

## **Copyright Undertaking**

This thesis is protected by copyright, with all rights reserved.

#### By reading and using the thesis, the reader understands and agrees to the following terms:

- 1. The reader will abide by the rules and legal ordinances governing copyright regarding the use of the thesis.
- 2. The reader will use the thesis for the purpose of research or private study only and not for distribution or further reproduction or any other purpose.
- 3. The reader agrees to indemnify and hold the University harmless from and against any loss, damage, cost, liability or expenses arising from copyright infringement or unauthorized usage.

#### IMPORTANT

If you have reasons to believe that any materials in this thesis are deemed not suitable to be distributed in this form, or a copyright owner having difficulty with the material being included in our database, please contact <a href="https://www.lbsys@polyu.edu.hk">lbsys@polyu.edu.hk</a> providing details. The Library will look into your claim and consider taking remedial action upon receipt of the written requests.

Pao Yue-kong Library, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

http://www.lib.polyu.edu.hk

# VALORISING POLYSACCHARIDE-RICH WASTE INTO VALUE-ADDED CHEMICALS IN GREEN SOLVENTS

SHANTA DUTTA

# PhD

The Hong Kong Polytechnic University 2022

# The Hong Kong Polytechnic University Department of Civil and Environmental Engineering

# Valorising Polysaccharide-rich Waste into Value-added Chemicals in Green Solvents

Shanta Dutta

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

May 2022

## CERTIFICATE OF ORIGINALITY

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it reproduces no material previously published or written, nor material that has been accepted for the award of any other degree or diploma, except where due acknowledgement has been made in the text.

Shanta Dutta

#### Abstract

The anticipated transition of our society from a fossil resource-dependent linear economy to a bio-based circular economy requires considerable research efforts on valorising waste-based feedstock such as lignocellulosic biomass and food waste for greener production of value-added products, energy, and chemicals. These wastes are enriched in polysaccharides such as cellulose and starch that are deemed suitable and potential for value-added chemical production. However, it is crucial to develop cost-effective and time-efficient valorisation technologies for complex waste substrates. This thesis focused on the development of facile and efficient technology to valorise polysaccharide-rich waste to value-added chemicals through catalytic conversion under diverse green solvent systems.

Solvent is a significant parameter that influences catalytic conversion through interactions with reactants and regulation of product selectivity in the system. Therefore, appropriate solvents could enhance the conversion of polysaccharide-rich waste to bio-based chemicals. However, high-performance industrial solvents often pose direct and indirect risks to health, safety, and environmental components, which should be addressed by finding green yet reactive solvents for biorefinery applications. This research demonstrated that cellulosic paper wastes and starchy food waste could be efficiently valorised into sugars, levulinic acid (LA), hydroxymethylfurfural (HMF), and other valuable chemicals through tandem hydrolysis and dehydration/rehydration using the dilute sulphuric acid catalyst in green solvent systems under microwave heating.

Gamma-valerolactone (GVL) (used as a co-solvent, GVL/H<sub>2</sub>O) as a bio-derived, renewable, and green solvent demonstrated excellent performance as a reaction medium for LA production (32 mol%) from highly cellulosic paper towel waste. Further, diverse paper waste substrates with variable properties (feedstock characteristics originated due to varied paper manufacturing operations) were also deemed viable for platform chemical production under GVL/H<sub>2</sub>O solvent generating up to 27 wt% LA yield along with a considerable amount of HMF, and furfural, which is attractive to foster paper waste valorisation at industrial scale. Such notable performance of GVL solvent could be attributed to its positive enhancement in cellulose solvation, maintaining the solubility of the desired products, while preventing polymerisation/condensation of derivatives and by-product formation.

Depolymerisation, which is a bottleneck for the efficient valorisation of cellulosic waste, could be enhanced by using CO<sub>2</sub>-derived organic carbonate solvents (*i.e.*, propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC)) as reaction medium. This research demonstrated the efficiency of these emerging green solvents for sugar production, up to 25 mol% in PC/H<sub>2</sub>O compared to 11 mol% in H<sub>2</sub>O-only solvent under mild reaction conditions (130 °C, 20 min). Enhanced sugar yield could be attributed to the higher availability of reactive protons in the catalytic system comprising carbonate solvents that facilitated efficient acid hydrolysis of recalcitrant cellulosic fibres. Moreover, a substantial build-up of auto-generated pressure in PC/H<sub>2</sub>O might be favourable for cellulose depolymerisation.

Furthermore, the valorisation of starch-rich food waste was optimised based on the knowledge acquired regarding catalytic conversion green solvent systems. This research highlighted that solvent effects, reaction pressure, and phase separation could be the critical factors for determining levulinic acid production from bread waste. The presence of polar aprotic solvents such as GVL and PC were instrumental in maintaining proton reactivity during catalytic conversion. In PC/H<sub>2</sub>O solvent, CO<sub>2</sub>-derived pressure generated by PC decomposition favours starch hydrolysis and subsequent dehydration (15-20 mol% LA, 130 °C, 20 min, 0.5 M H<sub>2</sub>SO<sub>4</sub>). Besides, LA yield was significantly increased by using biphasic GVL/H<sub>2</sub>O solvent (28 mol%, 150 °C, 15 min), promoted by NaCl as the phase modifier. These research efforts elucidated the roles and performance of green solvents, which could be potential alternatives to conventional industrial solvents for valorising polysaccharide-rich wastes in biorefineries.

### **Publications Arising from PhD Study**

#### **First Author Journal Papers of Waste Biomass Valorisation:**

- Dutta, S.; Zhang, Q.; Cao, Y.: Wu, C.; Moustakas, K.; Zhang, S.; Wong, K.H.; Tsang, D.C.W.\* Catalytic valorisation of various paper wastes into levulinic acid, hydroxymethylfurfural, and furfural: Influence of feedstock properties and ferric chloride. Bioresour. Technol., 2022, 357, 127376. [Impact Factor: 9.237; Grade A (Agricultural Engineering)]
- Dutta, S.; Yu, I.K.M.; Fan, J., Clark, J.H.; Tsang, D.C.W.<sup>\*</sup> Critical factors for levulinic acid production from starch-rich food waste: solvent effects, reaction pressure, and phase separation. Green Chem., 2022, 24, 163-175. [Impact Factor: 10.607; Grade A (Green & Sustainable Science & Technology)] [Journal Cover]
- Dutta, S.; He, M., Xiong, X.; Tsang, D.C.W.\* Sustainable management and recycling of food waste anaerobic digestate: A review. Bioresour. Technol., 2021, 341, 125915.
   [Impact Factor: 9.237; Grade A (Agricultural Engineering)]
- Dutta, S.; Yu, I.K.M.; Tsang, D.C.W.\*; Fan, A.; Clark, J.H.; Jiang, Z.; Su, Z.; Hu, C.; Poon, C.S. Efficient depolymerisation of cellulosic paper towel waste using organic carbonate solvents. ACS Sustain. Chem. Eng., 2020, 8, 13100-13110. [Impact Factor: 7.951; Grade A (Chemical Engineering)] [Journal Cover]
- Dutta, S.; Yu, I.K.M.; Tsang, D.C.W.\*; Su, Z.; Hu, C.; Wu, K.C.W.; Yip, A.C.K.; Ok, Y.S.; Poon, C.S. Influence of green solvent on levulinic acid production from lignocellulosic paper waste. Bioresour. Technol., 2020, 298, 122544. [Impact Factor: 9.237; Grade A (Agricultural Engineering)]
- 6. **Dutta, S.**; Yu, I.K.M.; Tsang, D.C.W.\*; Ng, Y.H.; Ok, Y.S.\*; Sherwood, J.; Clark, J.H. Green synthesis of gamma-valerolactone (GVL) through hydrogenation of biomass-

derived levulinic acid using non-noble metal catalysts: A critical review. Chem. Eng. J., 2019, 372, 992-1006. [Impact Factor: 11.529; Grade A (Chemical Engineering)]

#### **Co-author Journal Papers of Waste Biomass Valorisation:**

- He, M.; Zhu, X.; Dutta, S.; Khanal, S.K.; Lee, K.T.; Masek, O.; Tsang, D.C.W.\* Catalytic co-hydrothermal carbonization of food waste digestate and yard waste for energy application and nutrient recovery. Bioresour. Technol., 2022, 344, 126395. [Impact Factor: 9.237; Grade A (Agricultural Engineering)]
- Cao, Y., He, M., Dutta, S., Luo, G., Zhang, S. Tsang, D.C.W.<sup>\*</sup> Hydrothermal carbonization and liquefaction for sustainable production of hydrochar and aromatics. Renew. Sust. Energ. Rev., 2021, 152, 111722. [Impact Factor: 16.514; Grade A (Green & Sustainable Science & Technology)]
- Xiong, X., Yu, I.K.M., Dutta, S., Tsang, D.C.W.<sup>\*</sup> Valorisation of Humins from Food Waste Biorefinery for Synthesis of Biochar-supported Lewis Acid Catalysts. Sci. Total Environ., 2021, 775, 145851. [Impact Factor: 7.842; Grade A (Environmental Sciences)]
- Kumar, M.; Dutta, S.; You, S.; Luo, G.; Zhang, S.; Show, P.L.; Sawarkar, A.D.; Singh, L.; Tsang, D.C.W.\* A critical review on biochar for enhancing biogas production from anaerobic digestion of food waste and sludge. J. Clean. Prod., 2021, 305, 127143. [Impact Factor: 9.444; Grade A (Environmental Sciences)]
- O'Connor, J.; Hoang, S.A.; Bradney, L.; Dutta, S.; Xiong, X.; Tsang, D.C.W.; Ramadass, K.; Vinu, A.; Kirkham, M.B.; Bolan, N.S.\* A review on the valorisation of food waste as a nutrient source and soil amendment. Environ. Pollut., 2020, 272, 115985. [Impact Factor: 8.35; Grade A (Environmental Sciences)]

#### **Co-author Journal Papers of Other Waste Recycling**

 Wang, M.; Liu, K.; Dutta, S.; Alessi, D.S.; Rinklebe, J.; Ok Y.S.; Tsang, D.C.W.<sup>\*</sup> Recycling of lithium iron phosphate batteries: Status, technologies, challenges, and prospects. Renew. Sust. Energ. Rev., 2022, 163, 112515. [Impact Factor: 16.514; Grade A (Green & Sustainable Science & Technology)]

#### **Conference Proceedings/Abstracts of Waste Biomass Valorisation**

- Dutta, S.; Zhang, Q.; Yu, I.K.M.; Tsang, D.C.W.\* Levulinic acid production from lignocellulosic paper waste using green solvents, Waste Management and Valorisation for a Sustainable Future, Hybrid event, organized by Nature Research, October 26-28, 2021
- Dutta, S.; Yu, I.K.M.; Xiong, X.; Fan, J.; Clark, J.; Tsang, D.C.W.\* Efficient catalytic production of levulinic acid from starch-rich food waste: Influence of reaction pressure and phase separation, Sustainable waste management conference, virtual, organised by Institute for sustainability, 4-6 August 2021.
- Dutta, S.; Yu, I.K.M.; Xiong, X.; Tsang, D.C.W.\* Efficient catalytic production of levulinic acid from starch-rich food waste using a biphasic system, International Conference on Sustainable Biowaste Management, virtual, organised by Hong Kong Baptist University, 12-15 April 2021.
- Dutta, S.; Yu, I.K.M.; Xiong, X.; Tsang, D.C.W.<sup>\*</sup> Recycling bread waste into levulinic acid in binary monophasic and biphasic green solvents. 2<sup>nd</sup> Food Innovation and Engineering (FOODIE) Asia Conference, virtual, organised by AlChE, 23-24, November, 2020.

- Xiong, X.; Yu, I.K.M.; Dutta, S.; Tsang, D.C.W.\* Synthesis of Humins-derived Biochar Catalyst from Rice Waste Valorisation for Glucose Isomerisation. 20<sup>th</sup> International Conference on Heavy Metals in the Environment, virtual, 25-29 October, Seoul, Korea, 2020.
- Xiong, X.; Yu, I.K.M.; Dutta, S.; Tsang, D.C.W.<sup>\*</sup> Catalysis of Humins-Derived Biochar from Rice Waste Valorization for Glucose Isomerization. 2<sup>nd</sup> Food Innovation and Engineering (FOODIE) Asia Conference, virtual, organised by AlChE, 23-24, November 2020.
- Xiong, X.; Yu, I.K.M.; Dutta, S.; Tsang, D.C.W.<sup>\*</sup> Recycling Humins from Rice Waste Valorisation for Catalyst Synthesis in Biorefinery. the 2nd Engineering Sustainable Development Conference, 15-17 December 2020, virtual.

#### Acknowledgements

I would like to express my heartiest gratitude to Professor Daniel Tsang, my research advisor, who always inspires and encourages me to devote my best efforts to research and education. He leads the way to show us the strength and ability a person and a researcher could have and offers valuable opportunities to learn and develop essential skills and expertise. I am truly grateful for his indispensable help and continuous support throughout my PhD research journey. Besides, I would like to thank my research co-advisor Professor Chi Sun Poon for his guidance in enhancing my research works.

I feel very fortunate to have amazing groupmates who made this journey wonderful and supported me in my ups and downs. We learn from each other and accomplish together. Particularly, my sincere thanks go to Dr. Iris K.M. Yu for her guidance and indispensable help to continue the PhD journey and make it impactful. Besides, I highly appreciate all the lab technicians who are always willing to offer their support whenever we are in need and do their best to make our workplace safe and efficient. In particular, I would like to thank Mr W.S. Lam, who is very knowledgeable and offers practical advice regarding our analysis.

Special appreciation goes to my family members for their love, support, and immense help. My parents always made their best efforts to take care of me and my brother despite uncountable challenges in life. I am very thankful to have their love and protection. I also like to thank my parents-in-law for their support and understanding. Moreover, I feel blessed to have my loving husband who helped me in every way and made this journey possible. I must mention our wonderful son who embraced all the distress of our struggles and the devastating pandemic. We love you so much and wish we can fill your coming days with laughter and happiness. Besides, thanks to all our friends for their care and good wishes. Above all, thanks to the Almighty for all the blessings and opportunities in our life.

# **Table of Contents**

# Contents

Abstract	i
Publications Arising from PhD Study	iii
Acknowledgements	vii
Table of Contents	viii
Chapter 1: Introduction	11
1.1 Background	11
1.2 Scope and objectives	12
1.3 Thesis overview	13
Chapter 2: Literature Review	16
2.1 Introduction	16
2.2 Waste biomass substrates	17
2.2.1 Raw lignocellulosic biomass	17
2.2.2 Food waste	
2.3 Valorisation technologies	21
2.3.1 Composting	21
2.3.2 Enzymatic conversion	21
2.3.3 Anaerobic digestion	22
2.3.5 Integrated valorisation of anaerobic digestate	23
2.3.6 Pyrolysis	23
2.3.7 Hydrothermal conversion	24
2.3.8 Catalytic hydrolysis and dehydration	25
2.4 Value-added chemicals	27
2.4.1 Levulinic acid	27
2.4.2 Hydroxymethylfurfural	
2.4.3 Formic acid and furfural	
2.5 Influential reaction conditions	31
2.5.1 Microwave heating	31
2.5.3 Catalytic systems	31
2.5.4 Solvents systems	32
2.6 Research gaps and hypothesis	
Chapter 3: Materials and Methods	40
3.1 Waste substrates	40

3.2 Chemicals	41
3.2.1 Standard compounds	41
3.2.2 Catalysts	41
3.2.3 Solvents	42
3.3 Catalytic valorisation	43
3.3.1 Major experiments	43
3.3.2 Supplementary and control experiments	44
3.4 Sample analysis	45
3.4.1 Soluble products	45
3.4.2 Characterisation of solids	49
Chapter 4: Valorisation of Paper Waste in Green Solvents	51
4.1 Research questions	52
4.2 Results and discussion	54
4.2.1 Depolymerisation of paper towel	54
4.2.2 Effects of green co-solvent on LA production	57
4.2.3 Analysis of post-reaction solid residues	63
4.2.4 Energy consumption for LA production	67
4.2.5 Comparative perspective regarding solvent systems	68
4.3 Summary	69
Chapter 5: Influence of Feedstock Properties and Catalytic Systems	70
Abstract	70
5.1. Research questions	71
5.2. Results and discussion	74
5.2.1 Characteristics and composition of various paper wastes	74
5.2.2 Influences of paper waste properties on product yields	79
5.2.3 Comparative performance and product distributions in different catalytic sy	stems84
5.2.4 Perspectives regarding chemical production from various paper wastes	90
5.3 Summary	93
Chapter 6: Enhancement of Lignocellulose Depolymerisation	94
6.1 Research questions	95
6.2 Results and discussion	97
6.2.1 Depolymerisation of paper towel waste in PC/H <sub>2</sub> O solvent system	97
6.2.2 Comparative conversion in different carbonate solvent-water systems	
6.2.3 Role of carbonate solvents for effective depolymerisation	
6.2.4 Tandem dehydration-rehydration reactions	112
6.2.5 Energy requirement for sugar production	113

6.3 Summary	114
Chapter 7: Critical Factors for Levulinic Acid Production	115
7.1 Research questions	116
7.2 Results and discussion	119
7.2.1 Catalytic conversion of bread waste under bio-derived and CO <sub>2</sub> -derived solv	vents119
7.2.2 LA yield enhanced by in-vessel high pressure generated in $PC/H_2O$	126
7.2.3 Intensification of LA yield through phase separation	129
7.2.4 Perspectives on LA production and solvent recycling	136
7.3 Summary	139
Chapter 8: Conclusions and Recommendations	140
8.1 Conclusions	140
8.2 Recommendations and future work	142
Appendix A	146
Appendix B	147
Appendix C	149
References	150

# **Chapter 1: Introduction**

#### 1.1 Background

In recent decades, the growing demand for energy and resources has stimulated interest to recover materials and energy from waste biomass and provide sustainable alternatives to diminishing fossil-based resources (Savage, 2011; Luterbacher et al., 2014). Waste biomass generated in significant amounts might play an important role in our transition to a circular economy (Mak et al., 2020). Food waste is one of the major waste streams with an estimated annual generation of 931 million tons (at the consumer level) is turning into a significant environmental concern (UNEP, 2021), which should be managed to prevent pollution and associated resource loss. Besides, lignocellulosic biomass, such as woody waste and agricultural residues, is the most abundant resource with an estimated annual global production of approximately 170 billion tons (Petridis and Smith, 2018). Valorisation of these vast renewable resources is necessary to close the resource loop and ensure sustainability. However, the anticipated transition of our society from a natural resource-dependent linear economy to a bio-based circular economy would require considerable research efforts on valorising inexpensive and abundant waste-based feedstock (Mohan et al., 2019).

Compared to waste handling approaches such as incineration, and landfilling, various valorisation options using physical, chemical, and biological processing technologies have been preferred and investigated (Maina et al., 2017; Xiong et al., 2019). Conventional waste recycling techniques such as composting and anaerobic digestion were widely investigated for the production of biofertliser and biogas from food waste/organic wastes (Taherzadeh et al., 2019). Besides, microbial/enzymatic conversion is generally preferred for valorising food waste considering the reliability of the process and high selectivity for target products (P. Sharma et al., 2020). However, the above-mentioned valorisation process involves considerable time to achieve target products yet is very prone to be influenced by

climatic/process conditions, and therefore requires vigorous control (Tanger et al., 2013). However, the composition of polysaccharide-rich biomass/food waste makes them suitable candidates as starting materials for the production of biofuels and chemicals through thermochemical conversion (Yu and Tsang, 2017). Innovative valorisation processes are being investigated using various thermocatalytic conversions such as catalytic hydrolysis and dehydration, hydrothermal carbonisation, pyrolysis etc. Multiple value-added products/biobased chemicals could be achieved using catalytic hydrolysis and dehydration of biomass/food waste in a cost-effective and timely manner, including sugars, hydroxymethylfurfural (HMF), levulinic acid (LA), formic acid (FA) etc. (Chen et al., 2017b).

