study the effect of GVL on the hydrothermal decomposition of raw biomass, cellulose, cellobiose and glucose from the view of primary reactions and kinetics. The previous works have demonstrated that GVL/water is applicable to tune the reaction pathways of glucose decomposition under hydrothermal conditions (Chapter 4). And also, GVL suppresses the isomerization reactions of cellulose and cellulose derived compounds, but enhances

the hydrolysis reactions (Chapter 5–6). Moreover, hot-compressed GVL/water can enhance the sugar recovery from biomass decomposition compared to hot-compressed water. To further understand the role of GVL, comparison with the other widely used organic solvents need to be carried out. Thus, this study is carried out as a step forward to understand the effect of multiple organic solvents on the decomposition of biomass from our view of reaction mechanisms and kinetics with glucose and fructose as model compounds.

7.2   Yields of Products in Various Solvents

The yields of glucose and its major products, i.e., fructose, mannose, levoglucosan (LGA) and 5-hydroxymethyl-furfural (5-HMF), in water and other solvents are present in Figure 7.1. In agreement with the previous study in Chapter 4, glucose decomposition is suppressed in GVL/water compared with that in water. Moreover, this study indicates that the decomposition of glucose is also suppressed in acetone/water and 1,4-dioxane/water. For example, the conversion of glucose at 200 °C and 60 mins reduces from ~70% in water to ~62% in acetone/water and 1,4-dioxane/water. However, there is little difference observed between methanol/water, ethanol/water and water in terms of the conversion of glucose.

Several findings can be observed in terms of the yields of various products. To begin with, the yields of LGA in various solvents are different as shown in panel d–f of Figure 7.1. It can be seen that the glucose yields in GVL/water, acetone/water and 1,4-dioxane/water are higher than those in water, while the glucose yields in methanol/water and ethanol/water are similar as those in water. For example, glucose conversion at 200 °C and 40 min is ~47% in GVL/water, ~51% in acetone/water and ~53% in 1,4-dioxane/water, lower than ~61% in water, ~65 in methanol/water and ~63% in ethanol/water. The results suggest that glucose decomposition is suppressed in aprotic solvent/water mixtures, but not in protic solvent/water mixtures.

As for the products from glucose decomposition in hot-compressed solvent/water mixtures, fructose and 5-HMF are the main products while mannose and LGA are the minor products. All products increase with reaction time at low temperatures (i.e., 175 °C) in solvent/water mixtures, but decreases with reaction time at high temperatures (i.e., 225 °C), expect 5-HMF which shows continuous increases as reaction time increases. This is expected because 5-HMF can be produced from fructose, mannose and LGA via secondary reactions.

The yields of various products show large changes in different solvent/water mixtures. At temperatures ≤ 200 °C, it can be found that both the fructose and 5-HMF yields in the aprotic solvent/water mixtures are lower than those in water, while the LGA yield in the aprotic solvent/water mixtures is higher than that in water. For example, the 5-HMF yield in GVL/water, acetone/water and 1,4-dioxane/water at 200 °C and 40 min is ~24, ~18, ~16%, respectively, lower than those of ~31%, ~34, ~30% in water, methanol/water and ethanol/water, respectively. At increased temperatures (i.e., 225 °C), the 5-HMF yields in water and protic solvent/water mixtures first increase with reaction time, followed by decreases as reaction time further increases. In contrast, the 5-HMF yield still continues to increase with reaction time in aprotic solvent/water mixtures. This indicates that the secondary reactions of 5-HMF are more significant in water and protic solvent/water mixtures. As a result, the maximal 5-HMF yield achieved is ~45, ~50, ~55% in water, methanol/water and ethanol/water, respectively.

Compared to 5-HMF, the fructose yield is much lower, only ~7–9% in GVL/water, acetone/water and 1,4-dioxane/water at 200 °C and 20 min, lower than that of ~12–13% in water, methanol/water and ethanol/water under the same condition. Different as fructose and 5-HMF, the LGA yields in the aprotic solvent/water mixtures are higher than those in water and protic solvent/water mixture. For example, the yield of LGA at 200 °C and 20 min is ~3.8, ~2.9 and ~2.9% in GVL/water, acetone/water and 1,4-dioxane/water, respectively, higher than those of ~1.6, ~1.9, ~1.7% in water,

methanol/water and ethanol/water, respectively. Compared to other products, the mannose yield of mannose is little (<2%) and less affected by the solvent.

Figure 7.2 presents the yields of fructose (a–c) and its major products, i.e., 5-HMF (d–f), glucose (g–i) and mannose (j–l). It should be noted that LGA cannot be directly produced from fructose, so the major products from fructose decomposition are mainly glucose, mannose and 5-HMF. Similarly, the fructose decomposition is slightly supressed in aprotic solvent/water mixtures, while protic solvent has negligible effect on fructose decomposition. For example, fructose conversion at 200 °C and 40 min are ~84% in GVL/water, ~82% in acetone/water and ~82% in 1,4-dioxane/water, lower than ~90% in water, ~88 in methanol/water and ~87% in ethanol/water.