Considerable research interests were devoted to exploring innovative and effective ways to recycle food waste into useful materials and energy (Xiong et al., 2019). However, their facile, efficient, and greener production would be necessary for fostering sustainable production at the industrial scale (Soh and Eckelman, 2016). Sustainable biorefinery depends on the development of efficient processes to convert locally abundant, energy-rich renewable biomass into fuels, chemicals, and materials (Clark, 2019). Therefore, this thesis scrutinises the influential factors for catalytic conversion of polysaccharide-rich wastes through tuning system components, *i.e.*, feedstock, catalytic conditions, and solvent effects, to develop green and efficient waste valorisation processes.

#### **1.2 Scope and objectives**

Various polysaccharide-rich wastes were upcycled for the production of value-added chemicals using mineral acid (*e.g.*, H<sub>2</sub>SO<sub>4</sub>) and metal chloride (*e.g.*, FeCl<sub>3</sub>) catalysts under microwave heating. Considering the abundance of cellulose yet an underutilised waste-based feedstock, paper waste was employed as a substrate for producing sugars, HMF, and LA. Besides, bread waste served as the representative starch-rich feedstock for catalytic

valorisation. The investigations particularly focused on the application of green solvents as reaction medium, and a variety of binary green solvent systems (organic solvent/water) were explored during catalytic valorisation of the selected polysaccharide-rich wastes. Detailed experimental evidence was provided and discussed considering product yields and solid characterisation to elucidate solvent effects and associated influential factors.

The objectives of the thesis are listed below:

- To develop facile and green approaches for polysaccharide-rich waste valorisation through enhancing catalytic hydrolysis and dehydration/rehydration;
- To scrutinise the influences of the complex and diverse nature of the paper waste feedstock and demonstrate the viability of chemical production from different paper wastes with variable properties under diverse catalytic systems;
- > To enhance catalytic depolymerisation of highly crystalline cellulose in paper waste;
- > To identify potential organic solvents with desirable green characteristics and demonstrate/elucidate their performance/contribution regarding chemical production;
- > To reveal critical factors for optimising levulinic acid production.

#### **1.3 Thesis overview**

This thesis contains eight chapters in total (**Figure 1.1**). Following **Chapter 1** as the introduction, **Chapter 2** is the literature review presenting a summary of conventional and emerging waste valorisation technologies directed toward value-added chemical production from polysaccharide-rich wastes. It discusses the potential of lignocellulosic paper waste and starch-rich food waste for catalytic production of sugars and platform chemicals such as HMF and LA. The chapter focuses on the identification of emerging green solvents and emphasises their potential role to design safe, facile, and effective valorisation technologies. As such,

research gaps are highlighted, which lay the cornerstone of this thesis. The overview of this thesis is presented in **Figure 1.1**.

**Chapter 3** describes the methodology, including collection and characterisation of waste substrates, experimental procedures including catalytic conversion process, sample preparation, and adopted analytical and characterisation methods for soluble and solid samples, solvent selection, which were designed based on the corresponding research questions.

**Chapters 4 – 7** investigate the influential factors for the catalytic valorisation of polysaccharide-rich waste substrates, *i.e.*, feedstock characteristics, reaction conditions, and solvent effects in determining effective conversion. The first step is to design facile approaches for the efficient valorisation of highly cellulosic paper waste by tuning reaction conditions with a particular focus on using green solvent as a reaction medium (**Chapter 4**), followed by investigating the influences of feedstock characteristics and catalytic systems on chemical production through exploring the conversion of different paper waste with variable properties (**Chapter 5**). Further, to enhance depolymerisation of highly crystalline cellulose under moderate conditions, paper waste conversion was conducted using emerging green solvents, *i.e.*, organic carbonate solvents (**Chapter 6**). Apart from the safety and greenness of the reaction medium, process intensification would be necessary for fostering chemical production on an industrial scale. Therefore, **Chapter 7** focuses on revealing critical factors for optimising levulinic acid production from starch-rich food waste by controlling the interplay of reaction conditions/ system components.

**Chapter 8** concludes the key findings in this thesis and suggests research prospects to achieve sustainable valorisation of biomass waste/food waste for closing the resource loop and realising a circular bioeconomy.



Figure 1.1 Overview of the thesis

## **Chapter 2: Literature Review**

#### Abstract

The growing demand for energy and resources is driving society to recover materials and energy from waste biomass and provide sustainable alternatives to fossil-based resources. Diverse valorisation pathways could be adopted for value-added products and energy production from waste biomass. Currently, considerable research interests have been directed towards the effective utilisation of waste biomass for the production of chemicals and fuels in the emerging biorefinery industry. Various polysaccharide-rich waste biomass such as lignocellulosic waste and food waste are deemed suitable for platform chemical production (*e.g.*, levulinic acid, hydroxymethylfurfural, etc.). However, their cost-effective and greener production would be necessary for fostering production at the industrial scale. This chapter briefly summarises various recognised and emerging valorisation technologies, then describes potential value-added chemicals that could be obtained through the catalytic valorisation of polysaccharide-rich waste biomass, and highlights the knowledge gap regarding their greener production in the biorefinery.

#### 2.1 Introduction

Waste generation from anthropogenic activities and industrial/agricultural production processes adversely affect the natural environment. To maintain a sustainable environment, waste should be managed considering the 3R principle, *i.e.*, reduce, reuse, and recycle (Joshi and Visvanathan, 2019). Prevention of waste generation should be prioritised. Besides, generated wastes could be transformed into resources using appropriate technologies. Waste valorisation is the process of converting waste materials into more useful products including chemicals, materials, and fuels. Valorisation is a sustainable technique that converts waste into

value-added products, which limits their disposal in landfills and eliminates greenhouse gas emissions (Mak et al., 2020). Valorising waste biomass might deliver double benefits through lessening the burden of waste management problems and providing useful bio-based products thereby turning bio-wastes into resources (Clark, 2019). Nevertheless, the transformation of our society from a fossil-dependent to a sustainable one would take considerable endeavours on valorising waste-based feedstock such as lignocellulosic biomass, food waste etc. for greener production of value-added products, energy and chemicals (Morone et al., 2019; Cao et al., 2021).

#### 2.2 Waste biomass substrates

#### 2.2.1 Raw lignocellulosic biomass

Lignocellulosic biomass, such as grass, woody waste, and agricultural residues, is the most abundant resource with an estimated annual global production of approximately 170 billion tons, and the utilisation of these renewable resources ensures a more sustainable society (Petridis and Smith, 2018). In terms of environmental protection, using lignocellulosic biomass could effectively abate greenhouse gas (GHGs) emissions, contributing to the mitigation of climate change by carbon sequestration (Yang and Tilman, 2020). The major components of lignocellulosic biomass are cellulose, hemicellulose, lignin, and extractives (proteins and inorganic compounds) (Yu et al., 2020a). Cellulose is the most abundant polysaccharide in nature (making up 40-50% of the dry weight of lignocellulose), mainly consisting of D-glucopyranose units linked by  $\beta$ -glycosidic bonds (Zheng et al., 2017; Fan et al., 2018). Hemicellulose is an amorphous biopolymer consisting of pentoses and hexoses (other than glucose), accounting for 30-50% of lignocellulose (Z. Chen et al., 2018; Zhou et al., 2018), whereas, lignin (10-30%) is an amorphous polymer composed of diverse building blocks (Cao et al., 2020; Liu et al., 2021).

Most of the frontier chemical/biofuel production strategies focused on the conversion of cellulosic and hemicellulosic fractions contained in biomass (Liu et al., 2020b; Usmani et al., 2020). These precursors are promising sources for producing lignocellulose-derived sugars (*e.g.*, glucose, xylose) and valuable chemicals such as bioethanol, hydroxymethylfurfural (HMF), levulinic acid (LA), furfural etc. (Chen et al., 2017b; Yu et al., 2018b, 2019). The valorisation of lignocellulosic biomass as a renewable feedstock has attracted considerable research interest in producing value-added chemicals and energy in recent years (Chen et al., 2017b; Yu et al., 2020a). Biomass offers numerous benefits as a sustainable alternative to diminishing petroleum-derived feedstock considering its abundance, low cost, renewability, and diversified applications. In addition, the utilisation of waste biomass contributes further toward sustainability as it does not compete with food production yet caters for the growing need for biorefinery (Serrano-Ruiz et al., 2011; Mak et al., 2020).

#### 2.2.2 Food waste

Appropriate and sustainable management of the growing amount of food waste (FW) is a big issue around the world. Approximately 931 million tonnes of food waste were globally generated in the year 2019 at the retail and consumer level (households and commercial food services), excluding food loss during post-harvest to distribution in the food supply chain (UNEP, 2021). Such an enormous amount of FW requires proper handling to minimise pollution risks and be diverted from landfill disposal (Xiong et al., 2019). Transforming FW into value-added products and energy offers a sustainable opportunity to utilise the vast waste stream for biorefinery applications and pave the way forward to realising a circular bioeconomy (Mak et al., 2020).

The conventional approaches applied for handling and treatment of FW include composting, incineration, and landfilling (C. Zhang et al., 2014). Landfilling is a conventional approach for FW disposal yet many countries restricted FW landfilling due to limited space,

emission of greenhouse gases, leachate pollution, etc. (Wambugu et al., 2019). For example, the EU has revised the landfill directive to reduce the dumping of organic waste at landfills to 35% and below, and Germany bans the dumping of all biodegradable waste at landfill sites (Cozzolino et al., 2017). Restricting FW landfilling is not only beneficial for the environment but also encourages a zero-waste approach toward sustainable development (Unger and Razza, 2018). Incineration of FWs is also common yet it is expensive and energy-intensive, which is not widely feasible, especially in low-income countries (C. Zhang et al., 2014). Considering the high water content in FW (70-90%) and the generation of air pollutants during incineration, this approach is not sustainable (Wambugu et al., 2019). Considering the projected increase in FW generation, environmental cost of waste disposal, and stringent environmental protocols, novel strategies would be required to advance the FW management practices around the world (Oladejo et al., 2019). At present, considerable interest is growing to utilise FW as feedstock to generate bioenergy/biofuel and valuable products via various biological and thermochemical methods (Yu and Tsang, 2017; Xiong et al., 2019).

Starch-rich foods such as rice, bread, and potatoes are commonly consumed around the world and constitute a significant proportion of global food waste (Yu et al., 2020b), which can serve as a potential feedstock for biorefineries. Recent studies demonstrated that catalytic production of sugars and platform chemicals could be an effective technique for recycling/valorising a considerable amount of starch-rich food waste generated globally (Yu et al., 2018b). In this research, bread waste was selected as the representative starch-rich feedstock for the catalytic production of LA.

#### 2.2.3 Paper waste

Paper waste is unavoidable in the modern world and constitutes a major waste stream accounting on average ~17% of the total solid waste generated globally (Kaza et al., 2018). The waste paper generated every year is accelerating rapidly and burdening landfills, whereas

a fraction of generated paper waste is being recycled for pulp production or other uses (Van Ewijk et al., 2018; Xu et al., 2021). Efficient recycling of paper waste could be even more challenging when proper recycling facility is scarce, such as in the case of Hong Kong. For instance, in the year 2020, 68% of the total generated waste paper ended up in landfills amounting to 0.95 million tons, whereas ~0.45 million tons of paper waste was recovered for recycling using local and non-local facilities (EDP HK, 2020). This situation drives society to find cost-effective and sustainable approaches to recycling and reusing paper waste for diverse value-added production.

Paper is typically manufactured from lignocellulosic raw materials, such as wood, bamboo, and non-wood agricultural residues (e.g., straw and bagasse) and therefore contains a high proportion of cellulosic fibres. Commonly used treatment (e.g., anaerobic digestion) techniques are deemed unsuitable due to the low degradability of cellulosic fibres in the paper. Therefore, developing efficient technology is necessary for paper waste treatment and valorisation (Antonetti et al., 2016; S. S. Chen et al., 2018). For example, paper towel is a widely used sanitary product, and a considerable amount of paper towel waste is generated worldwide, for example, it contributed to 5% of total waste generated at the Hong Kong International Airport. These waste papers could be readily separated at the source (e.g., commercial buildings, institutions, airport terminals), and hence easy to collect and transfer for potential valorisation. However, hygiene concerns and the low biodegradability of highly cellulosic fibres make paper towel waste unsuitable for pulp recycling and biological treatment options, e.g., anaerobic digestion and composting (Alvarez et al., 2009; S. S. Chen et al., 2018). In this case, thermo-catalytic treatment can be an effective and efficient way for the sanitation and valorisation of paper towel waste in a single process. Due to the high proportion of cellulose, paper waste could be potentially valorised in biorefineries (Jahan et al., 2021).

Although paper waste could be an attractive biorefinery substrate, its potential conversion to platform chemicals is yet to be explored to a large extent (Nzediegwu et al., 2021).

#### 2.3 Valorisation technologies

#### 2.3.1 Composting

Composting is a biological process by which organic waste could be managed and the generated product could be used as a fertiliser for plant growth. Composting refers to the breakdown of organic matter and humic substances by microorganisms under aerobic conditions. Composting of food waste and other feedstock occurs in the presence of water and oxygen and results in the release of dissolved organic matter. Composting can be optimised by the addition of biological inoculates such as bacteria and fungi (Ameen et al., 2016). The complete breakdown of organic matter eventually produces a mature, stable, and nutrient-dense compost product, making it beneficial to plant growth (Insam and De Bertoldi, 2007). Composting requires close monitoring of certain parameters including pH, oxygen, particle size, temperature, time, curing, moisture content, and C/N ratio to optimise its potential to be used as a fertiliser (Adhikari et al., 2008; Waqas et al., 2018a). However, considering heterogeneous characteristics and moisture content of food waste, controlling process parameters and producing quality compost would require significant efforts (Cerda et al., 2018).

#### 2.3.2 Enzymatic conversion

Wastes containing polysaccharides (*e.g.*, cellulose, hemicellulose, and starch) could be valorised through microbial/enzymatic. In this biochemical pathway, polysaccharide-rich feedstock should undergo enzymatic or catalytic hydrolysis at first to release soluble sugars followed by microbial fermentation to generate target products (*e.g.*, ethanol, lactic acid, etc.) (Nguyen et al., 2013; Xiong et al., 2019). At present, simultaneous saccharification and

fermentation are often adopted to prevent the inhibition of enzymes by the products from the hydrolysis step. However, in the case of lignocellulosic feedstock, pre-treatment of the substrate is required to disrupt the lignin-carbohydrate complex and expose the cellulosic fibres for sugar production (Abdel-Rahman et al., 2011) thereby raising the process cost. Lignin may deposit on cellulose or interfere with enzymatic activity during hydrolysis. Besides, harsh conditions might be required to break down highly crystalline cellulosic fibres in the lignocellulosic feedstock. Lignocellulosic recalcitrance is a major bottleneck in terms of biochemical valorisation (Liu et al., 2019).

#### 2.3.3 Anaerobic digestion

Anaerobic digestion has increasingly become a preferable treatment option for sustainable organic waste management. Production of biogas via anaerobic digestion (AD) of organic wastes such as food waste (Giwa et al., 2019), and organic fraction of MSW (Rasapoor et al., 2020) have been investigated considerably. The produced biogas from AD can be upgraded to biomethane (CH<sub>4</sub>) and/or used in the generation of heat/energy (Chiappero et al., 2020), and the digestate residue can be utilized as fertilizer (Sanchez-Monedero et al., 2018). AD has been considered one of the suitable processes for waste biovalorisation built on the syntrophic mechanisms of microbial communities. Hydrolysis, acidogenesis, and methanogenesis are three key phases of AD, involving a diverse group of microbial communities (Fagbohungbe et al., 2017). Influential factors include feedstock concentration, inoculum (microbial) size, process temperature, solution pH, selection of additives, etc., which can regulate process parameters during AD (Pan et al., 2019). In comparison to composting, the use of FW as feedstock for the generation of bioenergy at the commercial level has the advantages of low carbon emissions, less secondary pollution generation, low operational costs, and less global warming potential (GWP) (Li et al., 2019).

#### 2.3.5 Integrated valorisation of anaerobic digestate

Digestate is the major byproduct of the AD process, which is a semi-stabilised solid mixture consisting of partially degraded organic matter, minerals, microbial biomass, carbohydrate, lipids, protein, etc. (Cesaro, 2021). For instance, food waste digestate (FWD) is characterised by the high contents of moisture, organic matter, nutrients, and protein (Grigatti et al., 2020; Opatokun et al., 2017). Owing to the rich amounts of salts and proteins in food waste, the FWD generated from the AD process contained a high concentration of phosphate (PO<sub>4</sub><sup>3-</sup>), ammonium (NH4<sup>+</sup>), Na<sup>+</sup>, K<sup>+</sup>, and Cl<sup>-</sup> ions (Cheong et al., 2020). Thus, recycling the FWD into renewable and value-added products such as biofertiliser, solid biofuel, and carbonbased materials shows great potential for diverse environmental applications. Composting is considered an effective strategy for valorising FWD into biofertiliser (Du et al., 2018). Furthermore, pyrolysis is an emerging option for digestate conversion into biochar, bio-oil, and pyrolytic gas in an oxygen-limited environment. Hydrothermal carbonisation is another increasingly popular alternative to stabilise the waste biomass with high moisture content using relatively low energy input. The concept of the Back to Earth Alternative (BEA) can be adopted for digestate management with a well-designed strategy to meet specific requirements (Peng and Pivato, 2019). Compared to AD alone, integration of AD with digestate pyrolysis/hydrothermal carbonisation can boost the net energy generation and elevate its soil amendment quality with environmental and economic advantages (Antoniou et al., 2019)(Antoniou et al., 2019).

#### 2.3.6 Pyrolysis

Biochar production through pyrolysis could be an attractive option for waste biomass management, where the substrate is dried and heated at 300–950 °C in an oxygen-limited environment. In recent years, biochar as a carbon-negative material has attracted extensive public interest and scientific attention application considering diverse applications, especially

for soil amendment, synthesis of functionalised materials, and renewable energy sources. (Xiong et al., 2017). Pore size, pore volume, specific surface area, pH, elemental composition, surface functional groups, etc. are key physicochemical properties of biochar, which affect its environmental applicability and functionality (Saffari et al., 2020; Wan et al., 2020). Biochar characteristics are critically influenced by the types of selected feedstock, such as food waste and lignocellulosic waste. Tuneable physicochemical characteristics of biochar make it a promising material as fertilizer, soil amendment, catalyst support, adsorbent, microbial habitats, pH buffer, and electron carrier for enhancing the efficiency of the AD process (Oliveira et al., 2017; Ponnusamy et al., 2020). However, considering high moisture content, pyrolysis of lignocellulosic and food waste would be challenging as a considerable amount of energy is required for feedstock drying ultimately raising the process cost.

#### 2.3.7 Hydrothermal conversion

Lignocellulosic biomass and food waste, though abundant in reserve for bioenergy production, have their drawbacks due to high moisture, bulk volume, and low heating value (H. B. Sharma et al., 2020). Hydrothermal processing is an effective and advanced technology that can directly convert carbon-rich et high moisture content feedstock into water medium, thus eliminating the energy-intensive feedstock drying step which is a pre-requisite for pyrolysis and gasification (Yang et al., 2020). This process is endothermic and usually carried out under subcritical or supercritical water conditions, where the feedstock is fractionated into valuable constituents through hydrolysis, depolymerisation, and condensation. Water is the greenest solvent, and it can simultaneously act as a reactant and a suitable medium for acid-catalysed reactions to break down the biomass into small fractions by the high concentration of  $H^+$  ions generated from subcritical water (Zhao et al., 2019). Hydrothermal carbonisation (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG) are involved in the processes for the selective production of carbonised solids (*i.e.*, hydrochar), liquid bio-

oils, and fuel gases depending on the operating temperatures (Gu et al., 2020; Tekin et al., 2014). HTC is usually conducted at a relatively moderate temperature (180–250 °C) and with auto-generated pressure (Akarsu et al., 2019). HTC could offer advantages in energy efficiency and emission control compared with pyrolysis and gasification. Potential uses of hydrochar include soil amendment, functional materials for catalysis and remediation, and use as a solid fuel. HTC could customise hydrochar as a carbon-rich functional material with a tunable structure through various controlled chemical processes. However, technological difficulties may be encountered during the reactions at a high solid loading rate, such as high energy consumption and rate-limiting heat and mass transfer. By contrast, in the case of the HTL process, the high-pressure requirement may present a major technical challenge for scaling up due to the safety consideration and capital-intensive equipment requirement. (Cao et al., 2021).

#### 2.3.8 Catalytic hydrolysis and dehydration

Thermochemical conversion such as catalytic hydrolysis and dehydration is a potential pathway for valorising polysaccharide-rich waste in an efficient and timely manner (Tanger et al., 2013). Acid-catalysed hydrolysis of lignocellulose is preferred over enzymatic hydrolysis due to facile penetration of acid catalyst into the lignocellulosic structure, lower resistance from lignin, and faster production of sugars (Lenihan et al., 2010). Recent studies demonstrated that catalytic production of sugars and platform chemicals could be an effective technique for recycling/valorising a considerable amount of lignocellulosic waste (**Figure. 2.1**) and starchrich food waste generated globally (Yu et al., 2017b). The chemical conversion process of cellulose/starch conversion involves multiple consequential reactions that are often accelerated over acidic or basic catalysts. Releasing sugars through acid hydrolysis of lignocellulose or starch is the entry point for valorisation (Rinaldi and Schüth, 2009), followed by isomerisation or direct dehydration of sugars to furanic derivatives such as HMF, which is subsequently rehydrated to form LA and FA. Hydrolysis of polysaccharides to glucose and dehydration

reactions are commonly catalysed by Brønsted acidic sites, whereas glucose isomerisation to fructose can be promoted over Lewis acids or Brønsted bases (Yu and Tsang, 2017; S. S. Chen et al., 2020).



Figure. 2.1 Conversion of lignocellulosic waste biomass into sugars and chemicals under Brønsted acidic catalysis.

The feedstock characteristics and variability of biomass/food waste, the reactivity of substrates (*e.g.*, crystalline or amorphous cellulose), degree of polymerisation etc. might significantly influence hydrolysis and subsequent dehydration reaction (Cheng et al., 2011; Li et al., 2016). To attain sustainable production of sugars and chemicals, appropriate feedstock selection is necessary. Besides, reaction conditions such as solution acidity, temperature, duration, solvents etc. directly influence the selectivity and yield of products (Yu and Tsang, 2017). Catalytic conversions are often accompanied by side reactions under high temperature and acidity, which generate heterogeneous solid residues, denoted as humins, via repolymerisation and irreversible aldol condensation among sugars and derivatives (Cheng et al., 2018; Filiciotto et al., 2019). Therefore, it is imperative to carefully design the process and tune the reaction conditions to maximise the desired product yields (Chen et al., 2017b; Xiong et al., 2019).

#### 2.4 Value-added chemicals

The composition and characteristics of polysaccharide-rich wastes make them suitable as a starting material for catalytic production of value-added chemicals. C5 or/and C6 sugars (mainly glucose and xylose) could be obtained through the hydrolysis of lignocellulosic waste and starchy food waste that could be turned into platform chemicals such as HMF, LA, FA, and furfural through subsequent dehydration/rehydration reactions (Chen et al., 2017b; Yu and Tsang, 2017). These bio-based chemicals are highly potential for diverse applications as discussed below.

#### 2.4.1 Levulinic acid

LA is one of the top bio-derived platform chemicals with diverse applications, *e.g.*, pharmaceuticals, plasticisers, solvents, fuels, and personal care products (Chen et al., 2017b; Hayes and Becer, 2020). Besides, LA serves as a building block for the production of various value-added derivatives such as gamma-valerolactone (GVL),(Dutta et al., 2019) succinic acid, diphenolic acid, (Antonetti et al., 2016; Pileidis and Titirici, 2016), alkyl levulinates, 2-methyl-tetrahydrofuran, etc. (Hayes and Becer, 2020). LA could be generated by the acid catalysis of cellulose or C6 sugars involving the production of HMF as an intermediate (Antonetti et al., 2016; Chen et al., 2017b). Alternatively, it can form via the acid catalysis of hemicellulose or C5 sugars with furfural as an intermediate (Alonso et al., 2013b). Polysaccharide-rich wastes have a high potential for LA production through tandem hydrolysis and dehydration (Chen et al., 2017a, 2017b) following the pathways mentioned above. A variety of waste biomass has been explored for the production of LA, for instance, food waste (Chen et al., 2017a; Wang et al., 2015), paper waste (S. S. Chen et al., 2018; Nzediegwu et al., 2021), rice husk and straw (Bevilaqua et al., 2013) and so on. Representative studies regarding LA production from waste biomass are presented in **Table 2.1**.

Starting from C6 sugar, sucrose, and cellulose, the maximum theoretical yield of LA could be achieved is 64.4 wt%, 67.8 wt%, and 71.6 wt% assuming complete conversion (Antonetti et al., 2016). Nevertheless, the actual achievable yield of LA from sugars or biomass might be significantly lower as the catalytic process is prone to be influenced by system components such as feedstock characteristics, reaction temperature and duration, catalyst concentration, and solvent system (Mukherjee et al., 2015; Chen et al., 2017b). For instance, concerning LA production from biomass, feedstock with high carbohydrate content, low recalcitrance possibly low lignin content is preferred (Rivas et al., 2016). Regarding catalyst selection, mineral acids are still the most cost-effective and efficient for LA production, while solid acid catalysts have been explored yet their efficiency for LA production is often restricted by mass transfer, catalyst deactivation and recycling issues (Antonetti et al., 2020b). However, efficient separation and purification of LA are necessary for the possible recovery of mineral acid catalysts and further conversion of LA to valuable derivatives such as GVL, which can be negatively affected by the presence of mineral acid (Wettstein et al., 2012; Lui et al., 2019). A viable strategy could be using the biphasic solvent system comprising two immiscible layers. The aqueous layer contains the acid catalyst and serves as the reactive phase, while the organic layer acts as the extractive phase, facilitating simultaneous production and extraction of LA, which might enhance LA yield and selectivity (Wettstein et al., 2012; Wang et al., 2020).

Besides, solid by-byproduct or humin formation through side reactions is an issue, which should be essentially addressed to achieve a higher yield and selectivity for LA (Boonyakarn et al., 2019). Therefore, the time/cost-efficient production of LA while keeping the by-product formation at a minimum needs significant research effort to design a highperformance system by manipulating system parameters.

Substrate	Catalyst	Reaction condition	Solvent	Heating system	LA yield	Reference
Giant reed	HCl (1.68 wt%)	190 °C, 20 min	H <sub>2</sub> O	microwave	22 wt%	(Antonetti et al., 2015)
Wheat straw	HCl	200 °C, 1 h	H <sub>2</sub> O	conventional	19.3 wt%	(Galletti et al., 2012)
	H <sub>2</sub> SO <sub>4</sub>	209.3 °C, 37.6 min	H <sub>2</sub> O	conventional	19.9 wt%	(Chang et al., 2007)
Grape pomace	HCl	190 °C, 20 min	H <sub>2</sub> O	microwave	4.7 wt% / 50.8 mol%	(Antonetti et al., 2020a)
Paper towel waste	$H_2SO_4(1 M)$	150 °C, 60 min	– H <sub>2</sub> O	microwave	40 mol%	(S. S. Chen et al.,
	Amberlyst 36	150 °C, 20 min			30 mol%	2018)
Waste plant biomass	H <sub>2</sub> SO <sub>4</sub> (1 M)	150 °C, 60 min	GVL/H <sub>2</sub> O	microwave	20 mol%	(Guan et al., 2020)
Cotton straw	SBA-SO <sub>3</sub> H	180 °C, 6 h	H <sub>2</sub> O	conventional	18 mol%	(Lai et al., 2011)
Vegetable waste	Amberlyst 36	150 °C, 5 min	H <sub>2</sub> O	microwave	17 mol%	(Chen et al., 2017a)
Corncob residue	FeCl <sub>3</sub>	180 °C, 2 h	H <sub>2</sub> O	conventional	48.5 mol%	(Wang et al., 2018)
Food waste	H <sub>2</sub> SO <sub>4</sub>	130 °C, 8 h	GVL/H <sub>2</sub> O	conventional	30.2 wt%	(Lui et al., 2019)
Delignified rice husk	Mn <sub>3</sub> O <sub>4</sub> /hierarchical ZSM-5 zeolite	130 °C, 8 h	40% H <sub>3</sub> PO <sub>4</sub>	conventional	39.7 wt%	(Pratama et al., 2020)
Bagasse	HCl (4.45 wt%)	220 °C, 45 min	H <sub>2</sub> O	conventional	22.8 Wt%	(Yan et al., 2008)

**Table 2.1** Representative studies on levulinic acid production from polysaccharide-rich wastes

#### 2.4.2 Hydroxymethylfurfural

Besides, HMF is the intermediate product generated during sugar conversion to LA, which is by itself a high potential C6-platform chemical that concerned comprehensive investigation in recent years (Yabushita et al., 2014; Mika et al., 2018). HMF is a versatile chemical which can be further upgraded to multiple derivatives such as 2,5 furandicarboxylic acid, dimethylfuran, ethoxymethylfurfural and many more valuable chemicals following selective catalytic schemes. These derivatives served as building blocks for diversified applications such as biofuels, resins, polymers, solvents, pharmaceuticals etc., and such diverse applications of HMF make it an attractive and high-value product (market price 100 USD kg<sup>-1</sup>, source: Alibaba) (Mukherjee et al., 2015; Yu and Tsang, 2017). Considerable research efforts have been invested in HMF production in recent years from C6 sugars (glucose, fructose) and biomass/food waste using Brønsted and/or Lewis acid catalysts (Yang et al., 2015; Yu et al., 2016; Xiong et al., 2018).

#### 2.4.3 Formic acid and furfural

In contrast, FA, another valuable product is coproduced simultaneously with LA during HMF rehydration in equimolar concentration (Li et al., 2012; Yang et al., 2015). FA as a low molecular organic acid can act as a hydrogen storage platform and provide it during hydrogenation reactions for specific applications (Moret et al., 2014), such as LA hydrogenation to GVL (Varkolu et al., 2016). However, A non-stoichiometric formation of FA could also be expected during catalytic conversion of carbohydrates through alternative pathways in addition to HMF rehydration (Flannelly et al., 2016). Besides, furfural is generated from the hemicellulosic fraction of lignocellulosic waste mainly through acid catalysed conversion of xylose, which could serve as a building block for a great variety of chemicals thereby making furfural a top C5-platform molecule derived from biomass (Gürbüz et al., 2013; Mika et al., 2018).

#### 2.5 Influential reaction conditions

#### 2.5.1 Microwave heating

A variety of heating systems have been employed for catalytic conversion including oil bath, hydrothermal system, microwave etc. Among them, microwave reactors are recognised to be more energy-efficient, which can directly heat the reactant solution compared to traditional reactors that involve convection and conduction for heat dispersal (Yu and Tsang, 2017). Therefore, a microwave reactor could be helpful for process intensification considering efficient heat transfer and rapid decomposition of recalcitrant and complex lignocellulosic substrates (Chen et al., 2017b). A higher sugar yield was reported using microwave-assisted cellulose hydrolysis compared to that of conventional heating under the same reaction conditions attributed to the interactions between microwave radiation and the CH<sub>2</sub>OH group of cellulose (Fan et al., 2013). Besides, a recent study demonstrated positive interactions between microwave and starch specifically during the starch gelatinisation stage (Yu et al., 2020c) which is promising and could be utilised for the effective valorisation of starch-rich wastes. However, careful attention should be paid to solvent selection for microwave conversion as the heating of the reactants is directly influenced by the solvent's ability to absorb microwave radiation (Yu and Tsang, 2017; Pandey and Shrivastava, 2018).

#### 2.5.3 Catalytic systems

Considering the low cost and high catalytic activity for tandem hydrolysis and dehydration reactions, mineral acids such as H<sub>2</sub>SO<sub>4</sub> and HCl are generally used for catalytic conversion from diverse biomass feedstock including food waste, paper waste, etc. (Xu and Huang, 2014; Antonetti et al., 2016; Chen et al., 2017a). For sugar production, dilute acid hydrolysis is preferred over concentrated acidic one considering low acid consumption, less reactor corrosion, and facile separation of acid and sugars end of the process (Zhou et al., 2021). Furthermore, metal chlorides have attracted considerable attention for catalytic performance

due to their Lewis acidity and generated Brønsted acidity in solution, safety, low cost, and recoverability compared to mineral acids (Yu et al., 2016; Di Fidio et al., 2020). Specifically, chlorides can promote the dehydration of fructose to HMF through stabilisation of the protonated transition state by Cl<sup>-</sup> (Mellmer et al., 2019). Fe-based catalyst has been widely used for biomass pretreatment, emphasising its influence on the degradation of cellulose and hemicellulose (Du et al., 2020; Yao et al., 2021). For instance, FeCl<sub>3</sub> was reported for hydrolysis and dehydration of various cellulose-rich biomass substrates to produce LA (Wang et al., 2018; Di Fidio et al., 2020). Various laboratory-prepared and commercial solid acid catalysts (sulphonated resins) also demonstrated potential for catalytic conversion of polysaccharide-rich substrates (Cao et al., 2018b; Yu et al., 2019). However, the efficacy of solid catalysts is still far behind the activity of homogenous mineral acid catalysts, which needs considerable improvement before their large-scale applications (Zhou et al., 2021).

#### **2.5.4 Solvents systems**

The solvent is a significant parameter that influences catalytic conversion through interactions with reactants and regulation of product selectivity in the reaction system, therefore, appropriate solvents can enhance the valorisation of lignocellulosic waste to chemicals. The selection of a suitable solvent is necessary, as it not only serves as a reaction medium but also influences the catalytic process through solvent-solute interactions, adjusting the reactivity of proton, suppressing the byproduct formation, etc. (Dyson and Jessop, 2016).

Appropriate reaction conditions and solvent selection are critical for selective and costeffective production of value-added chemicals (Antonetti et al., 2020b). As an environmentally benign and green solvent, water has been preferred and utilised extensively for biomass fractionation and chemical production (Cao et al., 2018b; Licursi D. et al., 2018). However, harsh reaction conditions, *i.e.*, high temperature and acidity, are required when using water as the reaction medium resulting in an energy-intensive process and high byproduct (humin)
formation. Besides, various conventional organic solvents such as dimethylsulfoxide (DMSO) (Chen et al., 2017a), tetrahydrofuran (THF), dimethylformamide (DMF) (Antonetti et al., 2016), and ionic liquids have been employed as reaction medium owing to their influence on the acidic protons, high reactivity of reagents and product selectivity, as well as their capability to enhance tandem catalytic reactions for biomass conversion (Antonetti et al., 2016; Chen et al., 2017a; Yu et al., 2018b)

Despite excellent performance and wide applications, conventional organic solvents DMSO, DMF, THF, etc., are widely considered "non-green" due to their direct or indirect detrimental effects considering safety (handling and application, volatile organic carbon (VOC) emission), health and environmental criteria (toxicity and bioaccumulation). Therefore, the use of alternative "green" solvents, especially those which are renewable/bio-derived, safe for handling/application, and involve less emission and environmental impact are recommended for biorefinery applications (Prat et al., 2016; Gao et al., 2020). However, apart from the green characteristics of solvents, it is imperative to identify suitable and highperformance solvents for the effective and efficient catalytic production of value-added chemicals. In this case, it is vital to evaluate solvent performance considering their effect on the solubility of reagent, mass transfer during catalytic reaction that affects reaction rate and selectivity, and solvent interaction with catalysts and substrates (Dyson and Jessop, 2016). Properties and applications of selected green solvents are discussed below.

## 2.5.4.1 Gamma-valerolactone (GVL)

The distinct physicochemical properties and renewable origin of gamma-valerolactone (GVL) have provided opportunities for diversifying its applications. GVL is a C5-cyclic ester ( $C_5H_8O_2$ ), naturally existing, safe, biodegradable, and nontoxic chemical which can be utilised as a food additive; green solvent, and fuel additive (T. Horváth et al., 2008; Bereczky et al., 2014). Researchers have investigated the catalytic hydrogenation of LA to obtain GVL by

using various catalysts, solvents, and hydrogen donors, resulting in different reaction pathways and yields of GVL. Noble metal catalysts, such as ruthenium (Ru) (Abdelrahman et al., 2014; Molleti et al., 2018), iridium (Ir) (Deng et al., 2013), palladium (Pd) (Amarasekara and Hasan, 2015), and platinum (Pt) (Putro et al., 2015), have been extensively explored owing to their high activity during LA hydrogenation, with carbon-supported Ru catalysts being the most extensively used. Besides, non-noble metal catalysts, such as Cu, Ni, Fe, Al, Mg, and Zr-based catalysts are preferred over precious metal catalysts because of their abundance in nature and economic sustainability and are potentially examined for GVL synthesis (Chia and Dumesic, 2011; Obregón et al., 2014; Gupta and Kantam, 2018). GVL is a potential fuel additive, and its combustion energy is similar to that of ethanol (29.7 MJ/kg) (Alonso et al., 2013a). However, GVL has lower energy density and cetane number and higher water solubility, which limit its direct application in transportation fuel production (Tang et al., 2014). However, the performance of GVL as a fuel additive was very similar to that of common biofuel ethanol (T. Horváth et al., 2008). GVL could be mixed with gasoline and diesel fuels and useful for emission reduction (Bereczky et al., 2014). Furthermore, GVL is a potential precursor for producing other chemicals, including methyl-tetrahydrofuran (Me-THF) and 1,4-pentandiol (Choi et al., 2015), alkyl valerates (Lange et al., 2010), adipic acid (precursor for nylon) via pentanoic acids (Tuck et al., 2012), and other derivatives.

Apart from its application as a chemical derivative and fuel additive, GVL has been recognised as a green, nontoxic, and efficient solvent because of its high biodegradability, low toxicity (Lethal Dose 50% (LD<sub>50</sub>), oral for rat 8800 mg kg<sup>-1</sup>), very low peroxide formation rate, useful polarity properties, and could be derived from biomass feedstock (T. Horváth et al., 2008; Moity et al., 2012). GVL has a low melting point (-31 °C), a high boiling point (207 °C), and a high flash point (96 °C) that minimizes the ignition hazard. Further, its vapour pressure is considerably low at high temperatures (3.5 kPa at 80 °C), which minimises emission

hazard and safeguard the handling of the chemical. In the CHEM21 solvent selection guide (Prat et al., 2016), GVL exhibits a better score in terms of safety compared to tetrahydrofuran (THF) which is a popular solvent for chemical conversion. While THF is very prone to peroxide formation, *i.e.*, 160 mg L<sup>-1</sup> in 20 days at room temperature (> 100 mg L<sup>-1</sup> as the safety limit), it has been reported that GVL does not form peroxides for a month at 60 °C (Fábos et al., 2009). However, for health and environment criteria, GVL was assigned health and environmental scores of 5 or higher by default (**Table A.1**) considering its high boiling point that reflects the energy-intensive separation process, and its comprehensive health and environmental assessment is yet to be conducted following the standard protocol (Prat et al., 2016).