The yields of various products also change greatly in different solvent/water mixtures. The yields of three products all increase with reaction time for all solvent/water systems. However, the formation of 5-HMF from fructose decomposition is considerably promoted in aprotic solvent/water mixtures, while the formation of glucose and mannose is suppressed. For example, the 5-HMF yield in GVL/water, acetone/water and 1,4-dioxane/water at 200 °C and 40 min is ~57, ~54, ~57%, respectively, higher than those of ~47%, ~48, ~51% in water, methanol/water and ethanol/water, respectively. In contrast, the glucose yield in GVL/water, acetone/water and 1,4-dioxane/water at 200 °C and 40 min is ~2.6, ~4.1, ~3.3%, respectively, lower than those of ~5.4%, ~5.3, ~6.2% in water, methanol/water and ethanol/water, respectively. The mannose yield has a similar trend as glucose, but its yield is slightly lower, i.e., <2% in aprotic solvent/water mixtures and <3% in water and protic solvent/water mixtures.
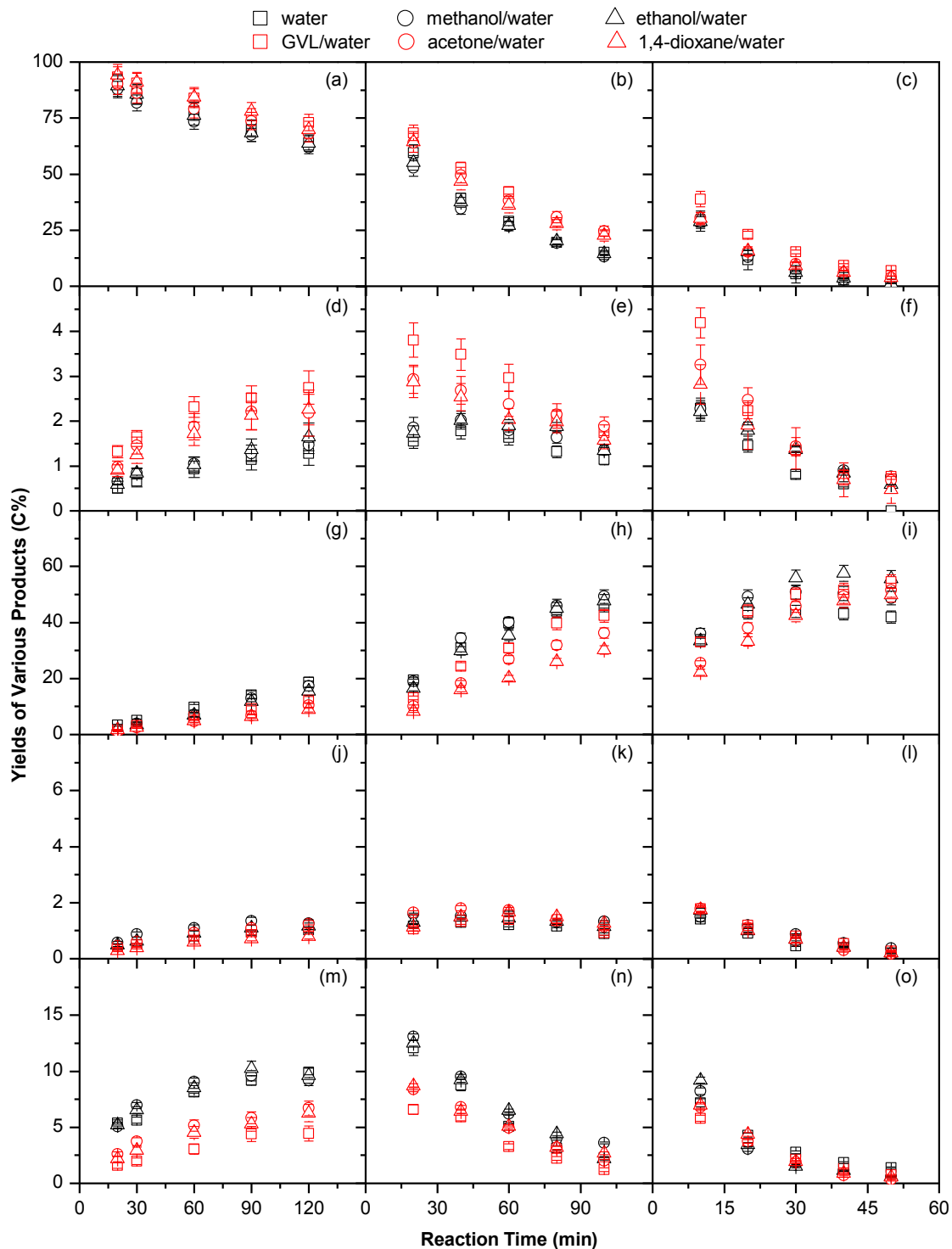
Figure 7.1: Yield of various products from glucose transformation at various solvent systems. (a) glucose yield at 175 °C; (b) glucose yield at 200 °C; (c) glucose yield at 225 °C; (d) 5-HMF yield at 175 °C; (e) 5-HMF yield at 200 °C; (f) 5-HMF yield at 200 °C; (g) fructose yield at 175 °C; (h) fructose yield at 200 °C; (i) fructose yield at

225 °C; (j) LGA yield at 175 °C; (k) LGA yield at 200 °C; (l) LGA yield at 225 °C; (m) mannose yield at 175 °C; (n) mannose yield at 200 °C; (o) mannose yield at 225 °C.

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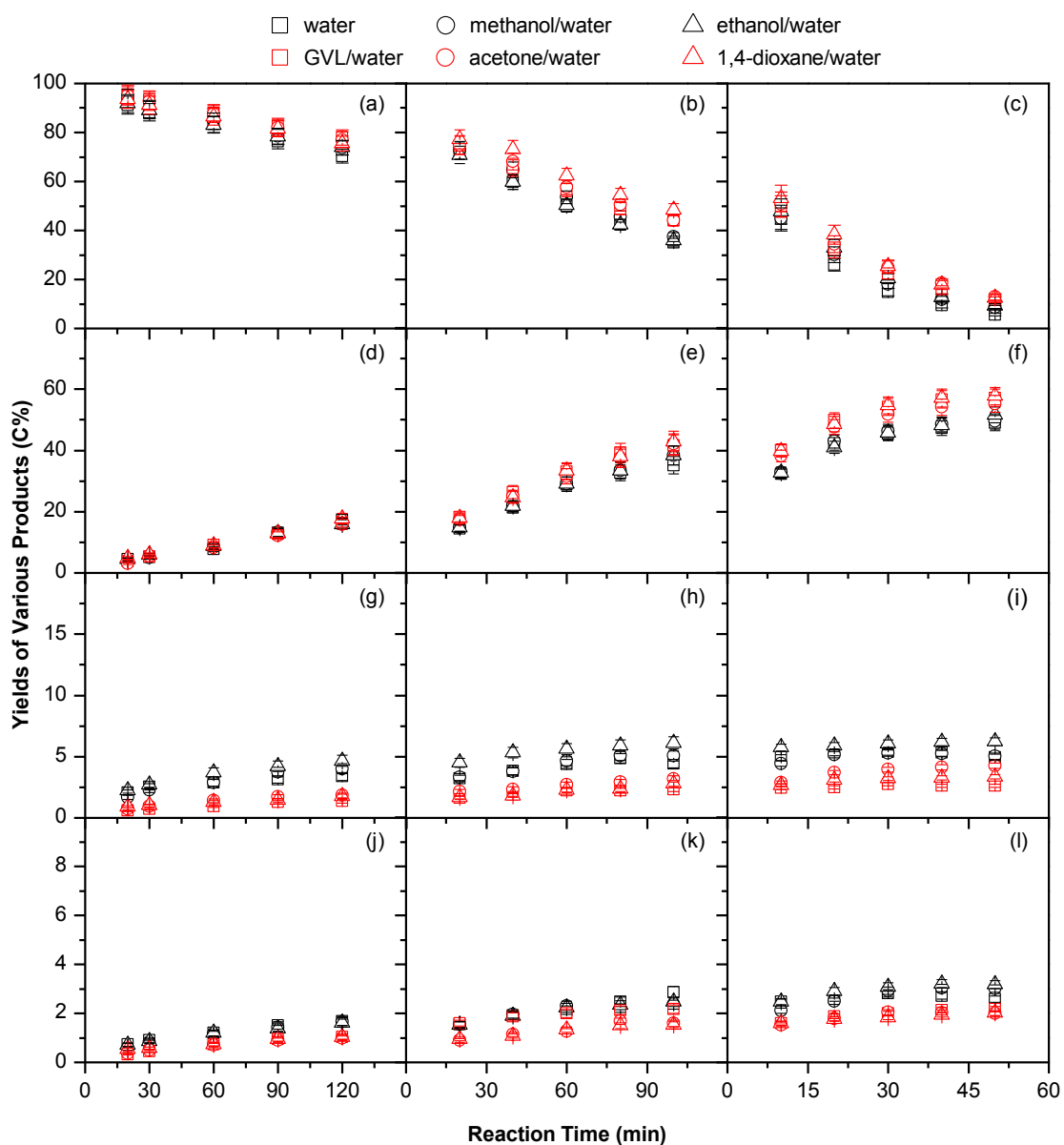
Figure 7.2: Yields of various products from fructose conversion in various solvent systems. (a) fructose yield at 150 °C; (b) fructose yield at 175 °C; (c) fructose yield at 200 °C; (d) 5-HMF yield at 150 °C; (e) 5-HMF yield at 175 °C; (f) 5-HMF yield at 200 °C; (g) 5 glucose yield at 175 °C; (h) glucose yield at 200 °C; (i) glucose yield at

225 °C; (j) mannose yield at 175 °C; (k) mannose yield at 200 °C; (l) mannose yield at 225 °C.