The use of GVL has been reported for enhancing various biorefinery reactions and synthesising biomass-derived chemicals (Table 2.2). Organosolv pretreatments using GVL/water solvent are reported to deconstruct the biomass to separate C5/C6 sugar and lignin (Timokhin et al., 2020), which may overcome the recalcitrance of lignin fractions in lignocellulosic biomass. In an experiment conducted by Lê and co-workers, a GVL/water mixture was used for the fractionation of *Eucalyptus globulus*, resulting in 80% total recovery of cellulose, hemicellulose, and lignin (Lê et al., 2016a). Meanwhile, Luterbacher et al. (2014) reported a high yield of carbohydrates (70% to 90%) based on corn stover, hardwood, and softwood using bio-derived GVL, water as the solvent, and dilute H<sub>2</sub>SO<sub>4</sub> as the catalyst. Recent studies reported the favourable effects of GVL solvent for acid or salt-catalysed transformation of carbohydrates to LA and HMF, e.g., achieving a high yield of levulinic acid (Alonso et al., 2013a; Mellmer et al., 2014a). The high polarity of GVL solvent can increase hydrolysis rates compared to the reaction carried out in the water (Mellmer et al., 2014a, 2019). A GVLcontaining medium was reported to maintain the activity of the Sn catalyst in bread waste conversion to HMF (yield of 20 mol%) (Yu et al., 2018b). Wettstein et al. (2012) developed a biphasic system that comprised GVL and an aqueous solution of HCl for cellulose

Experiment	Catalyst	Yield	Reference
Cellulose to LA and FA	HCl	70%	(Wettstein et al., 2012)
Carbohydrates from corn stover, hardwood, and softwood	H <sub>2</sub> SO <sub>4</sub>	70% to 90%	(Luterbacher et al., 2014)
Fructose, glucose, and sucrose to HMF Fructose, glucose, and sucrose to LA and FA	H <sub>2</sub> SO <sub>4</sub>	75% 50% to 70%	(Qi et al., 2014)
CO <sub>2</sub> to amines	GVL	84%	(Song et al., 2016)
Fractionation of <i>Eucalyptus globulus</i> wood in GVL/water		80% recovery rate for cellulose, hemicellulose, and lignin combined	(Lê et al., 2016a)
Bread waste to HMF	SnCl <sub>4</sub>	20 mol%	(Yu et al., 2018b)
Xylose to furfural	$H_2SO_4$	75% (selectivity)	(Mellmer et al., 2014b)
Hemicellulose to furfural	H-Modernite	80%	(Gürbüz et al., 2013)
Xylose and cornstalk to furfural	Sulphonated carbon	78.5%, 60.6%	(Zhang et al., 2016)
Glucose to HMF	Amberlyst 70, Sn- beta	59%	(Gallo et al., 2013)
Corncob, xylan, and xylose to furfural	FeCl <sub>3</sub> .6H <sub>2</sub> O	66.8%, 68.6%, anf 86.5% respectively	(L. Zhang et al., 2014)
Biomass (from plant microbial fuel cell) to LA	H <sub>2</sub> SO <sub>4</sub>	20 mol%	(Guan et al., 2020)
Wood biomass fractionation	-	40.3% cellulose with ~90% purity	(Fang and Sixta, 2015)
Food waste to LA	H <sub>2</sub> SO <sub>4</sub>	30.2 wt%	(Lui et al., 2019)

 Table 2.2 Representative studies on biomass/sugar conversion using GVL as the solvent

deconstruction to form LA and FA, which eventually produced GVL in a high yield (70% from LA/FA) and the higher product yield was attributed to the enhanced solubilisation of cellulose in GVL solvent. Representative studies regarding the applications of GVL as a solvent are summarised in **Table 2.2**, highlighting its versatility in serving a wide variety of biorefinery reactions involving bio-based chemicals and feedstocks. In view of the green attributes and efficiency for the valorisation of lignocellulose to chemicals reported in the literature, GVL could be potentially investigated as a reaction medium to obtain high LA production from complex lignocellulosic and starchy food waste substrates.

# 2.5.4.2 Organic carbonate solvents

Among the recommended less 'classical' solvents listed in the CHEM21 solvent selection guide (**Table A.1**), organic carbonates are considered highly potential green solvents for the replacement of traditional industrial solvents. Organic carbonate solvents, such as propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC) exhibit high biodegradability, low toxicity, and good safety score (stable under ambient conditions, low volatility, and flammability) (**Table 6.1**), while their synthesis involves the utilisation of carbon dioxide (CO<sub>2</sub>) (Schäffner et al., 2008; Parker et al., 2014; Prat et al., 2016). Such environment-friendly features and CO<sub>2</sub> exploitation in manufacture make organic carbonates attractive for potential biorefinery applications.

According to the safety, health and environmental ranking, DMC is recognised as a non-toxic and the greenest carbonate solvent (Prat et al., 2016) and reagent for multiple applications (Aricò and Tundo, 2010). For instance, DMC was used as a solvent for base-catalysed depolymerisation of lignin (Dabral et al., 2018), and transformation/synthesis of bio-based molecules/polymers as an agent for methylation or methoxycarbonylation (Fiorani et al., 2018). In contrast, cyclic carbonates such as PC and EC possess remarkable polarity ( $\pi$  = 0.83) which is a desirable attribute of solvents for catalytic hydrolysis and dehydration (Jessop et al.,

2012; Prat et al., 2016). The polar and aprotic nature of PC and EC solvents suggests their potentiality as alternatives for highly polar yet non-green industrial solvents such as DMSO, THF, DMF etc. A few studies have reported an improved rate of catalytic biomass conversion using PC (Yu et al., 2018b), EC (Yamada et al., 2007; Shin et al., 2009), and DMC (Dabral et al., 2018) in the reaction media. However, there is a lack of comparison among these carbonate solvents to understand their prospective roles in assisting the catalytic conversion of recalcitrant and complex lignocellulosic wastes and starchy food wastes, which requires a comprehensive investigation.

## 2.5.4.3 Other potential solvents

Common/classical solvents such as alcohols and acetone are recommended for industrial synthesis (Prat et al., 2016). The utilisation of alcohols particularly isopropanol and isobutanol could be sustainable considering their potential manufacture from renewable biomass resources. Several studies demonstrated the effectiveness of those solvents for catalytic conversion of carbohydrates to vital platform chemical HMF (Mushrif et al., 2012; Moity et al., 2012; Agutaya et al., 2020). In contrast, acetone is a low-cost solvent which is mostly used for effective fractionation of lignocellulose (Smit and Huijgen, 2017) and conversion of biomass to platform chemicals (Hu et al., 2012; Motagamwala et al., 2019). Besides, deep eutectic solvents (DES) are gaining attention recently as a reaction medium for platform chemical production considering their environment-friendly properties, biodegradability, favourable effects on cellulose de-crystallisation etc. Besides, DES can serve as both solvent and reagents, and mild reaction conditions might be adopted for catalytic conversion considering the low melting point of DES attributed to hydrogen bonding in the solvent system (Smith et al., 2014; Gunny et al., 2015; Morais et al., 2020). However, the application of DES for the effective valorisation of complex waste-based substrates warrants further investigation.

# 2.6 Research gaps and hypothesis

Though considerable research efforts have been directed toward valorising waste for the production of valuable products, finding high-value and sustainable approaches for polysaccharide-rich waste recycling/upcycling would be necessary for cost-/time-efficient production of diverse chemical and biofuel. This review suggested rigorous research efforts to manipulate the reaction system for the highly efficient production of value-added chemicals. Besides, it is necessary to understand the feedstock characteristics to evaluate their viability for targeted chemical synthesis. Moreover, considering its crucial contribution to catalysis, it is important to devote research efforts to identifying potential solvents as safe yet reactive reaction mediums targeted at catalytic valorisation of waste substrates. Therefore, this thesis aims to investigate and elucidate the critical system parameters for the green and efficient valorisation of polysaccharide-rich waste for value-added chemical production.

In **Chapter 4**, facile and efficient valorisation technology was developed for the selective production of platform chemicals from cellulosic paper waste through manipulating system parameters, *i.e.*, reaction temperature and solvent system. The viability of diverse paper feedstock for platform chemical production was assessed in **Chapter 5** reflecting on the influence of substrate composition and characteristics under multiple catalytic conditions. **Chapter 6** focused on the depolymerisation of highly cellulosic and crystalline feedstock, which is a bottleneck for sugar production and subsequent up-gradation to platform chemicals. Then in **Chapter 7**, critical factors for the production of vital platform chemical levulinic acid from starchy food waste were scrutinised under green solvent systems. This thesis provides a crucial understanding of system components for developing green and efficient biorefinery technology.

# **Chapter 3: Materials and Methods**

# Abstract

This chapter presents the description of various polysaccharide-rich waste substrates and a list of chemicals used for investigation. Experimental procedures including catalytic conversion process, sample preparation, and adopted analytical technics and characterisation methods for soluble and solid samples are documented in detail.

## **3.1** Waste substrates

**Chapter 4**: Virgin pulp (VPT) and recycled pulp paper towel (RPT) wastes collected from the Terminal Hall of the Hong Kong International Airport waste papers were utilised for the experiment. Paper towel wastes were dried in an oven at 105°C for 48 h and milled (German Pool, Pro-6) to achieve fibre-like consistency and stored in airtight bags for further characterisation and catalytic conversion. The lignocellulosic composition and crystallinity of VPT and RPT as determined following existing protocols are presented in **Table 4.1**.

**Chapter 5**: Papers were purchased from commercial suppliers and utilised as feedstock in the experiment to distinguish the characteristics of various paper types, paper raw materials, pulping processes, and other relevant treatments. Various paper feedstock were selected considering information about paper characteristics from literature and their availability in the market. Besides, paper towel wastes collected from the Hong Kong International Airport (HKIA) were also used for investigation. In total, nine types of paper feedstock were investigated in this study, *i.e.*, HKIA paper towels, napkins (wood-derived), napkins (bambooderived), printing/office paper, newspaper, packaging paper, tracing/parchment paper, paper food box (sugarcane derived), and paper mould. All papers were processed following the methods reported above. To facilitate the experimental results and discussion, paper substrates were grouped into two categories. Relevant information about paper properties was collected

as revealed by the suppliers or otherwise collected from existing literature as applicable, measured crystallinity and lignocellulosic compositions of various paper wastes are presented in **Table 5.1**.

**Chapter 6**: Virgin pulp paper towel waste collected from the Terminal Hall of the Hong Kong International Airport was used for the investigation.

**Chapter 7**: In this chapter, bread waste served as the representative starch-rich feedstock for the catalytic production of LA. Bread waste was collected from catering outlets in the Hong Kong International Airport (HKIA) and dried, ground, sieved through a 0.3 mm mesh, and stored in an airtight container for further experimental use. The bread waste contained 72.6% available carbohydrates, 4.2% total dietary fibre, 14.8% protein, 6.1% total fat, 2.3% ash, and 41.5% total organic carbon (TOC) on a dry mass basis (Yu et al., 2018b).

# **3.2 Chemicals**

#### **3.2.1 Standard compounds**

The standard compounds/chemicals for catalytic reaction (supplementary tests for improved understanding of conversion process) and calibration of analytical equipment included levulinic acid (98%), formic acid (98%), mannose (98%), and cellobiose (Alfa Aesar); glucose (99%, UNI-chem, China); fructose ( $\geq$ 99%) and maltose monohydrate (98%) (WAKO);  $\alpha$ -cellulose, furfural (99%) and hydroxymethylfurfural (HMF;  $\geq$ 99%) (Sigma Aldrich); and levoglucosan (98%, Fluorochem). All standard compounds/chemicals were used as received without any alteration.

## **3.2.2 Catalysts**

Various concentrations (0.135 to 0.5 M) of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%, Honeywell Fluka) and FeCl<sub>3</sub>·6H<sub>2</sub>O (98%, Sigma Aldrich). were employed as catalysts for paper and food

waste conversion. Concentrations of catalyst were selected based on the catalytic activity reported in the existing literature and as required to achieve target products (sugars and derivatives) from selected paper and food waste.

#### 3.2.3 Solvents

As introduced in **Chapter 2**, the greenest solvent H<sub>2</sub>O and other conventional and emerging green organic solvents were utilised for the catalytic valorisation of paper and food waste, such as gamma-valerolactone (GVL) (99%, Sigma-Aldrich), acetone (99%, Anaqua, USA), propylene carbonate (99%, Aladdin), ethylene carbonate (99%), dimethyl carbonate (99%) (Alfa Aesar), and isopropanol (IPA) (99%, Honeywell). Binary solvent systems (organic solvent-water) were used to improve the green attribute of solvent systems for polysacchariderich waste valorisation. For catalytic conversions (except for selected cases of biphasic reaction), a 1:1 ratio of organic solvent-water was used, *i.e.*, 50% water was replaced by organic solvent thereby reducing the use of expensive organic solvent, which is comparatively greener than using 100% organic solvent. Besides, water plays an important role in biomass conversion by directly taking part in reactions such as catalytic hydrolysis for the production of sugars. Furthermore, our previous research demonstrated 1:1 ratio of an organic solvent-water system could be conducive to bio-based chemical production. Solvents were selected based on the following criteria:

- Recommended green attributes based on health, safety, and environmental criteria presented in the CHEM21 solvent selection guide (Prat et al., 2016)
- Activity/performance reported in the literature
- Renewable origin: bio-derived, CO<sub>2</sub>-derived
- Polarity for microwave absorption

**Chapter 4**: Gamma-valerolactone, and acetone as green co-solvents were employed in this study and the solvent systems are denoted as GVL/H<sub>2</sub>O, and acetone/H<sub>2</sub>O respectively.

**Chapter 5**: Gamma-valerolactone, as the green co-solvent was employed in this study and the solvent systems, are denoted as GVL/H<sub>2</sub>O.

**Chapter 6**: Propylene carbonate, ethylene carbonate, and dimethyl carbonate as green cosolvents were employed in this study and the solvent systems are denoted as PC/H<sub>2</sub>O, EC/H<sub>2</sub>O and DMC/H<sub>2</sub>O respectively.

**Chapter 7**: Gamma-valerolactone, propylene carbonate, and isopropanol as green co-solvents were employed in this study and the solvent systems are denoted as GVL/H<sub>2</sub>O, PC/H<sub>2</sub>O, and IPA/H<sub>2</sub>O respectively.

# **3.3 Catalytic valorisation**

# 3.3.1 Major experiments

**Chapter 4, 5**, and **6**: The catalytic conversion of paper waste substrates was conducted under microwave heating (EthosUp Microwave Reactor, Milestone, at maximum power of 1.9 kW, 100 ml vessel). To perform catalytic tests, the selected paper or food waste substrate (5 wt/v %) was loaded to water or a mixture of organic solvent and water (solvent ratio, 1:1; total volume, 10 ml), and selected catalyst within a Teflon vessel and sealed, then heated (using microwave control settings) to reach the desired reaction temperature (ranges between 120 to 200 °C for different studies) following a constant ramping rate (32 °C min<sup>-1</sup>), followed by a holding period of 1–20 min, and cooling period of 15–30 min using mechanical ventilation. The in-vessel reaction temperature and autogenous pressure were recorded using a standard thermocouple and pressure data-logger, respectively in the microwave reactor. The reacting vessels were subjected to autogenous pressure with a maximum pressure set as 50 bar for the

microwave reactor, and no external pressure was applied during catalytic conversion. Each experimental run was conducted in duplicates to ensure reliable analysis.

Chapter 7: To perform catalytic tests using a monophasic system, 0.5 g bread waste (5 wt/v%), a mixture of organic solvent (PC/GVL/IPA) and water (total volume 10 ml; solvent ratio 1:1 for monophasic reaction), and 0.5 M H<sub>2</sub>SO<sub>4</sub> were loaded in Teflon vessel and sealed, then heated to reach the desired reaction temperature (110-150°C) following the procedures described in the previous section. The reaction conditions were selected based on the latest studies on starch-rich food waste conversion (Yu et al., 2018b, 2020b) and adjusted if necessary based on the experimental observations. After analysing the results obtained from different monophasic solvent systems, GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O solvents were investigated for biphasic reactions. As GVL and IPA were completely miscible in water, 30 wt%(aq) NaCl was applied as a phase modifier to prepare the biphasic system (Wettstein et al., 2012; Jiang et al., 2019), and catalytic tests were conducted following the conditions mentioned above. It should be noted that the concentration of H<sub>2</sub>SO<sub>4</sub> referred to the whole solvent system (*i.e.*, consistent for all experimental runs with different solvents, both monophasic and biphasic), whereas the concentration of NaCl refers to the reaction phase only, which was denoted as NaCl<sub>(aq)</sub>. To analyse the influence of the reaction phase and extraction phase on catalytic performance in the biphasic system, different ratios of water and organic solvent (1:1, 1:3, 3:1) were applied for the conversion. Control runs without bread waste substrate were performed for solvent systems under the selected conditions. Standard thermocouple and pressure data-logger were used during catalytic reactions to monitor and record the in-vessel reaction temperature and autogenous pressure, respectively.

## **3.3.2 Supplementary and control experiments**

**Chapters 4**: Conversion of standard sugars (*i.e.*, glucose and xylose) were conducted in different solvent systems following the method mentioned above (**Section 3.3.1**) at 180°C to

understand the solvent effect on model compounds and to compare with paper towel conversion. Control experiments without paper towels were carried out in all solvent systems at 200°C for comparative analysis.

**Chapter 6**: Paper towel waste conversion in DMSO/H<sub>2</sub>O and standard cellulose conversion in PC/H<sub>2</sub>O were conducted for comparative assessment following the above-stated method (**Section 3.3.1**). To explore the role of carbonate solvents in depolymerisation, paper towel waste was treated in PC/H<sub>2</sub>O (140°C, 10 min) without acid addition and then oven-dried at 60°C overnight. Then the pre-treated substrate was dried and subjected to microwave-assisted conversion in H<sub>2</sub>O (100%) (140°C, 10 min, 0.135 M H<sub>2</sub>SO<sub>4</sub>). Control runs without paper towel waste were carried out in all solvent systems at the same acid loading (0.135 M H<sub>2</sub>SO<sub>4</sub>) under selected reaction conditions.

**Chapter 7**: To substantiate the experimental results obtained in PC/H<sub>2</sub>O solvent, additional tests under the selected conditions were conducted using propylene glycol (PG) and water (PG/H<sub>2</sub>O, 1:1) for comparison.

# **3.4 Sample analysis**

#### **3.4.1 Soluble products**

After the catalytic run, reacted solution was centrifuged to separate liquid and solids, and a soluble sample was withdrawn from each replicate, diluted with deionised water (DIW), and filtered through a membrane filter (0.45  $\mu$ m) before analysis. Soluble products were detected and quantified through high-performance liquid chromatography (HPLC). To ensure the reliability of the analysis, blank and spiked samples with known concentrations of standard compounds were injected into the HPLC before analysing the samples.

**Chapters 4** and **7**: Detection and quantification of all soluble products were conducted employing an Aminex HPX-87 HPLC column (Bio-Rad) and Chromaster equipment consisting of a refractive index detector (Hitachi, Japan). The mobile phase comprises 0.01 M  $H_2SO_4$  at a 0.5 ml min<sup>-1</sup> flow rate at 50°C column temperature (Yu et al., 2017a).

**Chapter 5**: Detection and quantification of sugars, LA, and FA were conducted employing an Aminex HPX-87 HPLC column (Bio-Rad) (0.01 M  $H_2SO_4$  mobile phase, 0.5 ml min<sup>-1</sup> flow rate, 50°C) and Chromaster equipment consisting of a refractive index detector (Hitachi, Japan), while HMF and furfural were analysed by using ultraviolet and visible spectrophotometry (UV–VIS) detector with a UV wavelength set at 280 nm.

**Chapter 6**: Sugars were quantified by using an Agilent Hi-Plex Ca column and DIW (100%) as the mobile phase (0.4 ml min<sup>-1</sup>, 80 °C), after pH adjustment of samples (~7) by NaOH, while derivatives of sugars, including HMF, furfural, FA, and LA, were quantified using an Aminex HPX-87H column (Bio-Rad) (0.01 M H<sub>2</sub>SO<sub>4</sub> mobile phase, 0.5 ml min<sup>-1</sup> flow rate, 50°C).