In general, although detailed differences between solvents cannot be well discriminated, the addition of various organic solvents is shown to have different effect to the conversion of feedstocks and the yields of products for both monomers (i.e., glucose and fructose). Moreover, yields of various products from glucose and fructose in aqueous GVL, acetone and 1,4-dioxane are familiar with obvious comparison to that in water and aqueous alcohols (i.e. methanol and ethanol). The results suggest that the reaction pathways of both glucose and fructose are influenced of the addition of different organic solvents.

7.3   Selectivities of Primary Products in Various Solvents

It was studied in Chapter 4 that the detectable products (i.e., fructose, mannose, 5-HMF and LGA) account for ~85–90% of the primary selectivity in water and GVL/water. Herein, the selectivities of these products are calculated and present as a function of glucose conversion as shown in Figure 7.3. The selectivities of various products (especially fructose and 5-HMF) are greatly affected by the solvent system. For example, the initial selectivities of fructose in the protic solvent/water mixtures (i.e., ~65% at ~5% glucose conversion) are much higher than those in the aprotic solvent/water mixtures (i.e., ~30–40% at ~5% glucose conversion). In contrast, the initial selectivities of 5-HMF in the protic solvent/water mixtures (i.e., ~10–20% at ~5% glucose conversion) are much lower than those (i.e., ~25–35% at ~5% glucose conversion) in the aprotic solvent/water mixture. Similarly, the initial selectivities of LGA in the aprotic solvent/water mixtures (i.e., ~10–20% at 5% glucose conversion) are also higher than those in the aprotic solvent/water mixtures (i.e., ~5–6% at 5% glucose conversion). Compared to other products, the effect of solvent on mannose selectivity is negligible. The above results clearly indicate that the dehydration reactions to produce 5-HMF and LGA are largely enhanced in the aprotic

solvent/water mixture, at the expense of fructose formation. However, since the glucose decomposition is suppressed in the aprotic solvent/water mixture, resulting in a lower 5-HMF yield in the aprotic solvent/water mixture.

As the glucose conversion increases, the selectivities of fructose, mannose and LGA all continue to decrease, except for the 5-HMF selectivity which first increases with glucose conversion then decreases at high glucose conversions (>80%). Although the initial 5-HMF selectivity in the protic solvent/water mixture is much lower, the 5-HMF selectivity rapidly increases to the maximal value (i.e., ~58 and ~59% in methanol/water and ethanol/water, respectively), while is only slightly lower than that in the aprotic solvent/water mixture (i.e, ~62, ~64 and ~66% in GVL/water, acetone/water and 1,4-dioxane/water, respectively). This suggests that 5-HMF in the protic solvent/water mixture is produced from secondary reactions of primary products (mainly fructose) during glucose decomposition, while 5-HMF is produced from both primary and secondary reactions in the aprotic solvent/water mixture.

Figure 7.3: Selectivity of products from glucose decomposition in various solvent systems. (a) water; (b) 10% methanol; (c) 10% ethanol; (d) 10% GVL; (e) 10% acetone; (f) 10% 1,4-dioxane.

Moreover, the selectivities of various products from fructose decomposition are also present (Figure 7.4). Compared to those for glucose decomposition, the initial 5-HMF selectivities in water and protic solvent/water mixtures (i.e., ~50–55% at 5% glucose conversion) during fructose decomposition are much higher, indicating 5-HMF is a primary product from fructose decomposition in those solvent systems. However, the initial 5-HMF selectivities in aprotic solvent/water mixtures (i.e., ~65% at 5% glucose conversion) are even higher. In contrast, the initial glucose selectivities in water and protic solvent/water mixtures (i.e., ~25–28% at 5% glucose conversion) are much higher than those in aprotic solvent/water mixtures (i.e., ~12–15% at 5% glucose conversion). Therefore, the dehydration reaction to produce 5-HMF is also enhanced in the aprotic solvent/water mixture, but at the expense of isomerization reaction to produce glucose. The effect of solvent on mannose selectivity is also negligible.
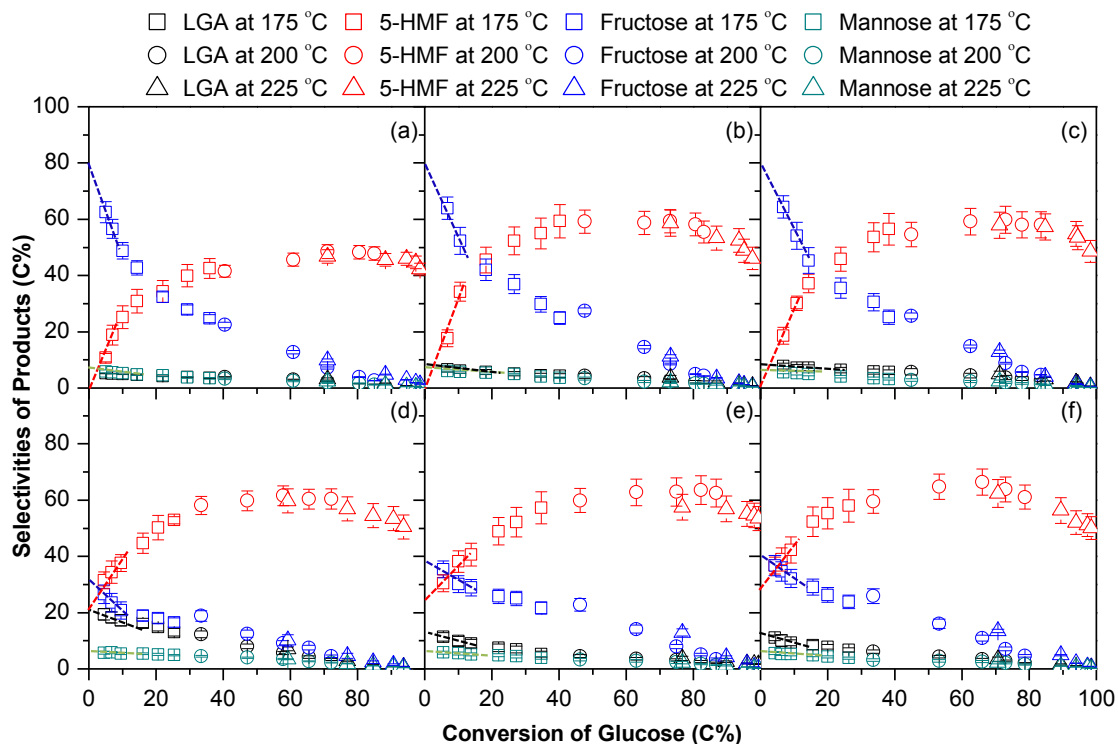