**Figure 3.1** Summary of experimental methodology illustrating catalytic conversion of polysaccharide-rich wastes, soluble product analysis, and solid characterisation technics used in this research

The yield of soluble products was calculated based on the carbon content (Eqn. 1) (S. S. Chen et al., 2018; Yu et al., 2018b) of the cellulosic or hemicellulosic fraction of a particular paper substrate,

Product yield (C mol%) = 
$$\frac{Conc_p (mg ml^{-1}) \times Vol (ml)/MW_p \times C_p}{C_s (mol)} \times 100$$
.....(1)

where  $Conc_p$  denotes the concentration of products (including disaccharide, glucose, fructose, LG, HMF, LA, FA, and furfural);  $MW_p$  and  $C_p$  represent the molecular mass and mole number of carbons in the corresponding product, respectively;  $C_s$  represent the mole number of carbon in the selected paper and food substrate, or mole number of sugars when using standard compounds for supplementary experiments (0.5 wt/v%).

**Chapters 4**: Soluble product yields were calculated based on the total organic carbon contents of a particular paper waste substrate. Notably, a volume loss varying from 5 to 20% (at different temperatures) was recorded for the acetone/H<sub>2</sub>O solvent system, which was accounted for in the yield calculation.

**Chapter 5**: The yield of C6 sugars, LA, FA, and HMF was calculated based on the cellulosic carbon content, while the yield of C5 sugars and furfural was calculated based on the hemicellulosic carbon content of the respective paper substrate.

**Chapters 6**: Soluble product yields were calculated based on the total organic carbon contents of the paper waste substrate. A volume loss of 5-20% (at different temperatures) was recorded for the binary organic carbonate solvent-water systems, which was taken into account for the product yield calculation.

**Chapters 7**: Soluble product yields were calculated based on the total organic carbon contents of a bread waste substrate. Notably, a volume loss of 5-15% (following various reaction

duration) was recorded for PC/H<sub>2</sub>O solvent, which was taken into account for calculating the soluble product yields. For biphasic systems, samples were obtained from each layer and prepared separately for analysis after dilution in DIW. Partition coefficients ( $R_x$ ) for a particular product such as LA ( $R_{LA}$ ) and FA ( $R_{FA}$ ) were calculated following Eq. (2),

Partition coefficient  $(R_x) = \frac{C \mod \% \text{ of product in the organic layer}}{C \mod \% \text{ of product in the aqueous layer}}$ 

.....(2)

## 3.4.2 Characterisation of solids

The total organic carbon content (TOC) of paper substrates and bread waste was analysed by a TOC-L analyzer (Shimadzu Corporation). The contents of hemicellulose, cellulose, and lignin in various types of papers were measured using the standard methods (GB/T 20805-2006, NY/T 1459-2007, and GB/T 20806-2006) (Cui et al., 2022), and the ash content in respective paper substrates was analysed following National Renewable Energy (NREL) protocol on a dry mass basis (Sluiter, 2008). The thermal behaviour of the papers was examined by a thermogravimetric analyzer (TGA, Rigaku Thermo plus EVO2) at a ramp rate of 10 °C min<sup>-1</sup> to 550 °C under the N<sub>2</sub> atmosphere, and the derivative thermogravimetric (DTG) curves were prepared for further analysis.

For selected reaction conditions, post-reaction solid residues were collected through centrifugation, decantation, washing with DIW (3 times), oven drying (48 h at 60°C), grinding, and afterwards stored in airtight containers for further characterisation. Untreated paper and bread waste samples and post-reaction solid residues were characterized by an X-ray diffractometer (XRD) (Rigaku Smartlab, 10-50° 20, rate:  $10^{\circ}$  min<sup>-1</sup> at 45 kV and 200 mA) and the crystallinity index (*CrI*) was calculated from the XRD patterns of respective paper following the method reported in the literature (S. S. Chen et al., 2018). Solid residues from paper waste conversion were also characterised through a scanning electron microscope (SEM)

(TESCAN VEGA3 XM), Brunauer–Emmett–Teller (BET) surface area analyzer (Micromeritics ASAP 2020 Plus Version 1.02.01), and Fourier-transform infrared spectroscopy (FTIR) (PerkinElmer, range: 4000cm<sup>-1</sup> to 400 cm<sup>-1</sup>, total 25 scans).

For paper and bread waste conversion, selected solid and liquid samples were examined using <sup>13</sup>C nuclear magnetic resonance (NMR) on a Jeol JNM-ECZ500R MHz spectrometer. A commercial 3.2 mm magic-angle spinning (MAS) NMR probe was used with a standard crosspolarisation MAS (CPMAS) pulse sequence. Paper waste residues were subjected to solid-state <sup>13</sup>C NMR (recorded with bulk powder samples) with the magnetic field strength of 11.6 T at 500 MHz involving 32.7 ms acquisition time, 2 ms contact time, and 5 s relaxation delay. Solid <sup>13</sup>C NMR of bread waste samples (both untreated and post-reaction solid residues) were performed using the MAS frequency was 10 kHz with relaxation delay, scan times, and contact time at 5 s, 1200-2000, and 2 ms, respectively. Liquid samples subjected to the selected reaction conditions were also analysed by <sup>13</sup>C NMR using D<sub>2</sub>O solution. Chemical shifts (δ) were given in ppm and measured relative to tetramethylsilane (TMS) as the internal standard.

# **Chapter 4: Valorisation of Paper Waste in Green Solvents**

# Abstract

This chapter focuses on the catalytic valorisation of lignocellulosic paper waste, which constitutes a major portion of municipal solid waste (MSW) to synthesise value-added chemicals. Green solvent systems comprising H<sub>2</sub>O and  $\gamma$ -valerolactone (GVL) or acetone were evaluated to produce levulinic acid (LA) from lignocellulosic paper towel waste at different temperatures using dilute H<sub>2</sub>SO<sub>4</sub>. At the highest reaction temperature (200°C), the H<sub>2</sub>O-only system achieved ~15 mol% of LA at maximum. while GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O co-solvent systems enhanced the depolymerisation of paper towel waste and the subsequent conversion to LA, with the highest yield amounted to ~32 mol%. The acetone/H<sub>2</sub>O solvent system yielded ~17 mol% LA at a lower temperature (180°C), while higher temperature-induced polymerisation of soluble sugars and intermediates, hindered further conversion to LA. In contrast, the availability of soluble sugars was higher in the GVL/H<sub>2</sub>O system, which favoured the production of LA at higher temperatures. A maximum ~32 mol% LA yield generated from paper towel waste in GVL/H<sub>2</sub>O (200°C, 5 min) could be attributed to the favourable effect of GVL solvent in disrupting cellulose crystallinity and enhancing solubility of generated products and preventing by-product formation during catalytic conversion.



Figure 4.1 Graphical abstract of Chapter 4

# **4.1 Research questions**

As introduced in **Chapter 2**, valorisation of lignocellulosic biomass remained challenging considering the complex nature and recalcitrance of cellulosic fibres. Paper waste represents a waste stream that can be easily separated at the source (*e.g.*, commercial/institutional buildings) yet commonly used treatment techniques (*e.g.*, anaerobic digestion) were deemed unsuitable due to the low degradability of cellulosic fibres. Besides, hygiene concerns particularly for sanitary papers such as paper towels further challenged its potential valorisation. Therefore, developing efficient technology was necessary for paper waste treatment and valorisation. However, considering the high content of cellulosic fibres ( $\sim$ 70%) in paper towels, it could be utilised as feedstock for thermocatalytic production of LA generally employing mineral acids such as H<sub>2</sub>SO<sub>4</sub>, HCl, or solid acid catalysts, and the acidic

conversion process could ensure the proper sanitisation of waste paper towels (Antonetti et al., 2016; S. S. Chen et al., 2018). Although paper waste could be an attractive biorefinery substrate, its potential conversion to platform chemicals was yet to be explored to a large extent.

The solvent is a significant parameter that influences catalytic conversion through interactions with reactants and regulation of product selectivity in the system, therefore, appropriate solvents could enhance the valorisation of lignocellulosic waste to chemicals (Dyson and Jessop, 2016; Yu et al., 2018b). Owing to the crucial contribution to catalysis, it was important to devote research effort to identifying potential solvents for specific catalytic reactions. As an environmentally benign and green solvent, water has been preferred and utilised extensively for biomass fractionation and chemical production yet harsh reaction condition is required to obtain considerable product yield, and additionally, high by-product formation might influence the product yield negatively (Cao et al., 2018a; Licursi D. et al., 2018). Besides, conventional organic solvents (e.g., dimethyl sulfoxide (DMSO), tetrahydrofuran (THF)) and ionic liquids were employed owing to their influence on the acidic protons, high reactivity of reagents and product selectivity, as well as their capability, to enhance tandem catalytic reactions for biomass conversion (Chen et al., 2017c; Yu et al., 2017a). However, these conventional solvents were considered problematic or even hazardous due to safety, health, and environmental implications (Prat et al., 2016). Therefore, the selection of an appropriate solvent is necessary for addressing their green characteristics while maintaining reactivity and product selectivity to achieve efficient and sustainable LA production.

This chapter examined the catalytic valorisation of lignocellulosic paper towel waste into LA in green co-solvents in a binary organic solvent-water (1:1 v/v) system (GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O) using dilute sulphuric acid (0.135 M H<sub>2</sub>SO<sub>4</sub>) as the catalyst at different temperatures. This chapter provides insights into the potential roles of green solvents in a catalytic biorefinery in addition to serving as a reaction medium and discusses interactions between the solvents and substrates to elucidate their significance in determining the depolymerisation of lignocellulosic fibre and the formation of LA.

# 4.2 Results and discussion

#### **4.2.1 Depolymerisation of paper towel**

The addition of the organic co-solvent to water medium (GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O) enhanced the depolymerisation of cellulose and hemicellulose in view of the higher total sugar yields, e.g., ~30-36% at 160-170 °C compared to ~18-22% in H<sub>2</sub>O only system (Figure 4.2). The maximum sugar yield at the H<sub>2</sub>O-only system observed at 190 °C (~35 mol%) was comparable to the total sugar yield at 170 °C in green co-solvent systems (~30-36 mol%), which suggests that the addition of green co-solvent increased the level of hydrolysis and decreased the energy required for reaction (a comparative discussion on energy consumption for LA production in different solvent systems is given in Section 3.4). Previous studies reported that binary organic solvent-water systems such as GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O provide a local phase separation near cellulose surfaces, where molecules of organic solvent preferentially bind to the hydrophobic surface while H<sub>2</sub>O molecules create bonds with the hydrophilic surface. Thus, organic solvent-water binary systems might lead to chemical modification at the cellulose surfaces inducing bond cleavage that improves cellulose hydrolysis (Smith et al., 2017; Song et al., 2018). However, detailed investigation through computational simulation would be needed to uncover mechanisms for specific catalytic reactions in future studies.

Considering the high yield of sugars,  $GVL/H_2O$  was the most efficient co-solvent for the depolymerisation of paper towel waste (~36-40 mol% at 170-180 °C). Enhanced depolymerisation of paper towel waste in the  $GVL/H_2O$  can be attributed to the combined

effects of GVL solvent on solvation of cellulose, disruption of cellulose crystallinity, and positive influence on glycosidic bond cleavage (Luterbacher et al., 2014; Mellmer et al., 2014a). It was reported that GVL can solubilise lignocellulosic biomass and disrupt the structure of crystalline cellulose, leading to increased production of sugars (Luterbacher et al., 2014). Besides, the polar aprotic nature of GVL helps to enhance the reactivity of protons through stabilisation of solvated protons compared to reaction conditions in H<sub>2</sub>O, thereby accelerating the reaction rate for biomass conversion during acid hydrolysis. GVL/H<sub>2</sub>O solvent has been reported to significantly decrease the activation energy for disaccharide (*e.g.*, cellobiose, maltose) hydrolysis by promoting glycosidic bond ( $\beta$ -1,4 and  $\alpha$ -1,4) cleavage, thereby providing a higher reaction rate compared to using 100% H<sub>2</sub>O as the solvent; the analogous effect was anticipated for cellulose hydrolysis (Mellmer et al., 2014a, 2014b).



**Figure 4.2** The yield of total sugars at different temperatures (160-200°C) in H<sub>2</sub>O, GVL/H<sub>2</sub>O, and acetone/H<sub>2</sub>O solvent systems from virgin pulp paper towels (reaction conditions: 5 wt% substrates, 0.135 M H<sub>2</sub>SO<sub>4</sub>, 5 min, solvent mixture 1:1).

A steady increase in total soluble products from VPT conversion was observed with increasing temperature (Figure 4.3) in the H<sub>2</sub>O-only system (~60 mol% at 200°C). In comparison, the yield of total soluble products for VPT (Figure 4.3) reached the maximum at 180°C for GVL/H<sub>2</sub>O (~51 mol%) and acetone/H<sub>2</sub>O (~47 mol%) which was ~20% higher than that of H<sub>2</sub>O-only system (~38 mol%) at the given temperature (180°C). The yield was comparable between green co-solvent systems, indicating similar reactivity of both co-solvent systems toward soluble products at 180°C. The total soluble product yield remained stable at 180-200°C for GVL/H<sub>2</sub>O solvent (~50 mol%), while for acetone/H<sub>2</sub>O solvent, a considerable drop in the total soluble product yield was detected at higher reaction temperatures (~39 mol% at 190-200°C). The decrease in total detectable products might indicate a higher tendency for insoluble by-products formation (e.g., humins) through polymerisation in acetone/H<sub>2</sub>O solvent at higher temperatures, in contrast, GVL/H<sub>2</sub>O system might have stabilised product solubility by preventing polymerisation of sugars and derivatives. For acetone/H<sub>2</sub>O solvent on average, 5-20% of the solvent loss was recorded during the experiment at different temperatures and char formation was observed at 180-200°C. Solvent loss in the acetone/H<sub>2</sub>O system might occur due to self-condensation of acetone or direct condensation of acetone with sugars and sugar derivatives (Smit and Huijgen, 2017), which might be related to lower total sugar yield in acetone/H<sub>2</sub>O co-solvent system. A previous study demonstrated that acetone generated the highest fraction of insoluble polymers among various organic solvents tested (e.g., alcohols, chloroform, DMSO) for acid-treatment of levoglucosan. In acid-catalysed reactions, acetone could produce different products through intramolecular aldol condensation that ultimately forms polymers, and condensation products can react with sugars leading to polymer formation (Hu et al., 2012). An isolated phase of products can form through precipitation in the system if the solvent cannot dissolve kinetic products during the reaction (Dyson and Jessop, 2016). In the acetone/H<sub>2</sub>O system, polymerisation might have restricted the amount of soluble sugars in

the reaction medium, and the solid polymers could result in char formation at higher temperatures, thus resulting in lower soluble product yield detected in liquid samples in the experiment.



**Figure 4.3** Product yields from paper towel conversion in (a)  $H_2O$ , (b) GVL/ $H_2O$  and (c) acetone/ $H_2O$  solvent system at different temperatures utilizing VPT and RPT (reaction conditions: 5 wt% substrate, 0.135 M  $H_2SO_4$ , 5 min, solvent mixture 1:1).

#### 4.2.2 Effects of green co-solvent on LA production

In general, all solvent systems showed an increasing trend for LA yields from paper towel waste with increasing temperature in the presence of dilute  $H_2SO_4$  (0.135M) catalyst (Figure 4.4), in accordance with the literature (Wettstein et al., 2012; Chen et al., 2017c). The lower temperature of 160-180°C was efficient for sugar production, and LA emerged at a higher temperature of 180-200°C. At the highest reaction temperature (200°C), LA yields of 15-32 mol% were obtained in this study that is comparable to those reported in the previous studies on biomass conversion, such as paper towel waste (LA yield ~30-46 mol%) (S. S. Chen et al., 2018), paddy straw (LA yield ~24 wt%) (Yan et al., 2008), and paper sludge (LA yield ~15-32 wt%) (Galletti et al., 2012); though a precise comparison of results achieved in different studies was difficult considering different reaction conditions employed (*e.g.*, temperature, solvent, catalyst loading).



**Figure 4.4** LA yield at different temperatures (160-200°C) in H<sub>2</sub>O, GVL/H<sub>2</sub>O, and acetone/H<sub>2</sub>O solvent systems from virgin pulp paper towel (reaction conditions: 5 wt% substrates, 0.135 M H<sub>2</sub>SO<sub>4</sub>, 5 min, solvent mixture 1:1).

Although H<sub>2</sub>O-only solvent generated a considerable yield of sugars (~60 mol% at 180°C) with 0.135 M H<sub>2</sub>SO<sub>4</sub> catalyst, it generated only ~2-15% LA yield at 180-200°C (Figure 4.3), which was similar to the values mentioned in previous studies (Chen et al., 2017b; Alonso et al., 2013a). In comparison, GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O green co-solvent systems achieved higher LA yields, which were approximately 29-32 mol% at maximum, highlighting the presence of GVL and acetone favoured the tandem dehydration-rehydration reactions. Comparing the co-solvent systems, acetone/H<sub>2</sub>O gave a considerable yield of LA (~17 mol%) from VPT at a lower temperature (180°C), whereas GVL/H<sub>2</sub>O could not generate a significant LA yield until 190°C (~20 mol%). Although GVL/H<sub>2</sub>O provided the most efficient sugar yield (e.g., ~40 mol% at 170°C), the system generated insignificant LA yield at lower temperatures (~2 to 4 mol% at 160-180°C), which suggested that dehydration of sugars to HMF might be the bottleneck during paper towel conversion in GVL/H<sub>2</sub>O at the given reaction temperature. In contrast, considerable LA yield was observed for acetone/H<sub>2</sub>O at 180°C, suggesting that dehydration of sugar to HMF was faster in acetone/H2O compared to rehydration of HMF to LA. Our recent study showed that acetone/H<sub>2</sub>O could provide a faster sugar-to-HMF conversion compared to other organic solvent-water systems such as DMSO/H<sub>2</sub>O and THF/H<sub>2</sub>O (Yu et al., 2017a). Moreover, faster sugar conversion in the acetone/H<sub>2</sub>O system could be attributed to the significant pressure build-up in the reaction vessel, which was ~30 bar on average during the reaction at 180°C (Figure 4.5), as the boiling point of acetone is low (56°C). High *in-situ* pressure was found to accelerate the conversion of biomass/sugars (Duo et al., 2016; Yu et al., 2018b). In comparison, the average in-vessel pressure recorded for GVL/H<sub>2</sub>O system was ~12 bar during reaction at 180°C (Figure 4.5), so in situ pressure might not have a noticeable effect on catalytic conversion in the system. Apart from the pressure effect, acetone/H<sub>2</sub>O solvent might contribute to and enhance tandem catalytic steps during sugar dehydration to HMF and subsequent rehydration to LA. However, further experimental

evidence supplemented with mechanistic simulation would be needed to support the postulation and uncover the role and contribution of solvents to facilitate catalytic reactions.



**Figure 4.5** Temperature and pressure profile during the reaction (paper towel conversion) in (a)  $GVL/H_2O$  and (b) acetone/H<sub>2</sub>O system (reaction conditions: 5 wt% substrates, 0.135 M H<sub>2</sub>SO<sub>4</sub>, 5 min, 180°C, solvent mixture 1:1).

For GVL/H<sub>2</sub>O solvent, the reactions were accelerated with an increase in temperature (190-200°C), and a higher yield was achieved (LA yield ~20-32 mol%). Despite the faster conversion of sugars to LA (17 mol%) at 180°C, the acetone/H<sub>2</sub>O system did not provide a significant increase in LA yield (~29 mol%) when the reaction temperature was further

increased to 200°C. In comparison, GVL/H<sub>2</sub>O system generated 8 times higher yield (~32 mol%) at 200°C compared to that of 180°C (~4 mol%). The lower yield of LA in acetone/H<sub>2</sub>O could be attributed to the polymerisation of sugars and condensation products in the solvent system, which might have restricted the availability of soluble sugars during catalytic reactions at a higher temperature (Hu et al., 2012). In contrast, the good performance of the GVL/H<sub>2</sub>O solvent system for tandem catalytic reactions could be attributed to the interactions among substrate, solvent, and an acid catalyst, as GVL was reported to solubilise recalcitrant cellulose and products generated during the deconstruction of cellulose (Alonso et al., 2013b; Mellmer et al., 2014a).