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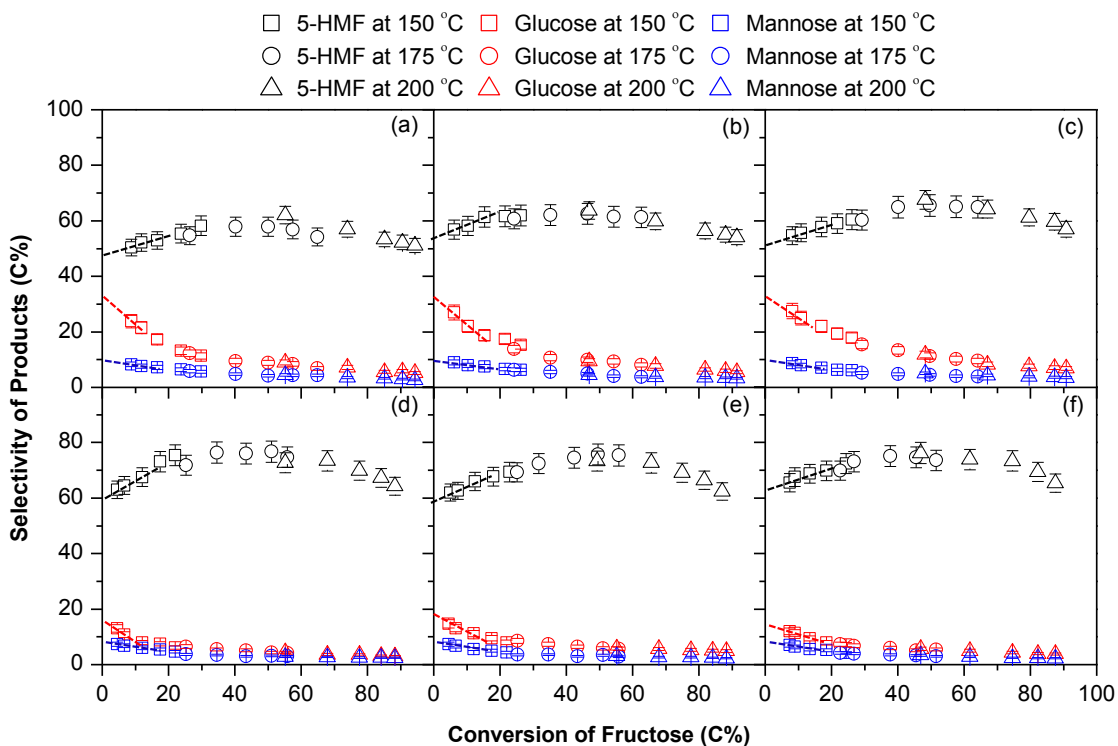
Figure 7.4: Selectivity of products from glucose decomposition in various solvent systems. (a) water; (b) methanol/water; (c) ethanol/water; (d) GVL/water; (e) acetone/water; (f) 1,4-dioxane/water.

Further efforts are taken to obtain the contributions of corresponding primary reactions based on the delplot method[198, 243] to understand the reaction pathways of glucose and fructose in various solvents. The contributions of reactions of glucose in various solvents are shown in Figure 7.5 and Figure 7.6. Obviously, the isomerization to fructose (~78–82%) is the dominant primary reaction of glucose decomposition in water, methanol/water and ethanol/water; while the dehydration to LGA (~5%) and the isomerization to mannose (~6%) are minor primary reactions. However, in the aprotic solvent/water mixtures (i.e., GVL/water, acetone/water, and 1,4-dioxane/water), the isomerization to fructose (~30–40%) is drastically suppressed and the dehydration to LGA (~14–20%) is largely enhanced compared with those in water. Similar as that in GVL/water, the dehydration to 5-HMF is also a primary reaction of glucose decomposition in acetone/water and 1,4-dioxane/water, with contributions of ~25%. Therefore, the results suggest that the addition of the aprotic solvent can significantly change the glucose decomposition reaction pathways, promoting the dehydration to 5-HMF and LGA but suppressing the isomerization to fructose, while the effect of protic solvent is smaller.

Similar findings can be found for fructose decomposition. For example, the addition of the aprotic solvent (i.e., GVL, acetone and 1,4-dioxane/water) increases the selectivity of dehydration reaction to 5-HMF from ~47% in water to ~60–63% in aprotic solvent/water mixtures, but reduce the selectivity of isomerization reaction to glucose from ~35% in water to ~18–20% in aprotic solvent/water mixtures. While those selectivities in methanol/water and ethanol/water almost remain unchanged.

Therefore, the reaction pathways of glucose and fructose decomposition in solvent/water mixture can be summarized as follows. The addition of aprotic solvent can significantly change the reaction pathways of glucose and fructose decomposition,

i.e., increasing the selectivities of dehydration reactions but decreasing the selectivities of isomerization reactions. Particularly, the dehydration to 5-HMF becomes a major primary reaction of glucose decomposition in aprotic solvent/water mixture, while it is only a secondary reaction in water and protic solvent/water mixture. In contrast, the effect of protic solvent addition on glucose and fructose decomposition is smaller.
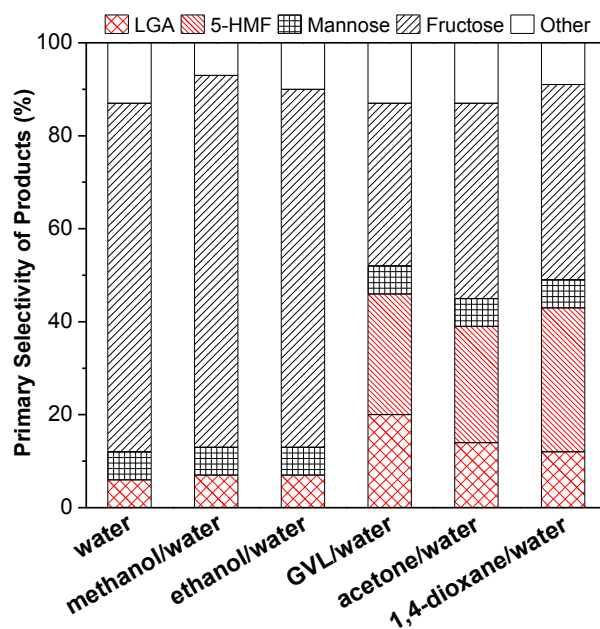
Figure 7.5: Contributions of various primary reactions of glucose decomposition in water and various aqueous organic solvents.

Interestingly, within the two categories, the solvents are also found to have similar effect on the reaction pathways of fructose. In brief, the contributions of dehydration from fructose to 5-HMF are significantly higher in GVL/water, acetone/water and 1,4-dioxane/water (~55–60%) than those in water, methanol/water and ethanol/water (~40–46%); while the contributions of isomerization from fructose to glucose are lower in the former solvents (~18–22%) compared with those in the latter ones (~30–35%).
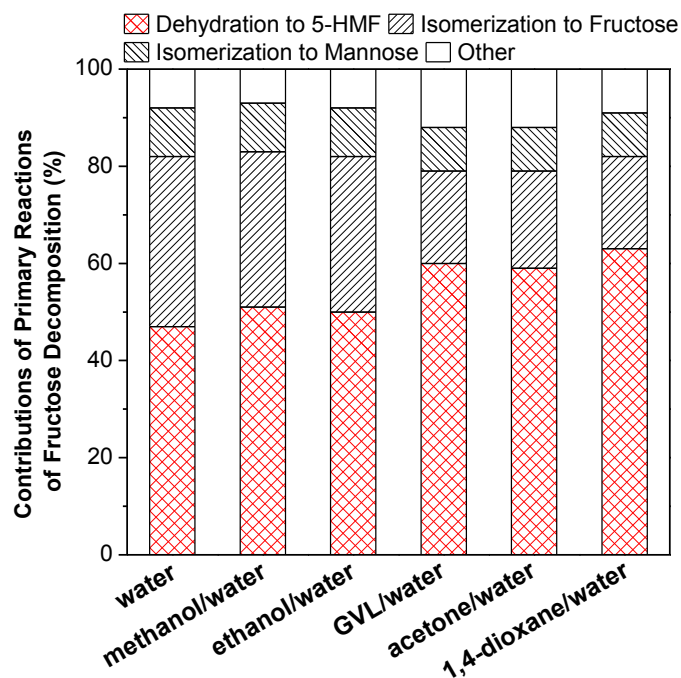
Figure 7.6: Contributions of various primary reactions of fructose decomposition in water and various aqueous organic solvents.

7.4   Kinetics of Glucose and Fructose Decomposition in Various Solvents

The possible different effect between aprotic and protic solvents to the kinetics is further studied as follows. Familiar to the kinetics of glucose in water and GVL/water in the previous study (Chapter 4), the kinetics of fructose and glucose decomposition in various solvents follow the fist-order reaction kinetics (shown in Figure 7.7 and Figure 7.8).

Figure 7.7: Correlation between –Ln[C(t)/C(0)] and reaction time t for glucose decomposition in various solvent mixtures. (a) water; (b) methanol/water (10/90); (c) ethanol/water (10/90); (d) GVL/water (10/90); (e) acetone/water (10/90); (f) 1,4-dioxane/water (10/90). C(0) and C(t) represent the primary concentration and the concentration of glucose after a reaction time t at various solvent systems and temperatures.

The reaction rate constants were further calculated, and the results of glucose and fructose decomposition are presented in Tables 7.1 and 7.2, respectively. It can be found that the addition of aprotic solvent largely reduces the reaction rate constant of both glucose and fructose decomposition in the solvent/water, while the addition of aprotic solvent only has a small effect. For example, the reaction rate constant of glucose decomposition at 200 °C reduces largely from 0.0181 min^{-1} in water to 0.0101–0.0121 min^{-1} in aprotic solvent/water, but only slightly reduces to 0.0165–0.0168 min^{-1} in protic solvent/water. Compared to that of glucose, the reaction rate constant of fructose decomposition at 200 °C is much larger, but still reduces from 0.0505 min^{-1} in water to 0.0338–0.365 min^{-1} in aprotic solvent/water and 0.0446–0.472 min^{-1} in protic solvent/water. Comparing the reaction rate constants of glucose

and fructose decomposition in different solvent systems at 200 °C, it can be seen that the reaction rate constant of fructose is almost 3 times higher than that of glucose under the same conditions. Therefore, once fructose is produced during glucose decomposition, its further decomposition can rapidly convert fructose into 5-HMF. This explains the rapid increase of 5-HMF selectivity (see Figure 3) at the early stage of glucose conversion in protic solvent/water mixture, in comparison to the slow increase in 5-HMF selectivity during glucose decomposition in aprotic solvent/water mixture.

The kinetic parameters of glucose and fructose decomposition in hot-compressed solvent/water mixture were also estimated based on the Arrhenius plots (Figure 7.9), and the results are presented in the same tables. It can be seen that both activation energy and pre-exponential factor decrease in aprotic solvent/water, while those in protic solvent/water almost remain unchanged. For example, the activation energy of glucose decomposition reduces from ~117 and ~101 kJ/mol in water to ~107 and ~95 kJ/mol in aprotic solvent/water and protic solvent/water, respectively. Although the addition of aprotic solvent reduces the activation energy of sugar decomposition in the solvent/water mixture, the reaction rate constant is still lower compare to that in the protic solvent/water mixture, mainly due to the significant reduced pre-exponential factor. Obviously, the addition of aprotic solvent reduces the availability of active sites for decomposition reactions (i.e., via isomerization).
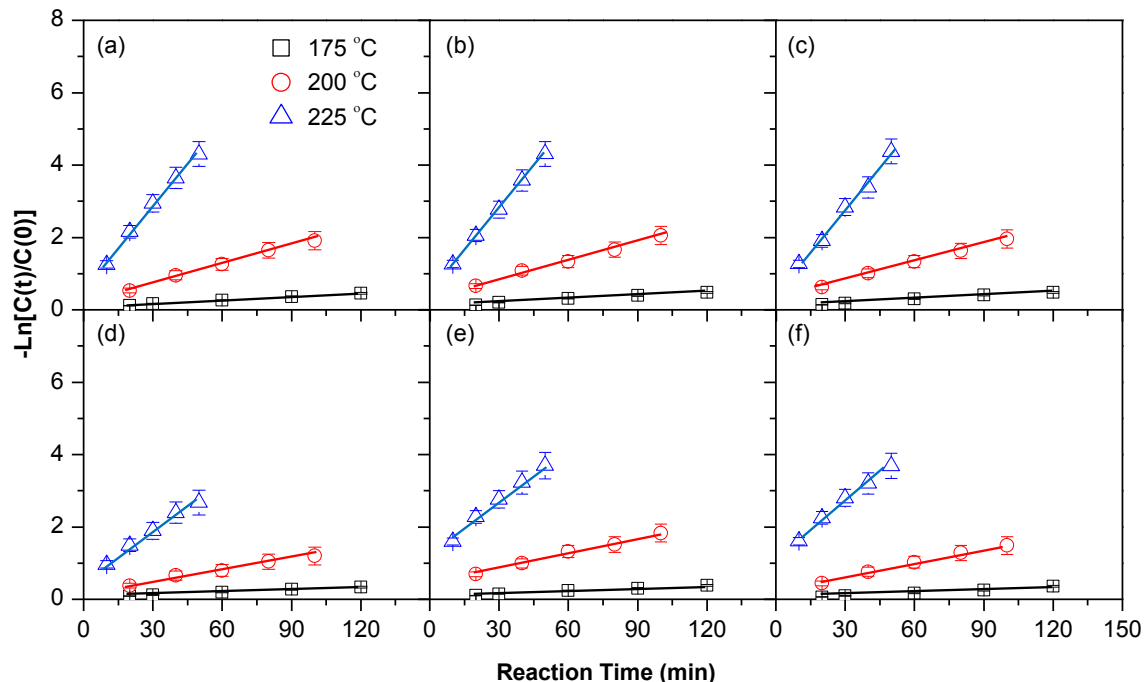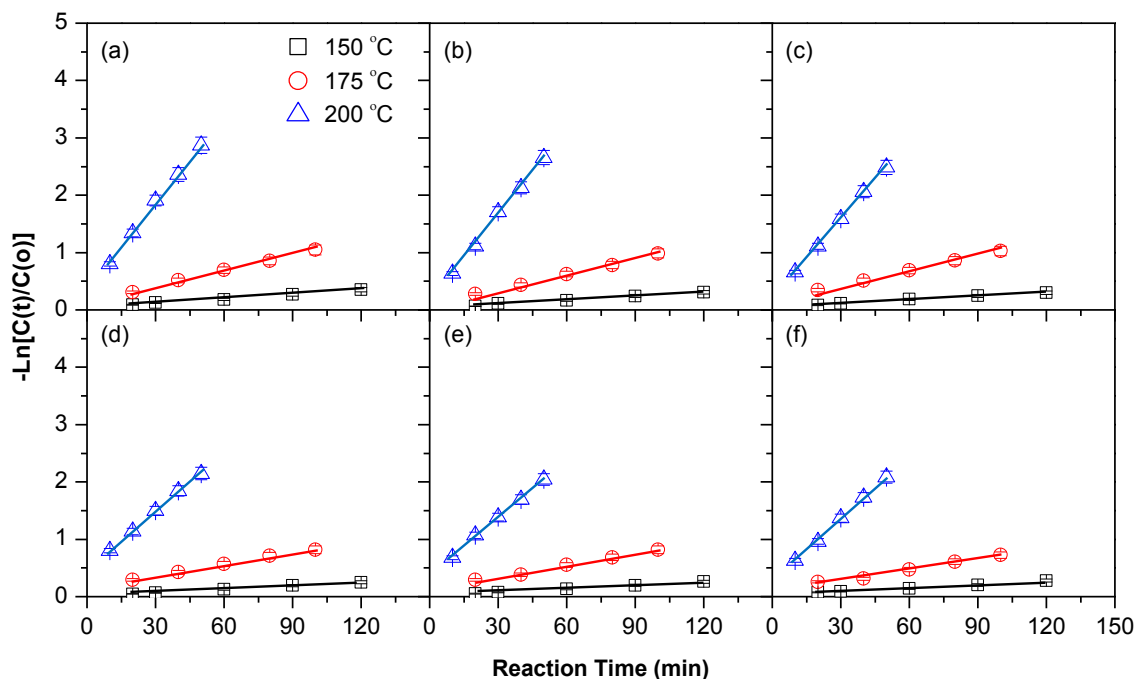
Figure 7.8: Correlation between –Ln[C(t)/C(0)] and reaction time t fructose decomposition in various solvent mixtures. (a) water; (b) methanol/water (10/90); (c) ethanol/water (10/90); (d) GVL/water (10/90); (e) acetone/water (10/90); (f) 1,4-dioxane/water (10/90). C(0) and C(t) represent the primary concentration and the concentration of glucose after a reaction time t at various solvent systems and temperatures.