**Figure 4.6** Conversion of standard sugars (glucose and xylose) in different solvent systems (reaction conditions: 5 wt% substrate, 0.135 M H<sub>2</sub>SO<sub>4</sub>, 5 min, 180°C, solvent mixture 1:1).

To probe the effect of solvent on paper towel conversion, supplementary tests were done with glucose (standard compound) at 180°C in all solvent systems. Using glucose as feedstock, both GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O solvent systems produced ~16 mol% of LA at 180°C (**Figure 4.6**). In comparison, the LA yield from paper towel waste was lower in GVL/H<sub>2</sub>O (~4 mol%) than that in acetone/H<sub>2</sub>O (~17 mol%). Generally, standard sugars are easier to be converted to HMF and LA compared to lignocellulosic substrates considering the complex structure combining cellulose, hemicellulose, and lignin. Considering the faster conversion of lignocellulosic paper wastes observed in acetone/H<sub>2</sub>O solvent, it might be possible that a fraction of the LA produced was subsequently degraded when standard sugar (glucose) was used as the substrate.

In general, the conversion of RPT was slightly higher than that of VPT in H<sub>2</sub>O and acetone/H<sub>2</sub>O solvent systems (**Figure 4.3a, c**). This could be ascribed to the relatively shorter fibre length and lower crystallinity of RPT fibres (65.5%) compared to VPT (67.1% crystallinity), as amorphous cellulose and short fibres are easier to be deconstructed (S. S. Chen et al., 2018). In contrast, GVL/H<sub>2</sub>O showed slightly lower conversion for recycled pulp at 160-170°C, while at higher temperatures GVL/H<sub>2</sub>O provided almost the same conversion for both types of paper towel wastes (**Figure 4.3b**). It should be noted that RPT contained more lignin (11.8%) (**Table 4.1**) and lignin solubility is high in GVL/H<sub>2</sub>O solution in the case of GVL concentration ranging between 50-65 wt% (Lê et al., 2016b), and reactions may slow down due to high solute-solvent solvent interactions (Dyson and Jessop, 2016) between lignin and GVL.

Туре	Cellulose	Hemicellulose	Lignin	Crystallinity index (CrI)
VPT	78.1% (13.03)*	20.6% (3.44)*	1.3%	67.1
RPT	67.4% (11.23)*	20.8% (3.45)*	11.8%	65.5

**Table 4.1** Characteristics of the paper towel waste used for catalytic conversion

\* Number in the parentheses represents the mole number of carbon for 0.5 g of corresponding paper towel waste; VPT and RPT were manufactured from different raw materials/sources

Results from paper towel waste conversion revealed that hemicellulose conversion remained facile in all solvent systems for both VPT and RPT (**Figure 4.3**), as efficient production of xylose was recognised and consequently dehydrated to furfural. Furfural production occurred to a greater extent at a lower temperature (160°C) than that of LA, indicating that deconstruction of hemicellulose and subsequent conversion to furfural were less energy-intensive compared to cellulose. At 190-200°C a higher yield of furfural was observed for GVL/H<sub>2</sub>O (~9-11 mol%) while a lower furfural yield was observed for acetone/H<sub>2</sub>O (~3-4 Col%). It was worth noting that GVL could decrease the rate of furfural degradation (Alonso et al., 2013b), which was reflected by the results of this study. In contrast, acetone might react with furfural and form condensation products (Hu et al., 2012). Our supplementary test with xylose (standard compound) (**Figure 4.6**) revealed that ~50 Col% total soluble products were detected in the solution and a considerable amount of black solid was observed at the end of the reaction in the acetone/H<sub>2</sub>O system.

#### 4.2.3 Analysis of post-reaction solid residues

As observed during the experiment, a higher amount of solid residue was observed after reaction in 100% H<sub>2</sub>O, which can be related to the lower depolymerisation and lower LA yield in water as a large fraction of lignocellulosic fibre might remain unreacted or generate humins. As solid residue was collected and measured for reaction at 180°C, it was observed that reaction in GVL/H<sub>2</sub>O solvent generated 50% less solid residue compared to the H<sub>2</sub>O-only system. For the acetone/H<sub>2</sub>O system, the formation of char was observed at the bottom of the reaction vessel, but the exact fraction of solids was not possible to quantify. Less quantity of unreacted solids in the GVL/H<sub>2</sub>O solvent system indicated higher solubility and conversion of paper towel waste during the reaction.

To understand the changes in paper towel wastes in different solvent systems, a solidstate <sup>13</sup>C NMR (CP/MAS) analysis was conducted on the remaining solids after reaction and paper towel waste before reaction (Appendix). NMR spectra of paper towel waste and postreaction solid residue resemble the resonances observed in the spectrum of isolated cellulose, which could be related to the high cellulosic fractions in paper towel waste (78.1% in VPT waste). The chemical shifts are given by <sup>13</sup>C CP/MAS NMR spectrum (**Figure 4.7**) of cellulose ranges from 100-108, 80-93, 70-80, and 57-70 ppm could be assigned to C<sub>1</sub>, C<sub>4</sub>, C<sub>2,3,5</sub> and C<sub>6</sub> signals of cellulose, respectively (Atalla and VanderHart, 1999; Kono et al., 2002; Foston, 2014; Alcántara et al., 2016). Considering the peak attribution and diversity of cellulosic biomass, NMR peaks obtained from unreacted solid samples might be assigned as follows: the peak at 101 ppm is assigned to C<sub>1</sub>, peaks at 79 and 85 are assigned to C<sub>4</sub>, peaks at 71 and 68 are assigned to C<sub>2,3,5</sub>, and peaks at 61 and 58 are assigned to C<sub>6</sub> signals of cellulose, respectively.



**Figure 4.7** Solid-state (CP/MAS) <sup>13</sup>C NMR spectra for paper towel waste and spectra for solid residue subjected reactions in acetone/H<sub>2</sub>O, GVL/H<sub>2</sub>O, and H<sub>2</sub>O (reaction conditions: 5 wt% substrates, 0.135 M H<sub>2</sub>SO<sub>4</sub>, 5 min, 180°C).

The C<sub>4</sub> peak of NMR spectra is commonly used for extracting the structural information of cellulose. A broad peak ranged from 80-85 ppm represents C<sub>4</sub> cellulose amorphous carbon, whereas a comparatively sharp peak from 85-92 ppm represents C<sub>4</sub> crystalline carbon (Foston, 2014; Zhu et al., 2016). The C<sub>4</sub> peaks (85 and 79 ppm) of the <sup>13</sup>C NMR spectrum of paper towel waste before reaction shows that the intensity of amorphous carbon was relatively high compared to that of crystalline carbon. In contrast, the spectra of solid residue after reaction in different solvents show alteration in relative intensities of amorphous and crystalline carbon. Following acid hydrolysis in different solvents, the intensity of crystalline carbon increased while the intensity of amorphous carbon decreased compared to that of untreated paper towel waste. This shift indicated that amorphous carbon was consumed during the reaction to produce sugar and the relative crystallinity increased because the crystalline phase gave relatively high resonance (Samuel et al., 2010; Zhu et al., 2016). An increase in crystallinity was also reported after acid hydrolysis of biomass as amorphous carbon is more susceptible to degradation (Bernardinelli et al., 2015). The change in relative intensities of crystalline and amorphous carbon is less pronounced in the solid residue obtained from a reaction involving an H<sub>2</sub>O-only solvent system, however, it was more pronounced in green co-solvent systems involving GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O. Similar changes in relative intensities of crystalline and amorphous phases could be observed for the C6 peak of spectra. This phenomenon indicates that a higher amount of cellulosic carbon was converted during reaction in GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O solvent systems compared to 100% H<sub>2</sub>O, which was in good agreement with the total yield of soluble products that are 38 mol% for H<sub>2</sub>O-only solvent system and ~50 mol% for GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O co-solvent system.



**Figure 4.8** XRD patterns of solid residue subjected to reactions in acetone/H<sub>2</sub>O, GVL/H<sub>2</sub>O, and H<sub>2</sub>O (reaction conditions: 5 wt% substrates, 0.135 M H<sub>2</sub>SO<sub>4</sub>, 5 min, 180°C).

The XRD patterns of solid residue (**Figure 4.8**) in different solvent systems were also analysed to reveal the changes in cellulose crystallinity (Appendix). The diffraction peaks were identified at  $15^{\circ}$ ,  $22.5^{\circ}$  and  $34.5^{\circ}$  corresponding to (110), (200) and (004) planes of Type-I crystalline cellulose (Lu et al., 2015). The calculated *CrI* values (**Table 4.2**) demonstrated the changes in crystallinity after reaction compared to untreated paper towel waste, yet significant alteration in cellulose crystallinity was not observed. Evaluating *CrI* values for solid samples in different solvent systems showed a relatively high crystallinity for GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O compared to the H<sub>2</sub>O-only system. This suggested a higher degree of hydrolysis of amorphous cellulose in co-solvent systems that leave behind the crystalline form in cellulose structure, thus the relative crystallinity increased in solids (Cheng et al., 2011).

Reaction conditions	CrI
Untreated paper towel waste	67.1
H <sub>2</sub> O	46.9
GVL/H <sub>2</sub> O	50.5
acetone/H <sub>2</sub> O	49.1

**Table 4.2** Crystallinity index (*CrI*) of VPT subjected to reaction in different solvents (reaction conditions: 5 wt% substrates, 0.135M H<sub>2</sub>SO<sub>4</sub>, 5 min, 180°C, solvent mixture 1:1)

## 4.2.4 Energy consumption for LA production

Energy consumption per unit of LA production was evaluated for different scenarios (Table 4.3) based on the power consumption rate recorded in the microwave reactor used for experiments (Figure B.1). This calculation reflects the actual reaction conditions used in the study (reaction conditions: 5 wt% substrate, 0.135 M H<sub>2</sub>SO<sub>4</sub>, 5 min, and solvent mixture 1:1), which may differ with variations in substrate and catalysts loading. Energy consumption has been evaluated for ramping (up to the designated temperature) and holding during the reaction (constant temperature) (Figure 4.5). In general, most energy was consumed during the ramping period compared to the holding period at a constant reaction temperature for all solvent systems (Table 4.3). By evaluating different solvent systems at 180°C, it was observed that energy consumption per unit of LA produced was considerably lower in organic solvent-water binary systems (~1.6-7 kWh g<sup>-1</sup>) compared to H<sub>2</sub>O-only systems (~20 kWh g<sup>-1</sup>). Acetone/H<sub>2</sub>O was the most energy-efficient (~1.6 kWh g<sup>-1</sup>) solvent system for unit production of LA at 180°C. For reaction at 200°C, energy consumption values were comparable for GVL/H2O and acetone/H<sub>2</sub>O (~1 kWh g<sup>-1</sup>), which was 60% lower than that of the H<sub>2</sub>O-only system (~2.3 kWh g<sup>-1</sup>). These results suggested that the addition of green co-solvents such as GVL and acetone can decrease the actual energy cost per unit of LA production from paper towel waste, which

is encouraging the development of a cost-effective process for waste valorisation to produce

valuable chemicals.

Table 4.3 Energy consumption for LA production in different solvent systems (reaction
conditions: 5 wt% substrates, 0.135 M H <sub>2</sub> SO <sub>4</sub> , 5 min, solvent mixture 1:1)

Solvent	Temperature (°C)	Energy consumption (kWh)		Energy consumption per unit of LA production	
		Ramp	Reaction	Total	$(kWh g^{-1})$
H <sub>2</sub> O	180	0.09	0.04	0.12	20.67
	200	0.10	0.03	0.13	2.34
GVL/H <sub>2</sub> O	180	0.08	0.03	0.11	7.13
	200	0.09	0.04	0.13	1.04
Acetone/	180	0.08	0.04	0.11	1.63
$H_2O$	200	0.09	0.03	0.12	1.02

# 4.2.5 Comparative perspective regarding solvent systems

Comparing organic solvent-water binary solvent systems, GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O provided advantages from different viewpoints. To achieve a higher LA yield from lignocellulose at a lower temperature, acetone/H<sub>2</sub>O could be efficient whereas GVL/H<sub>2</sub>O provides a slower conversion of sugars. To maintain the availability of soluble sugars and further enhancement of LA yield, the GVL/H<sub>2</sub>O system was more beneficial than acetone/H<sub>2</sub>O. Green co-solvent systems can be further tuned for optimum LA production considering reaction temperature, duration, and acid concentration. Additional experiments could be performed to reveal conversion kinetics for different co-solvent systems to optimise the waste valorisation process. Moreover, to obtain a sustainable biomass conversion process, recovery of solvent is important; in that case, the acetone/H<sub>2</sub>O system falls short owing to considerable solvent loss (up to 20%) during the reaction. Working with acetone at high temperatures might also raise safety concerns as its flashpoint is very low (-18°C) (Prat et al., 2016), which can be an issue concerning its significance as a green solvent. Hence, careful attention should be given
to selecting green co-solvent systems for biomass-to-chemical conversion considering reaction conditions, product selectivity, environmental impact, and safe handling of chemicals at work.

## 4.3 Summary

This chapter investigated the catalytic valorisation of lignocellulosic paper towel waste and analysed the influences of organic solvent-water binary green solvent systems on acid hydrolysis LA production. Depolymerisation of fibres and yield of LA was enhanced by green co-solvents compared to 100% aqueous condition. This research implies that GVL and acetone solvents have good potential for catalytic conversion of paper waste with effective depolymerisation of highly crystalline cellulosic fibres and selective conversion of sugar to LA. These results contribute toward the development of a simple, energy-efficient, and scalable technology for the valorisation of considerable amounts of cellulosic paper waste worldwide paving the way toward a circular bioeconomy.

# Chapter 5: Influence of Feedstock Properties and Catalytic Systems

#### Abstract

Lignocellulosic paper waste constitutes a major waste stream globally, which should be valorised for chemical production. Paper properties, *e.g.*, feedstock composition, cellulosic crystallinity, and thermal stability/degradability vary with raw materials and pulping processes. **Chapter 4** of this thesis demonstrated the efficient catalytic valorisation of paper towel waste facilitated by green solvent. However, the influence of variable paper properties on catalytic reactions was unexplored, which might affect the viability of chemical production from the diverse paper feedstock. This chapter. investigated LA, HMF, and furfural production by H<sub>2</sub>SO<sub>4</sub> and FeCl<sub>3</sub> catalysed conversion of nine types of paper wastes in a green solvent system (1:1 GVL/H<sub>2</sub>O). At 160-180 °C for 1-20 min, ~23-27 wt% LA yield was achieved from sanitary papers, tracing/parchment paper, and paper food boxes mainly containing crystalline cellulose, while a lower LA yield (~10-20 wt%) was obtained from other paper wastes with high contents of ash and lignin. A higher selectivity towards HMF (~12 mol%) was achieved in the presence of FeCl<sub>3</sub>. A furfural yield of ~4-7.5 wt% was also obtained from the hemicellulose content. This study elucidated crucial factors and desirable characteristics of paper waste for catalytic valorisation.



Figure 5.1. Graphical abstract of Chapter 5

## **5.1. Research questions**

The amount of paper waste generated every year is rapidly accelerating and burdening landfills, although a fraction of paper waste is being recycled for pulp production or other uses (Van Ewijk et al., 2018; Xu et al., 2021). In Hong Kong and other densely populated cities, efficient recycling of paper waste can be even more challenging when proper recycling facility is scarce due to high land premium and labour cost. For instance, in the year 2020, 68% of the total generated waste paper ended up in landfills amounting to 0.95 million tons, whereas ~0.45 million tons of paper waste was recovered for recycling using local and non-local facilities (EDP HK, 2020). This situation drives society to find high-value and sustainable approaches to paper waste recycling/upcycling for diverse chemical and biofuel production.

Paper is typically manufactured from lignocellulosic raw materials, such as wood, bamboo, and non-wood agricultural residues (*e.g.*, straw and bagasse). Due to the high proportion of cellulose, paper waste can be potentially valorised in biorefineries (Jahan et al., 2021). Modern paper pulp manufacturing processes are generally categorised as mechanical and chemical pulps. Mechanical pulping exerts mechanical force or pressure to crush fibres in raw materials, and a considerable amount of lignin can be retained during the papermaking process, leading to lower strength of paper. Therefore, mechanical pulping is mostly used for making non-permanent papers, such as newsprint (Biermann, 1996). Chemical pulping typically applies alkaline regimes, dilute aqueous acids, or organic solvents to promote delignification by breaking the linkages between lignin and carbohydrates (Sewsynker-Sukai et al., 2020). Acidic sulphite pulping involves the treatment of woods with various sulphite or bisulphite salts to make papers (*e.g.*, tracing/parchment paper). Traditional pulping processes are mostly performed with alkaline additives, for example, kraft pulping (NaOH/Na<sub>2</sub>S) (Cao et al., 2021), which is the most dominant process for manufacturing a wide variety of papers, such as printing paper or office paper, packaging paper, and sanitary papers (*e.g.*, napkins and tissues). In addition, waste paper can be used as raw materials for obtaining pulp through reuse/recycle loops (Bajpai, 2015; Zimmerman et al., 2020).

Although paper waste can be an attractive biorefinery substrate, its potential conversion to platform chemicals is yet to be explored to a large extent. **Chapter 4** of this thesis demonstrated the efficient catalytic valorisation of paper towel waste facilitated by green solvent. However, the influence of variable paper properties on catalytic reactions was unexplored, which might affect the viability of chemical production from the diverse paper feedstock. Among them, LA, HMF, and furfural are vital platform chemicals with multiple applications, *e.g.*, solvent, pharmaceuticals, personal care products, plasticisers, and building blocks for several value-added derivatives and fuels (Yu et al., 2016; Espro et al., 2021). Depending on different types of biomass and pretreatments involved in pulping processes, paper wastes would have variable properties, such as cellulose crystallinity, feedstock composition, and presence of inorganic impurities, which might influence the catalytic valorisation process as well as the yield and distribution of target products. For example, a high lignin content may cause resistance to paper utilisation, and its critical role has been recently

highlighted in biomass conversion (Yoo et al., 2020). It was necessary to expose the cellulose surface by removing lignin for the effective conversion of waste papers to LA and HMF. However, limited information about paper properties and their influence on subsequent conversion could be found in the existing literature. Therefore, a comparative evaluation of different paper types for LA and HMF production was necessary for advancing our understanding of paper waste valorisation in biorefinery.

Currently, mineral acids (e.g., H<sub>2</sub>SO<sub>4</sub> and HCl) provides the most viable option for LA production from biomass substrates (Antonetti et al., 2020b), and the acid-catalysed conversion of biomass reactions could be enhanced in polar aprotic solvents. In particular, GVL, a biomass-derived product, was used as a polar aprotic solvent that could increase the hydrolysis rates compared with the reaction carried out in the water (Mellmer et al., 2014a, 2019). Organosolv pretreatment using GVL/H<sub>2</sub>O solvent was reported to deconstruct the biomass to separate C5/C6 sugar and lignin (Timokhin et al., 2020), which might overcome the recalcitrance of lignin fraction in the paper and enable effective conversion. In addition, metal chlorides such as FeCl<sub>3</sub> have attracted considerable attention for biomass catalysis owing to their abundance, occupational safety, low cost, and better recoverability compared to mineral acids. It would be useful to disrupt hydrogen bonds within cellulose and destabilise the crystalline structures (Du et al., 2020). Furthermore, considerable Lewis acidity of FeCl<sub>3</sub> and Brønsted acidity generated in the solution make it a suitable catalyst for promoting hydrolysis and dehydration of cellulose-rich biomass substrates for the production of LA, HMF, and furfural (Yu et al., 2016; Wang et al., 2018; Di Fidio et al., 2020). FeCl<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> might be used as a combined catalytic system to investigate whether synergetic effects could be achieved during biomass conversion. Therefore, FeCl<sub>3</sub> as a catalyst could be beneficial to develop costeffective and time-efficient valorisation technologies for complex paper wastes.