Moreover, calculation based on Arrhenius equation indicates that the overall activation energies for the decomposition of glucose (~117 kJ mol^{-1}) and fructose (~100 kJ mol^{-1}) are slightly lower in aprotic/water than that in water and aprotic/water (~107 and ~95 kJ mol^{-1} for glucose and fructose, respectively). In conclusion, this study indicates that the presence of aqueous aprotic solvents result to lower reaction rates, pre-exponential constants, and activation energies compared with that in water and aqueous alcohols under catalyst-free conditions.
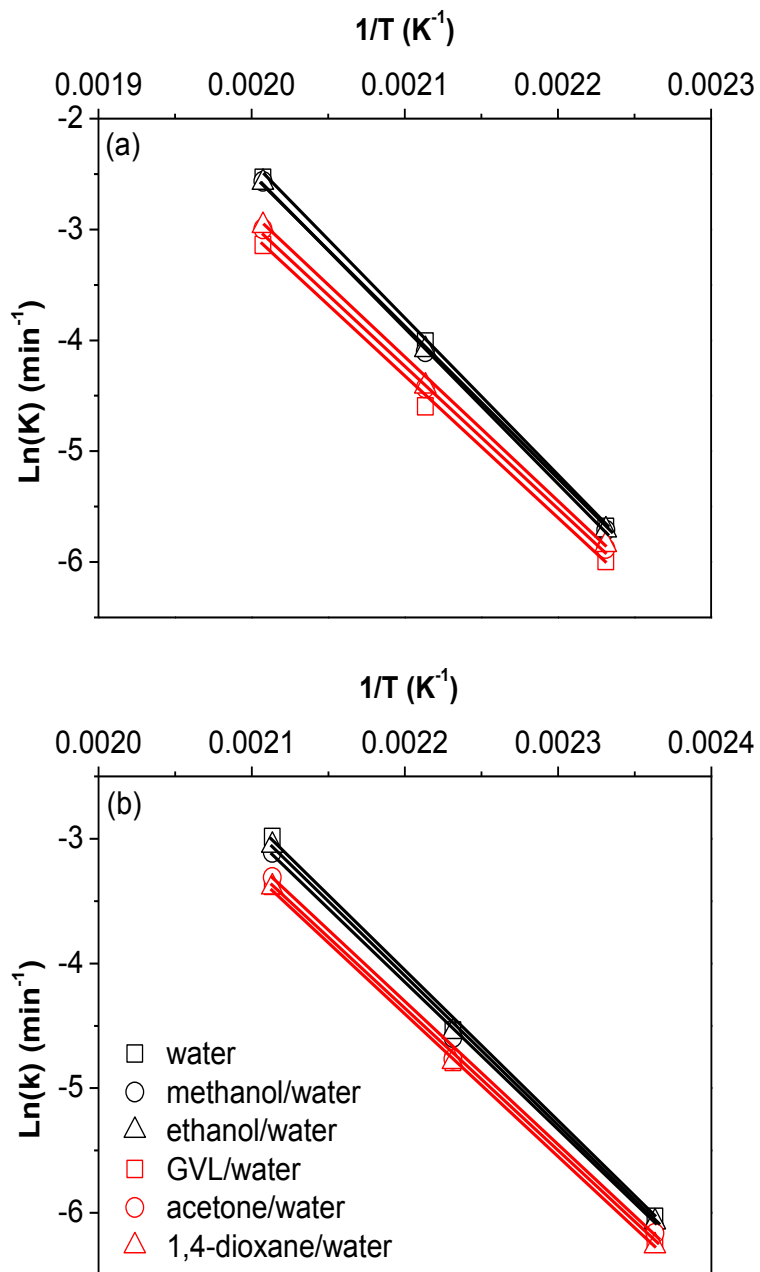
Figure 7.9: Arrhenius plots of glucose (a) and fructose (b) decomposition in water and various aqueous organic solvents.

Table 7.1: Reaction rate constant, activation energy and pre-exponential constant for glucose decomposition in different solvent systems

Solvent	reaction rate constant (min^{-1})			activation energy (kJ mol^{-1})	pre-exponential constant (min^{-1})
	175 °C	200 °C	225 °C		
water	0.0034	0.0181	0.0794	117	1.5E+11
methanol/water	0.0033	0.0178	0.0769	116	1.2E+11
ethanol/water	0.0033	0.0175	0.0760	117	1.3E+11
GVL/water	0.0025	0.0101	0.0433	106	5.1E+09
acetone/water	0.0028	0.0119	0.0500	107	7.9E+09
1,4-dioxane/water	0.0029	0.0121	0.0515	107	7.7E+09

Table 7.2: Reaction rate constant, activation energy and pre-exponential constant for fructose decomposition in different solvent systems

Solvent	reaction rate constant (min^{-1})			activation energy (kJ mol^{-1})	pre-exponential constant (min^{-1})
	150 °C	200 °C	225 °C		
water	0.0024	0.0104	0.0505	101	7.2E+09
methanol/water	0.0022	0.0101	0.0446	100	5.4E+09
ethanol/water	0.0023	0.0106	0.0472	101	4.8E+09
GVL/water	0.0020	0.0083	0.0341	94	8.0E+08
acetone/water	0.0019	0.0085	0.0338	95	8.8E+08
1,4-dioxane/water	0.0021	0.0080	0.0365	96	9.8E+08

7.5   Discussion on the Effect of Different Solvents

The above results have clearly shown the distinct effect of aprotic and protic solvents on glucose and fructose decomposition in hot-compressed solvent/water mixture. The effects of aprotic solvents on glucose and fructose decomposition in hot-compressed solvent/water mixture are complicated, since the solvents can affect the chemical thermodynamics of sugar decomposition reaction via solvent-solute intermolecular interactions with reactants, intermediates, products and catalyst.[238] The current study reveals the important role of aprotic solvent in enhancing the sugar

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dehydration into 5-HMF, providing new insights into the effect of different solvents on sugar decomposition in hot-compressed solvent/water mixture.

First, the aprotic solvent can affect the equilibrium of different sugar tautomers in the reactants. Previous studies[213, 214, 244] have reported that different forms of sugar tautomers are present in the sugar solution, such as open-chain form, the pyranose (six-membered ring) and the furanose (five-membered ring) forms of α- and β-types. In water, the pyranose forms of the α- and β-types are dominate in glucose solution, while the pyranose and furanose forms of the β-type are dominate in fructose solution.[214] It is known that 5-HMF is a primary product from fructose decomposition in HCW, but not a primary product from glucose decomposition in HCW. This suggests that the furanose forms play important roles in 5-HMF formation from sugar decomposition, since furanose forms are present in the fructose solution but not the glucose solution.[214] The importance of furanose form in enhancing 5-HMF formation during fructose decomposition under acidic conditions has been recently confirmed via an in situ NMR analysis.[245] In an aprotic solvent like dimethyl sulfoxide (DMSO), the furanose forms of α- and β-types are largely increased for fructose,[213] especially the β-furanose which was reported to be the most stable tautomer in DMSO probably due to the formation of intramolecular hydrogen bonds.[244] In this study, the primary selectivity of 5-HMF is largely increased during fructose decomposition in the aprotic/water solution, further supporting the important role of the furanose forms in enhancing 5-HMF formation from fructose dehydration. In contrast, there are only small changes in the forms of fructose tautomers for protic solvents like methanol,[213] explaining the little effect of protic solvent on fructose dehydration to produce 5-HMF. Therefore, it is very likely that the furanose forms are increased for glucose in the aprotic solvent/water solution, resulting in the formation of 5-HMF as a primary product from glucose decomposition in hot-compressed aprotic solvent/water mixture. However, further research is required to confirm the increase of the furanose forms for glucose solution in the aprotic solvent.

Second, the aprotic solvent can also affect the formation mechanism of various products (i.e., 5-HMF, fructose) from sugar decomposition. For glucose decomposition in HCW, 5-HMF is produced from the secondary decomposition of fructose. However, the reaction mechanism of direct 5-HMF formation from glucose decomposition in the aprotic solvent/water is unclear. Previous molecular dynamic (MD) calculation[246] indicated that direct glucose dehydration into 5-HMF in acidic solution is initiated by protonation of the C2-OH and the breakage of C2-O2 bond followed by the formation of the C2-O5 bond. The presence of aprotic solvent seems to change the local arrangement of solvents around the glucose molecules, thus facilitating the formation of 5-HMF.[247] The reaction mechanisms of fructose decomposition in different solvents have been also investigated by molecular dynamic simulations.[213, 248-251] In water, 5-HMF formation likely follows the acid-catalyzed dehydration mechanism since protons are present in water.[249] In DMSO, it was proposed that fructose is first converted into some precursors catalyzed by DMSO, before the formation of 5-HMF.[248] While in the DMSO/water mixture, there are strong interactions between fructose and DMSO/water, which seem to enhance the acid-catalyzed dehydration mechanism.[251] It is likely due to the high reactivity of water molecules (so-called "solitary water") dissolved in organic solvents, which have unique properties because of the absence of the hydrogen bonding.[252] However, more theory studies are required to achieve mechanistic understanding in the role of aprotic solvent in enhancing direct dehydration reaction to produce 5-HMF during glucose decomposition in aprotic solvent/water mixtures.

The presence of aprotic solvent also suppresses the fructose formation from glucose decomposition in hot-compressed solvent/water mixture. In water, previous MD simulations[207] have reported that glucose isomerization is also initiated by protonation of the C2-OH to form a furanose aldehyde intermediate, followed by a hydride transfer from C2 to C1 on the furanose aldehyde and the subsequent rehydration of the C2 carbocation. In the aprotic solvent/water mixture, the solvent strongly competes with water in the first solvation shell of glucose and push significant amount of water to the second coordination shell, leading to significant

change in the local arrangement of solvents around the glucose molecules.[247] Due to the reduced water molecules around the glucose molecules, the hydride transfer to produce fructose becomes difficult, thus reducing the fructose selectivity during glucose decomposition in hot-compressed aprotic solvent/water.

Third, the aprotic solvent can also affect the stability of formed products (i.e., 5-HMF) from sugar decomposition. Previous simulation studies[250, 253] have revealed that aprotic solvents like DMSO prefer to coordinate around 5-HMF, thus providing a shielding effect to prevent the further rehydration to levulinic acid and formic acid or condensation to form humins. Therefore, the higher 5-HMF selectivity in the aprotic solvent/water mixture is at least partly due to the high stability of 5-HMF in the aprotic solvent/water mixture, further proving that aprotic solvent/water mixture is a promising solvent system to produce 5-HMF from sugar products.
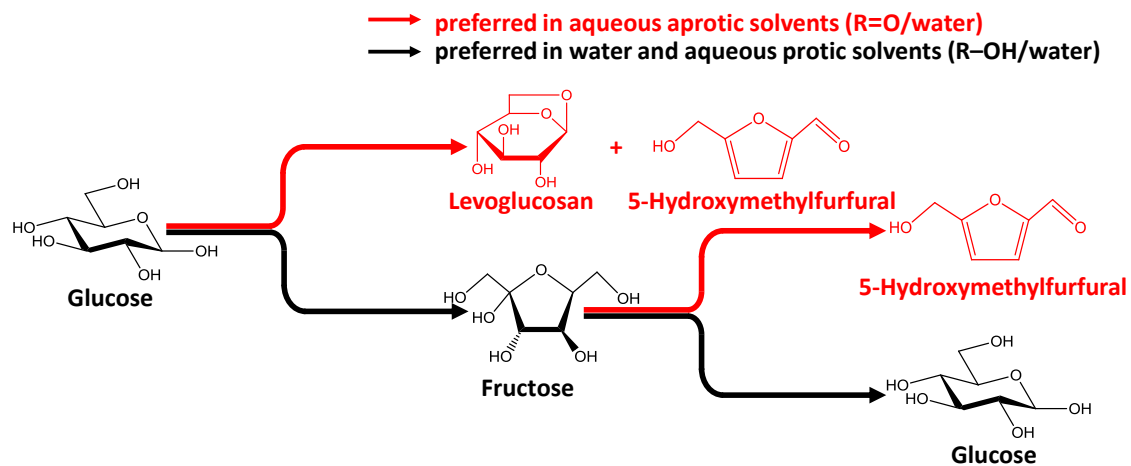
Figure 7.10: Reaction pathways of glucose and fructose in aqueous aprotic and protic solvents

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7.6   Conclusions

This chapter investigates the decomposition of glucose and fructose in hot-compressed solvent/water mixtures to provide some new insights into the solvent effect of various organic solvents on hydrothermal decomposition of sugars. The results clearly demonstrate the distinct effect of aprotic solvent on sugar decomposition in solvent/water mixture. Although the addition of aprotic solvent (i.e., GVL, acetone, and 1,4-dioxane) suppresses the sugar decomposition, it largely increases the selectivities of dehydration products and decreases the selectivities of isomerization products. Particularly, direct dehydration to 5-HMF becomes a primary product during glucose decomposition in aprotic solvent/water mixture. In contrast, the addition of protic solvent (i.e., methanol, ethanol) has little effect on primary sugar decomposition in hot-compressed solvent/water mixture. The distinct effect of aprotic solvent is likely due to its strong intermolecular interactions with reactants and products, leading to the changes of sugar tautomers in the reactants, the modification of reaction pathways as well as the stabilization of dehydrated products such as 5-HMF. This study demonstrates that the aprotic solvent/water mixture is promising to tune the reaction pathways of sugar decomposition for the production of biofuels and biochemicals.