This chapter investigated the microwave-assisted, high-throughput conversion of various types of paper wastes using H<sub>2</sub>SO<sub>4</sub> and FeCl<sub>3</sub> catalysts and a green solvent (GVL/H<sub>2</sub>O, 1:1). Nine types of paper substrates, originally manufactured by mechanical or chemical pulping, were selected in this study to investigate the feedstock viability for platform chemical synthesis, which is mostly unexplored at present. The paper properties, including feedstock composition, cellulosic crystallinity, and thermal stability were investigated to identify the desirable characteristics of paper wastes for chemical production under microwave-assisted catalytic systems. This study was designed to recognise the diverse compositions of the paper waste streams and assess the influence of compositional variation on the platform chemical production through manipulating the system components.

#### 5.2. Results and discussion

#### 5.2.1 Characteristics and composition of various paper wastes

Distinct characteristics and lignocellulosic composition of various paper wastes are presented in **Table 5.1** and **Figure 5.2**. The majority of the papers were manufactured from virgin wood, except for bamboo napkins and paper food boxes that were produced from sugarcane bagasse, whereas paper mould was manufactured from the waste paper pulp (**Table 5.1**). The newspaper was produced by combining ~70-80% mechanical pulp and ~20-30% chemical pulp, and the tracing/parchment paper was prepared by sulphite pulping. Kraft pulp was used for manufacturing other papers. Other than packaging paper and bamboo napkins, all papers originating from chemical pulp were bleached. To reveal the nature of cellulosic fibres, the untreated paper substrates were analysed using XRD. According to the XRD patterns, various paper substrates exhibited peaks at  $2\theta = ~16^{\circ}$  and  $22^{\circ}$  corresponding to natural cellulose I, indicating that the crystalline structure of cellulose was rarely changed after the paper manufacturing processes. In contrast, for paper mould, a small peak at  $2\theta = ~12^{\circ}$ 

corresponding to regenerated cellulose II was observed, *i.e.*, a slight transformation of cellulosic fibres happened during pulp recycling. Notably, compared to regenerated cellulose, cellulose I was thermodynamically prone to be converted (Cheng et al., 2011). The crystallinity index (*CrI*) of various paper wastes was calculated to present the crystalline phase proportion, as shown in **Table 5.1**. The lowest *CrI* value (53.3%) of newspapers reflected the low crystallinity and strength of cellulosic fibres, probably resulting from the extensive mechanical force used during mechanical pulping operation (Biermann, 1996). The highest *CrI* value (67.5%) observed for tracing/parchment paper was possibly due to the acid hydrolysis of unstable amorphous cellulose, thus increasing the relative crystallinity of the resulting substrate. The *CrI* values of sanitary papers such as paper towels and napkins ranged from 58 to 66%, while the remaining papers had comparable crystallinity, *e.g.*, ~56% for printing and packaging paper and ~60% for paper food box and paper mould.

	Paper wastes	Raw materials	Pulping process	Pulp bleaching	Crystallinity index ( <i>CrI</i> )
Category-1	HKIA paper towel	Wood, virgin	Chemical pulp, Kraft/sulfate	Bleached	66.4
	Napkin-1 (wood)	Wood, virgin	Chemical pulp, Kraft/sulfate	Bleached	60.5
	Napkin-2 (bamboo)	Bamboo, virgin	Chemical pulp, Kraft/sulfate	Not bleached	57.9
	Tracing/parchment paper	Wood, virgin	Chemical pulp, sulfite	Bleached	67.5
	Paper food box	Sugarcane bagasse	-	Not bleached	59.6
	Printing paper	Wood, virgin	Chemical pulp, Kraft-sulfate	Bleached	56.1
Category-2	Newspaper	Wood, virgin	Mechanical pulp 70-80% + Chemical pulp 20- 30%	Not bleached	53.3
	Packaging paper	Wood, virgin	Chemical pulp, Kraft/sulfate	Not bleached	56.4
	Paper mould	Waste paper	Recycled pulp prepared using mechanical force	Not bleached	59.7

**Table 5.1** Characteristics of various paper waste substrates (untreated)

The organic carbon content (wt%) of various paper feedstock was measured initially to evaluate the potential of waste paper as a carbon source for chemical production (Table C.1). It was found that the papers manufactured by chemical pulping (kraft and sulphite) had comparable carbon contents ranging from 37.7 to 40.7%, except the printing paper with the lowest amount of organic carbon (33.3%). In comparison, the newspaper contained the highest amount of organic carbon (43.9%), indicating the higher carbon retention by mechanical pulping, and comparatively, a higher carbon loss could be expected during the chemical pulping process. By further analysing the lignocellulosic composition of various paper wastes (Figure 5.2), the highest cellulose content was identified up to 87.2 wt% in the tracing/parchment paper, and the sanitary papers had similar cellulose and hemicellulose contents of approximately 83-85 wt% and 14-17 wt%, respectively. The high cellulose contents in the paper wastes showed great potential for the selective production of LA through hydrolysis of cellulose into C6 sugars with subsequent dehydration and rehydration to LA. A low lignin content (0.1-1.2 wt%) in the paper waste from kraft pulp manifested the efficiency of kraft pulping for delignification, which is believed to reduce the hindrance of lignin components and expose more carbohydrate substrates for further valorisation. In contrast, a high lignin content (26 wt%) was measured in the newspaper (mechanical pulping), which may correspond to a high organic carbon due to the high carbon content (60–65%) of lignin (Bengtsson et al., 2019). A notable amount of lignin (8 wt%) was also detected in the paper mould which was manufactured from recyclable waste papers. Although the source of the original waste papers was not identifiable, substantial lignin content in the paper mould implied that the original paper wastes might be manufactured through the mechanical pulping process.



**Figure 5.2** Cellulose, hemicellulose, lignin, and ash content of various paper waste substrates, (a) category-1 paper, (b) category-2 paper.

Apart from the major organic components, the paper towels, napkins, tracing/parchment paper, and paper food boxes also contained a small amount of ash or inorganic impurities (0.2-1 wt%) (**Figure 5.2**). In contrast, other paper wastes had higher ash contents, such as 5.2 wt% for newspaper, 12.2 wt% for packaging paper, 18.5 wt% for printing paper, and 26.1 wt% for paper mould, respectively. The ash content in papers might originate from the inherent metals in biomass feedstock and the addition of non-fibrous components, such as mineral fillers during paper manufacturing for the improvement of paper properties (*e.g.*, printability, opacity, and stability) and cost savings for materials and energy use (Agrawal

et al., 2021). Common mineral fillers for papermaking include limestone/precipitated calcium carbonate (CaCO<sub>3</sub>) and clay (Shen et al., 2011; Hubbe and Gill, 2016). The characteristic peak of CaCO<sub>3</sub> at  $2\theta = \sim 29.7^{\circ}$  in XRD patterns (L. Chen et al., 2020) was observed for paper wastes with high ash content, and the peak intensity was comparatively higher for printing paper than paper mould and packaging paper.

Considering the variability in overall composition and crystallinity of different paper wastes, it would be more practical to evaluate the product yields and recognise the influential properties by categorising the paper wastes into two groups with comparable compositional characteristics for our subsequent discussion. Category-1 represented the paper wastes consisting of comparatively higher contents of cellulose, higher crystallinity, and lower contents of lignin and inorganics, whereas Category-2 represented the paper wastes having lower cellulosic contents and lower crystallinity yet containing a substantial amount of lignin and ash (**Table 5.1** and **Figure 5.2**).

#### 5.2.2 Influences of paper waste properties on product yields

The catalytic conversion was conducted to evaluate product yield from different paper wastes under the reaction conditions of catalyst 0.5 M H<sub>2</sub>SO<sub>4</sub>, 160 or 180 °C, 0-20 min, GVL/H<sub>2</sub>O solvent (1:1), and the results are shown in **Figure 5.3**. In general, the conversion of various papers showed a similar trend for LA production. While using a lower temperature of 160 °C, LA yield and total cellulosic product yield (including LA, C6 sugars, HMF, and FA) increased steadily with increasing reaction duration. In contrast, the maximum total cellulosic product yield (49-64 mol%) was observed within 1 min reaction at 180 °C for all paper wastes, denoting efficient hydrolysis of the substrates under the selected reaction conditions. A considerable LA yield was obtained rapidly after 5 min of reaction at 180 °C, for instance, ~33-37.5 mol% from Category-1 substrates and ~21-46 mol% from Category-2 substrates. The total cellulosic product yield at 180 °C reached a plateau and started to decrease after 15-20 min of

reaction, probably due to the humins formation through condensation of intermediates and/or products at a prolonged reaction duration. Overall, the substantial LA yield achieved from various paper wastes in this study clearly indicated the viability and potential of the assorted paper waste stream for LA production.

Comparative differences in the product yields were more evident at 160 °C (**Figure 5.3**). In the case of Category-1, paper food boxes generated the maximum C6 sugar yield (42 mol%) and total cellulosic product yield (56 mol%) compared to the tracing/parchment paper, which provided 31 mol% and 47 mol% C6 sugar yield and total cellulosic product yield, respectively, at 160 °C and 5 min (**Figure 5.3a** and **5.5b**). Such variation in the hydrolysis performance could be attributed to the difference in cellulosic crystallinity of the tracing/parchment paper (*CrI* value: 67.5) and paper food boxes (*CrI* value: 59.6). The presence of highly crystalline cellulose in tracing/parchment paper might have constrained the hydrolysis process and resulted in a lower product yield.



**Figure 5.3** LA yield and total product yield (cellulosic fraction) from catalytic conversion of various paper waste substrates: (a) category-1 paper and (b) category-2 paper (5 wt/v% substrate, 0.5 M  $H_2SO_4$ , 160 or 180°C, 1-20 min, 1:1 GVL/ $H_2O$  solvent).

However, napkin-2 (bamboo) (*CrI* value 57.9) could not provide a higher product yield (46 mol%, 160 °C, 5 min) than other paper wastes, despite having the lowest cellulosic crystallinity among Category-1 substrates, which was probably due to the hierarchical structure of bamboo fibres with high thermal stability (*i.e.*, cellulose microfibrils reinforcing the intertwined hemicellulose-lignin matrix). The thermal behaviour of various paper wastes was validated by TGA. A small weight loss and a higher cellulose degradation temperature at approximately 346 °C were observed for bamboo napkins, while the designated peak appeared at a relatively lower temperature region (337 °C) for paper food boxes, indicating the enhanced thermal stability of bamboo-derived papers (**Figure 5.4a**). In particular, an increase in the fibre surface roughness and thermal stability of bamboo fibre after alkaline treatment was reported by a recent study (Chin et al., 2020), which might be relevant for bamboo napkins manufactured through kraft pulping. Therefore, higher energy input was required for the hydrolysis of thermally stable cellulosic fibres in certain types of paper wastes, which could ultimately affect the product yields.

In contrast, the thermal stability of the Category-2 substrates was not significantly different (**Fig. 5.4b**). Notably, the distinct shoulder peak of hemicellulose (~295 °C) and a sharp peak for cellulose degradation (~342 °C) (He et al., 2022) were observed in the DTG curve of paper mould. This was not the case for the other paper wastes where only a single peak represented the degradation of cellulose and hemicellulose as a whole. Therefore, the fibres in the paper mould were expected to undergo facile hydrolysis and generate a higher LA yield. However, the LA yield generated from the paper mould was significantly lower than the other Category-2 substrates. For example, the newspaper provided the maximum LA yield of 45.7 mol% within 5 min of reaction at 180 °C (**Figure 5.3b**). By contrast, only 21 mol% LA yield was achieved from the paper mould under the same reaction conditions, *i.e.*, the yield was 55% lower than the newspaper, and a longer reaction duration of 20 min was required to obtain a



Figure 5.4 TG and DTG curves of various paper waste substrates (untreated): (a) category-1 paper and (b) category-2 paper.

high LA yield (43.6 mol%). Such a significant disparity in LA yield could be ascribed to the differences in paper composition and cellulosic crystallinity. The newspaper with lower crystallinity (53.3%) could be more easily converted than the paper mould with higher crystallinity (59.7%). Moreover, different ash contents in the paper mould (26%) and the newspaper (5.2%) could be a crucial factor affecting the hydrolysis reaction. As mentioned, CaCO<sub>3</sub> could be the main phase for paper ash. Considering the acidic condition involved in this system, the dissolution of inorganic components and the release of Ca<sup>2+</sup> was accompanied by an increase in the solution alkalinity, which could hinder the acid-catalysed hydrolysis (Fang et al., 2018). In addition, alkali and alkaline earth metals in the ash of paper wastes, such as Ca, Mg, and K, could serve as base catalysts that may promote the condensation of intermediates and/or products through C–C coupling (Chaudhary and Dhepe, 2017; Wang et al., 2019). It could be deduced that the presence of mineral fillers in the paper wastes would negatively affect the production of LA and HMF. Such influence was also observed in the latest study where waste newspapers were pretreated with dilute acid prior to their conversion to LA to minimise the negative influences of alkaline substances (Nzediegwu et al., 2021).

#### **5.2.3** Comparative performance and product distributions in different catalytic systems

Subsequently, various catalytic systems (180 °C, 5 min) using H<sub>2</sub>SO<sub>4</sub>, FeCl<sub>3</sub> (0.25 and 0.5 M), and H<sub>2</sub>SO<sub>4</sub>-FeCl<sub>3</sub> (0.25 M each) were conducted to achieve high conversion of various paper wastes and selective production of desired products. Both H<sub>2</sub>SO<sub>4</sub> and FeCl<sub>3</sub> catalysts could efficiently promote the hydrolysis of paper wastes into sugars, C6 sugars (glucose) from the cellulosic fraction and C5 sugars (predominantly xylose and minor content of arabinose) from the hemicellulosic fraction that subsequently undergo dehydration to LA, HMF, and furfural (**Figure 5.5** and **5.6**). LA was the primary product detected in both systems as HMF derived from C6 sugars can be readily rehydrated to LA over Brønsted acidic sites, considering sufficient acidity in the reactant solution. Applying a lower concentration of H<sub>2</sub>SO<sub>4</sub> (0.25 M),

approximately 22-29 mol% LA yield was obtained from the Category-1 substrates (**Figure 5.5a**). It is noteworthy that LA yield in the 0.25 M H<sub>2</sub>SO<sub>4</sub> catalysed system was nearly comparable with the 15.6-24 mol% LA yield generated from the 0.25 M FeCl<sub>3</sub> catalysed system (**Figure 5.6a**), reflecting the analogous solution Brønsted acidity (derived pH ~1, in GVL/H<sub>2</sub>O solvent) observed for both catalysts. However, FeCl<sub>3</sub> might be less effective in the hydrolysis of highly crystalline tracing/parchment paper (*CrI* value 67.5), of which the yield of LA was comparatively lower with FeCl<sub>3</sub> catalyst (15.6 mol%) than that with H<sub>2</sub>SO<sub>4</sub> (22.3 mol%). It should be remarked that metal chlorides are safer and more easily recoverable compared to mineral acid catalysts, which is attractive from the sustainable biorefinery perspective (Di Fidio et al., 2020).

Employing H<sub>2</sub>SO<sub>4</sub> (0.25 M, 180 °C, 5 min) catalyst, a maximum of 7.5 mol% HMF was produced from the tracing/parchment paper among the Category-1 substrates, while 11 mol% HMF was obtained from the paper mould among the Category-2 substrates. In contrast, under the FeCl<sub>3</sub> (0.25 M, 180 °C, 5 min) catalytic system, a maximum of 11.7 mol% and 14.8 mol% HMF could be observed from the tracing/parchment paper and paper mould, respectively. The results indicated that the FeCl<sub>3</sub> catalyst was more selective for HMF production compared to the H<sub>2</sub>SO<sub>4</sub> catalyst, suggesting an important contribution of metal chlorides to HMF production. FeCl<sub>3</sub> acting as a Lewis acid showed the ability to attract electron pairs, leading to rapid catalytic reactions (Liu et al., 2020a). The metal cations in the aqueous solution could generate hydrolysed H<sub>3</sub>O<sup>+</sup>, which further enhanced the Brønsted acidity of the solution (Wang et al., 2018). Previous studies reported the crucial role of chloride salts in facilitating acid-catalysed biomass dehydration owing to the stabilised protonated transition state by chloride ions (Mellmer et al., 2019, 2014a). The increased HMF yields could be achieved using GVL/water solvent mixed with chloride salts. As a result, improved hydrolysis



efficiency could be achieved in this study by accounting for the efficient conversion of cellulose-enriched substrates into HMF and LA with FeCl<sub>3</sub> catalyst.

**Figure 5.5** Product yields from catalytic conversion of various paper waste substrates: (a) 0.25 M  $H_2SO_4$ , 180°C; (b) 0.5 M  $H_2SO_4$ , 160°C; and (c) 0.5 M  $H_2SO_4$ , 180°C (5 wt/v% substrate, 5 min, 1:1 GVL/ $H_2O$  solvent).



**Figure 5.6** Product yields from catalytic conversion of various paper waste substrates: (a) 0.25 M FeCl<sub>3</sub>; (b) 0.5 M FeCl<sub>3</sub>; and (c) 0.25 M H<sub>2</sub>SO<sub>4</sub> + 0.25 M FeCl<sub>3</sub> (5 wt/v% substrate, 180°C, 5 min, 1:1 GVL/H<sub>2</sub>O solvent).

It was noted that LA yield varied significantly among the Category-2 substrates using a lower acid concentration (~9-41 mol% using 0.25 M H<sub>2</sub>SO<sub>4</sub>, and ~4-30 mol% using 0.25 M FeCl<sub>3</sub>), which might be attributed to the varied contents of non-convertibles such as lignin and ash content. Hence, LA yields were plotted against the ash content of various paper wastes to examine the associated influences (Figure 5.7). A strong negative correlation (Pearson correlation coefficient, r = -0.9) was observed between ash content and LA yield, further demonstrating the negative impacts of indigenous mineral fillers in the paper wastes. Nevertheless, the influence of ash content was less pronounced for higher acidic conversion (0.5 M H<sub>2</sub>SO<sub>4</sub>). A substantial amount of LA could be obtained from both Category-1 (~33-38 mol%) and Category-2 (~21-46 mol%) substrates when using 0.5 M H<sub>2</sub>SO<sub>4</sub> (Figure 5.5c). Considering the moderate acidic concentration, temperature, and duration employed in this study, the obtained LA yield was promising compared to the existing studies that reported cellulosic substrate conversion. For instance, 15.4 wt% LA yield was reported from paper sludge under concentrated H<sub>2</sub>SO<sub>4</sub> at 200 °C temperature and 60 min of reaction duration (Galletti et al., 2012). However, a precise comparison among different studies was challenging owing to the differences in the reactor designs, feedstock characteristics, solvent selection, substrate loading, etc., employed for the biomass conversion. In addition, marginal changes in LA yield were observed between 0.25 M and 0.5 M FeCl<sub>3</sub> catalysed conversion (Figure 5.6a, **b**), which was in agreement with a previous study on corn stalk conversion to LA (Zhi et al., 2015). A slight decrease in the total cellulosic product yield under 0.5 M FeCl<sub>3</sub> catalyst implied the insoluble humin formation through condensation and polymerisation between sugars and derivatives.



**Figure 5.7** Correlation between ash content and LA yield in category-2 paper substrates using 0.25 M H<sub>2</sub>SO<sub>4</sub> or 0.25 M FeCl<sub>3</sub> (5wt/v% substrate, 180°C, 5 min, 1:1 GVL/H<sub>2</sub>O solvent).