Chapter 8: Conclusions and Recommendations

8.1   Introduction

Overall, this PhD study has provided new knowledge on and made original contributions to various aspects of hydrothermal processing of biomass and its derived sugars in hot compressed solvents under catalyst-free conditions. This chapter summarises the key findings from this PhD study and outlines the future works.

8.2   Conclusions

In general, hot-compressed gamma-valerolactone/water (HCGW) suppresses the isomerization reactions and enhances the hydrolysis reactions of cellulose and its derived oligomers, which effect increases the sugar recovery during biomass saccharification. Moreover, HCGW enhances the dehydration reactions and suppresses the isomerization reactions of biomass derived glucose and fructose, which effect enhances the conversion from monomers to 5-HMF. Further investigation suggests that aprotic solvents and protic solvents have different effect onto the conversion of biomass derived sugars.

8.2.1   Glucose Decomposition in HCGW under Catalyst-Free Conditions

- The dehydration reactions from glucose to 5-HMF and LGA are enhanced in GVL/water. Especially, the dehydration of glucose to 5-HMF is shown to be

a primary reaction in GVL/water. In contrast, isomerization from glucose to fructose is suppressed;

- Correlation between the reaction rates and GVL concentrations in GVL/water shows that the reaction rates of isomerization decrease with the increase of GVL concentrations; while dehydration reactions increase on the contrary;

- The activation energy of glucose conversion reduces in HCGW with the increase of GVL concentration;

- The changes in primary reaction pathways suggest that GVL can be applied to tune the reaction pathways from isomerization-dominated in water to dehydration-dominated in GVL/water.

8.2.2 Cellobiose Decomposition in HCGW under Catalyst-Free Conditions

- As the dominant primary reaction of cellobiose decomposition in water, the isomerization reaction to produce glucosyl-fructose (GF) is largely suppressed or even eliminated in HCGW, depending on GVL concentration;

- More importantly, GVL addition significantly promotes the hydrolysis reaction to produce glucose. The selectivity of hydrolysis reaction increases with GVL concentration, and stabilizes at ~80% when the GVL concentration increases to >10%;

- As a result, a high glucose yield of ~66% can be obtained from cellobiose at 25% GVL concentration and 200 °C. To the best of our knowledge, this is the highest glucose yield reported so far from cellobiose hydrothermal decomposition under acid-free conditions.

8.2.3 Cellulose and Biomass Decomposition in HCGW under Catalyst-Free Conditions

- Compared to water, GVL/water co-solvent is found to be more effective to hydrolyse cellulose with faster hydrolysis reaction rate and higher sugar recovery;

- Analyses of the primary liquid products from cellulose pyrolysis in HCGW by HPAEC-PAD indicate that GVL addition enhances hydrolysis reactions and suppresses isomerization reactions in the solid phase during cellulose hydrolysis in HCGW, leading to an increased sugar recovery (i.e., ~91%) and a higher yield of low-DP glucose oligomers (i.e., ~50% in 10% GVL/water for DPs up to 5) in the primary liquid products;

- Further hydrolysis experiments at reduced flow rates show that the presence of GVL also promotes hydrolysis reactions and inhibits isomerization reactions in the liquid phase, producing more low-DP glucose oligomers (i.e., ~63% in 5% GVL/water for DPs up to 5) without reduction in total sugar recovery;

- Finally, a near-compete sugar recovery of ~93% can be achieved from biomass hydrolysis at 250 °C in HCGW even at a low GVL concentration of 5%, demonstrating excellent performance of GVL/water co-solvent for biomass hydrolysis under acid-free conditions.

8.2.4 **Glucose and Fructose Decomposition in Various Solvents under Catalyst-Free Conditions**

- Analyses of the primary products indicate that aqueous GVL, acetone and 1,4-dioxane/water are preferred to suppress the isomerization and enhance the dehydration reactions of both glucose and fructose; while water and aqueous alcohols (methanol/water, ethanol/water) are preferred for the isomerization reactions of both monomers;

- Further discussion suggests that the present of aprotic solvents (R=O) enhances dehydration reactions and suppresses isomerization, which is contrary to the present of protic solvents (R-OH);

- Slight differences in the kinetics of glucose and fructose decomposition are demonstrated;

- This study suggests that the use of different co-solvents can tune the reaction pathways of biomass derived monomers for the generation of different biochemicals.

8.3   Recommendations

Based on the finding from this research, the following future researches are suggested to close the research gaps in this area:

- The analytical methods in this thesis mainly focus on the sugar products in liquid samples. Further improvements on analytical methods are necessary in future works to characterize more products including lignin and solids.

- An integrated process for continuous processing of biomass combined with products purification/separation in the case of GVL/water need to be developed in future studies.

- There are still other reactions such as reversion, retro-aldol condensation reactions under other reaction conditions (Chapter 2) need to be further understood to have a comprehensive understanding of solvent effects on biomass hydrothermal processing.

- This study carried out experiments on fructose, glucose, cellobiose, cellulose, and mallee wood. More works need to be carried out onto other biomass derived compounds such as lignin, hemicellulose, 5-HMF, and LGA.

- This study compared the solvent effect of GVL with other aprotic and protic solvents. There are more solvents need to be studied. For example, Ionic

Liquids (IL) are also widely used solvents for biomass processing (Chapter 2). The reaction mechanism and kinetics will also need to be investigated.

- The factors influencing the solvent effect of GVL need to further studied to alter the solvent effect via different approaches. For example, alkali and alkaline earth metallic (AAEM) species was reviewed in Chapter 2 to influence the hydrothermal decomposition of cellobiose. They may also cause effect to the performance of GVL.

- The use of HCGW achieved a high sugar recovery (~93%) from biomass (Chapter 6). Further studies need to be carried out to develop effective ways to separate the biomass derived products from the GVL/water binary solvents for the sustainable use of GVL.

- In the Chapter 7 of this thesis, only fructose and glucose were studied in different solvents. The decomposition mechanisms of cellobiose, cellulose, and biomass in these solvents need to be further understood.

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Insights into Hydrothermal Decomposition of Cellobiose in Gamma-Valerolactone/Water Mixtures

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Cite this: *Ind. Eng. Chem. Res.* 56, 28, 7957-7963

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Title: Solvent effect of gamma-valerolactone (GVL) on cellulose and biomass hydrolysis in hot-compressed GVL/water mixtures

Author: Bing Song, Yun Yu, Hongwei Wu

Publication: Fuel

Publisher: Elsevier

Date: 15 November 2018

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