Notably, several paper wastes provided the maximum LA yield (*e.g.*, 36 mol% for paper towels and tracing/parchment paper) when a combination of H<sub>2</sub>SO<sub>4</sub> and FeCl<sub>3</sub> (0.25 M each) was used as a catalyst (**Figure 5.6c**). This suggested the potential synergetic effects with a combination of Brønsted and Lewis acid catalysts for LA production, probably because they could catalyse the tandem reactions of isomerisation of glucose to fructose, dehydration to HMF, and rehydration to LA by lowering the overall energy barrier. A non-stoichiometric formation of FA (a co-product of HMF rehydration to LA) was particularly observed for the H<sub>2</sub>SO<sub>4</sub>-FeCl<sub>3</sub> catalysed system (FA: LA molar ratio ~1.6-1.7 for various paper wastes), suggesting excess FA formation through alternative pathways in addition to HMF rehydration (Flannelly et al., 2016).

Apart from LA, the conversion of paper wastes simultaneously generated a considerable amount of value-added products derived from the hemicellulosic fraction, such as

C5 sugars and furfural, which increased the total value of products obtained from the paper waste biorefinery. Among the Category-1 substrates, a maximum of 75.3 mol% furfural was synthesised from the bamboo napkins using the H<sub>2</sub>SO<sub>4</sub> catalyst (0.25 M, 180 °C, 5 min). Remarkably, the highest 83 mol% furfural along with 7 mol% C5 sugar yield could be achieved from the printing paper (Category-2), corresponding to a 90% conversion of total carbon in the hemicellulosic fraction of the printing paper (0.25 M H<sub>2</sub>SO<sub>4</sub>, 180 °C and 5 min). However, when 0.5 M H<sub>2</sub>SO<sub>4</sub> was employed for the conversion, a lower furfural concentration was generally observed for different paper substrates, suggesting that the produced furfural might be partially degraded under a higher solution acidity. Notably, furfural yield was comparatively lower in FeCl<sub>3</sub> catalysed system compared to H<sub>2</sub>SO<sub>4</sub>, which might be due to the rapid production and subsequent degradation of furfural by FeCl<sub>3</sub> catalyst containing both Lewis and Brønsted acidity (Ding et al., 2021). Therefore, a lower concentration of FeCl<sub>3</sub> and/or a lower temperature would be suggested if the furfural yield needs to be maximised from the paper wastes in future studies.

#### 5.2.4 Perspectives regarding chemical production from various paper wastes

Based on the above findings, it was perceived that the catalytic conversion of various paper wastes would be considerably influenced by their composition, crystallinity, and thermal stability of cellulosic fibre. The actual yield of products would vary considering the significant variations of lignocellulosic composition and contents of ash and lignin (that could not be converted to the target products) between Category-1 and Category-2 substrates. Therefore, the yields of target products (LA, HMF, and furfural) based on the weight of the substrate were calculated and compared between various paper wastes (**Table 5.2**). Under the selected reaction conditions (0.5 M H<sub>2</sub>SO<sub>4</sub>, 180 °C and 5 min), ~23-27 wt% LA yield could be achieved from the Category-1 substrates, *i.e.*, sanitary papers, tracing/parchment paper, and paper food boxes that possessed high cellulose content (~80-87 wt%) yet limited lignin and inorganics.

Conversely, LA yield was limited to ~10-20 wt% among the Category-2 substrates with a lower content of cellulose. For instance, the newspapers (Category-2) provided 30% less LA yield compared to the paper towels (Category-1). Moreover, the lowest LA yield (10.2 wt%) was obtained from the paper mould, which originated from recycled pulp and contained an excessive amount of ash (26 wt%) and a moderate amount of lignin (~8 wt%). The generated LA yield from the paper mould was ~60% lower than the paper towel under the same conditions. Although a maximum of ~20 wt% LA yield could be obtained from the paper mould when the reaction was prolonged to 20 min, the increase in process cost and energy consumption would impede LA production at a commercial scale. Therefore, paper wastes with low contents of ash and lignin would be desirable for LA production.

In addition to the primary product of LA, variable yields of HMF could be obtained from the Category-1 (~1-3.5 wt%) and Category-2 (~0.4-3.5 wt%) substrates. The maximum HMF yield was achieved from the bamboo napkins (Category-1) and the paper mould (Category-2). In addition, a notable furfural yield ~4-7.5 wt% could be obtained from the Category-1 substrates reflecting their comparable hemicellulose content. By contrast, the newspaper which had the highest hemicellulose content (23.6%) among the Category-2 substrates generated the lowest furfural yield (3.7 wt%) (**Table 5.2**). This could be attributed to the facile conversion of the hemicellulosic fraction of newspaper (manufactured by mechanical pulping) yet rapid degradation of newly produced furfural under the acidic condition. In other words, the reaction conditions would need to be tuned according to the target products of primary interest in the biorefinery. Based on the market price of the major products (LA 10 USD kg<sup>-1</sup>, HMF 100 USD kg<sup>-1</sup>, and furfural 2 USD kg<sup>-1</sup>; source: Alibaba), the total value of the produced chemicals could be estimated. For example, 1 kg of HKIA paper towel could generate chemicals that were worth a total value of 3.63 USD considering the LA, HMF, and furfural yields generated in this study, signifying the economic benefits of paper waste valorisation. However, to evaluate the

economic benefits of chemical synthesis from paper wastes, we should consider the consumption and recycling of catalysts and solvents required for the production process. Fractional distillation is a well-recognised and effective technique for the recovery of spent organic solvent. Solvent recovery and reuse would provide significant environmental benefits over virgin solvent manufacturing and waste solvent disposal (Dutta et al., 2022). Furthermore, FeCl<sub>3</sub> catalyst could be readily recovered as ferric hydroxide from the reacted solution and subsequently processed to obtain FeCl<sub>3</sub> for reuse (Di Fidio et al., 2020). In comparison, different approaches have been investigated for H<sub>2</sub>SO<sub>4</sub> recovery from the solution, including ion exclusion chromatography, solvent extraction, and electrodialysis (Wolfaardt et al., 2021).

	Substrate	LA yield	HMF yield	Furfural yield
		(wt%)	(wt%)	(wt%)
	HKIA paper towel	25.7	0.96	5.08
	Napkin-1 (wood)	26.6	1.34	5.69
Category-1	Napkin-2 (bamboo)	23.5	3.46	6.31
	Tracing/parchment paper	26.8	1.50	3.93
	Paper food box	23.1	1.27	7.46
	Printing paper	19.5	2.01	4.83
Catagomy 2	Newspaper	17.8	0.43	3.66
Category-2	Packaging paper	20.2	1.52	4.60
	Paper mould	10.2	3.44	4.27

**Table 5.2** Product yields from various paper waste substrates (0.5 M H<sub>2</sub>SO<sub>4</sub>, 180°C, 5 min, 1:1 GVL/H<sub>2</sub>O solvent)

Overall, this chapter highlighted that the paper waste stream has a high potential for platform chemical production. Variable properties of different paper waste considerably influence the yield and distribution of target products. In particular, this research substantiates the importance of feedstock selection and compositional analysis for specific product synthesis. Various waste biomass feedstock are attracting attention as renewable sources of chemicals, yet their complex structures and variability in composition remain a major challenge for scaling up the conversion of biomass to value-added products in biorefineries (Antonetti et al., 2016; Yu et al., 2020a; Cao et al., 2021). Hence, the fundamental understanding and science-informed selection of appropriate waste feedstock for cost-/time-efficient production and total component utilisation would pave the way toward a circular bio-economy.

## **5.3 Summary**

This chapter demonstrated the potential valorisation of different paper wastes for platform chemical production (up to ~27 wt% LA yield) and elucidated the critical paper properties for biorefinery applications. Owing to the lignocellulosic composition, sanitary papers, tracing/parchment paper, and paper food boxes with a high cellulose content were more viable for LA and HMF production using H<sub>2</sub>SO<sub>4</sub> and FeCl<sub>3</sub> catalysts under GVL/H<sub>2</sub>O green solvent. By contrast, high contents of lignin and mineral fillers impeded LA yield from the other paper wastes. Insights from this study could be beneficial for identifying suitable lignocellulosic candidates and scaling up paper waste valorisation.

## **Chapter 6: Enhancement of Lignocellulose Depolymerisation**

#### Abstract

This chapter investigated the depolymerisation of lignocellulosic paper towel waste using emerging green solvents such as organic carbonates. Organic carbonate solvents, i.e., propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC), which are low in toxicity and biodegradable, were investigated as 'green' co-solvents (PC/H<sub>2</sub>O, EC/H<sub>2</sub>O, DMC/H<sub>2</sub>O, solvent ratio 1:1) for depolymerisation of cellulosic paper towel waste. PC/H<sub>2</sub>O and EC/H<sub>2</sub>O enhanced the depolymerisation of paper towel waste and improved the total sugar yield (up to ~25 C mol%) compared to H<sub>2</sub>O only (up to ~11 C mol%) at mild reaction conditions (130°C, 20 min). The higher performance of PC/H<sub>2</sub>O and EC/H<sub>2</sub>O could be attributed to the higher availability of reactive protons in the catalytic system that facilitates efficient acid hydrolysis of recalcitrant cellulosic fibres. Moreover, a substantial build-up of in-vessel pressure by CO<sub>2</sub> release during the microwave-assisted reaction because of decomposition of PC or EC might have accelerated the conversion of paper towel wastes. PC and EC are prospective solvents for lignocellulosic biomass conversion considering their green features and notable catalytic performance, which have a good potential for substituting conventional organic solvents such as dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) that are often considered hazardous in terms of health, safety, and environmental implications.



Figure 6.1 Graphical abstract of Chapter 6

## **6.1 Research questions**

Depolymerisation is a crucial step to obtain sugars from lignocellulose which could be further upgraded to value-added chemicals and fuels in the biorefinery industry. It is essential to develop cost-effective technologies for lignocellulose depolymerisation to achieve a high sugar yield using mild reaction conditions with low energy requirements (Fan et al., 2013; Mellmer et al., 2014a). As demonstrated in **Chapter 4** and **Chapter 5**, depolymerisation of cellulose-rich waste usually requires a high reaction temperature or the use of concentrated mineral acid due to the recalcitrant nature of highly crystalline cellulosic fibres, which can be detrimental to the environment (Fan et al., 2013; Luterbacher et al., 2014). The use of organic solvents could facilitate lignocellulose conversion under mild reaction conditions, such as dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and ionic liquids (Shuai et al., 2016; Chen et al., 2017c). However, environmental and safety concerns were raised against these conventional solvents, and their substitution with greener solvents is recommended (Prat et al., 2016). More research efforts are needed to explore green alternatives that are environmentally benign without compromising the lignocellulose conversion efficiency. Recently, several studies have reported effective lignocellulose conversion using novel green solvents such as GVL (Yu et al., 2018; Guan et al., 2020). Considering the efficient performance of GVL green solvent in **Chapter 4**, this chapter focuses on investigating other recommended and emerging green solvents as the medium for waste biomass valorisation following the CHEM21 selection guide of classical and less classical solvents.

Organic carbonate solvents, such as propylene carbonate, ethylene carbonate, and dimethyl carbonate exhibit high biodegradability, low toxicity, and good safety score (stable under ambient conditions, low volatility, and flammability) (**Table 6.1**), while their synthesis involves the utilisation of carbon dioxide ( $CO_2$ ) (Schäffner et al., 2008; Parker et al., 2014; Prat et al., 2016). These environment-friendly features imply their suitability as potential green solvents for biomass valorisation. A few studies reported an improved rate of catalytic biomass conversion using PC (Yu et al., 2018b), EC (Yamada et al., 2007; Shin et al., 2009), and DMC (Dabral et al., 2018) in the reaction media. However, there was a lack of comparison among these carbonate solvents to understand their potential roles in assisting catalytic depolymerisation of lignocellulosic waste.

Properties	PC	EC	DMC	Reference
Boiling point (°C)	242	248	90	(Prat et al.,
Flash point (°C)	132	143	16	2016)
Polarity	0.83	-	0.45	(Zhang et al., 2013)
LD <sub>50</sub> (lethal dose)	34920	>5000	9000	(Schäffner
(oral) (rat) [mg kg <sup>-1</sup> ]				et al., 2008)
Biodegradability (d)	94% (29)	Readily	88% (28)	2000)
		biodegradable		
Solubility with water	240	214	139	
[g L <sup>-1</sup> ] (20°C)				

**Table 6.1** Properties of organic carbonate solvents

This chapter aimed to investigate the use of PC, EC, and DMC as green co-solvents in a binary organic solvent-water system for the conversion of paper towel waste catalysed by dilute sulfuric acid ( $H_2SO_4$ ) in mild reaction conditions. The study provided insights into the role of organic carbonate solvents in the sustainable and efficient valorisation of lignocellulosic feedstock in the biorefinery.

### 6.2 Results and discussion

#### 6.2.1 Depolymerisation of paper towel waste in PC/H<sub>2</sub>O solvent system

Catalytic conversion of paper towel waste in PC/H<sub>2</sub>O showed relatively slow depolymerisation at 120°C, achieving approximately 1-4 mol% of glucose, 3-6 mol% xylose, and 2 mol% of mannose during the 20-min reaction (**Figure 6.2a**). The production of xylose and mannose was more efficient than glucose, suggesting a lower energy requirement for the depolymerisation of hemicellulose compared to cellulose in PC/H<sub>2</sub>O. As the temperature increased to 130-150°C, a sharp increase in the maximal glucose yield was observed (~21-25 mol%) in 10-20 min (**Figure 6.2b-d**), which was promising and comparable to glucose yield obtained in previous studies using cellulosic substrate in the organic solvent-water system, for instance, ~10 mol% from vegetable waste (DMSO/H<sub>2</sub>O, 120°C, 5 min, 0.5 g Amberlyst 36) (Chen et al., 2017c), and ~14 mol% from Chinese Pennisetum (GVL/H<sub>2</sub>O, 180°C, 20 min, 1 M H<sub>2</sub>SO<sub>4</sub>) (Guan et al., 2020).

It was observed that the rate of glucose production increased at the point where the xylose yield started to decline (**Figure 6.2b-d**). For instance, at 130°C, the glucose production rate was ~0.28 mol min<sup>-1</sup> during 0-15 min of reaction while xylose yield was increasing. However, after 15 min, xylose yield started to decline, and a rapid improvement in glucose production rate (~3.3 mol min<sup>-1</sup>) was observed (**Table 6.2**). Cellulose fibres are usually covered by amorphous hemicellulose within lignocellulosic biomass, which needs to be dissolved to

improve the accessibility of cellulosic fibres to protons in homogeneous catalytic conditions (Shuai and Luterbacher, 2016). A sharp increase in glucose yield in parallel to the declining xylose yield might be because complete depolymerization of hemicellulose exposed more cellulose fibres for favourable proton attack to facilitate cellulose hydrolysis. Hemicellulose content is 21% of the total carbon in the paper towel waste, while the maximum total yield of hemicellulosic monomers and derivatives (*i.e.*, xylose, mannose, and furfural) detected in PC/H<sub>2</sub>O was ~16.5 mol% (140°C, 10 min), which indicated highly efficient depolymerisation of hemicellulose during the hydrolysis in the PC/H<sub>2</sub>O solvent.



**Figure 6.2** Product yields versus time during the catalytic conversion of paper towel waste in PC/H<sub>2</sub>O solvent system at different temperatures (a)  $120^{\circ}$ C, (b)  $130^{\circ}$ C, (c)  $140^{\circ}$ C, (d)  $150^{\circ}$ C, (Reaction conditions: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, solvent ratio: 1:1)

	Rate of glucose production (C mol min <sup>-1</sup> )		
Temperature	Before declining xylose yield	After declining xylose yield	
130°C	0.28	3.26	
140°C	0.80	3.45	
150°C	1.86	3.06	

**Table 6.2.** Rate of glucose production in PC/H<sub>2</sub>O

The PC/H<sub>2</sub>O solvent system generated a maximum total sugar yield of ~30 mol% (140°C, 15 min, and 150°C, 10 min) (**Figure 6.3a**). A gradual decrease in total sugar yield was detected after 15 min at 140°C and after 10 min at 150°C, indicating the secondary reactions of sugars, *e.g.*, dehydration to HMF and furfural and rehydration to LA. The negligible amount of fructose (~0.7-1.4 mol%) (**Figure 6.2a-d**) suggests that glucose was converted to HMF via direct dehydration, without isomerization to fructose as the intermediate step. Strong Brønsted acids favoured direct dehydration of glucose to HMF and had an insignificant effect on glucose-fructose isomerization (Yang et al., 2015; Chen et al., 2017c). The direct glucose dehydration was less feasible than that of xylose (to furfural), which was consistent with the previous findings (Enslow and Bell, 2015) and plausibly suggests a lower energy barrier for the latter reaction. The maximum total soluble product yield achieved was ~60 mol% (150°C, 10 min) (**Figure 6.3b**), implying efficient depolymerization of paper towel waste in the PC/H<sub>2</sub>O solvent.



**Figure 6.3** (a) Total sugar yields at 120-150°C in PC/H<sub>2</sub>O, and (b) total product yields at 120-150°C in PC/H<sub>2</sub>O, (Reaction conditions: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, solvent ratio: 1:1)

The crystallinity index (*CrI*) was calculated from the XRD patterns of post-reaction solid residues in the PC/H<sub>2</sub>O solvent system (120-150°C, 20 min) (**Figure 6.4**). The *CrI* increased from 66.4% for the untreated sample to 74.2% for residues obtained after heating at 120°C for 20 min, suggesting that most of the amorphous fraction was consumed for sugar production, and the proportion of crystalline fraction relatively increased. The small increase in BET surface area (7.26 m<sup>2</sup> g<sup>-1</sup> at 120°C vs 1.53 m<sup>2</sup> g<sup>-1</sup> for untreated sample) possibly resulted from pores newly created along with the dissolution of the amorphous matrix. At higher temperatures, the crystalline fraction decomposed given the decrease in *CrI* to 69.5% at 130°C

and to 64.5% at  $140^{\circ}$ C. The SEM images showed fibre breakdown with the increasing temperature in PC/H<sub>2</sub>O (**Figure 6.5**).



**Figure 6.4** XRD patterns, Crystallinity index (*CrI*) and BET surface area of untreated paper towel waste and post-reaction solid residue in PC/H<sub>2</sub>O solvent system at different temperatures 120°C, 130°C, 140°C, and 150°C (Reaction conditions: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, duration: 20 min, solvent ratio: 1:1)



**Figure 6.5** Scanning electron microscope (SEM) images of untreated paper towel waste (a&f) and post-reaction solid residue in PC/H<sub>2</sub>O solvent system at different temperatures 120°C (b&g), 130°C (c&h), 140°C (d&i), and 150°C (e&j) at 500x (a, b, c, d, e) and 5000x (f, g, h, i, j)) magnification (Reaction conditions: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, duration: 20 min, solvent PC/H<sub>2</sub>O (1:1))

#### 6.2.2 Comparative conversion in different carbonate solvent-water systems

Among the solvents investigated, PC/H<sub>2</sub>O and EC/H<sub>2</sub>O demonstrated enhanced depolymerisation of paper towel waste (total sugar yield up to ~25 mol% at 130°C) considering the conversion of paper towel waste in 100% H<sub>2</sub>O as the baseline (total sugar up to ~11 mol%). All solvents generated a similar glucose yield (~1-2 mol%) after 5 min of reaction at 130°C. Unlike reaction in H<sub>2</sub>O only, PC/H<sub>2</sub>O and EC/H<sub>2</sub>O demonstrated notable improvement in glucose yield when the reaction was extended to 20 min (up to ~20 mol% in PC/H<sub>2</sub>O) (**Figure 6.6a-d**). After a 20-min reaction (130°C), four times higher total soluble product yield (~41 Cmol%) was observed in PC/H<sub>2</sub>O compared to that of H<sub>2</sub>O alone (~11 mol%) (**Figure 6.7b**), demonstrating the effectiveness of carbonate solvent system for the deconstruction of lignocellulosic fibres of paper towel waste. Comparing the conversion in different carbonate solvent-water systems, EC/H<sub>2</sub>O was the most efficient solvent in terms of total sugar yield



**Figure 6.6** Product yields during the catalytic conversion of paper towel waste in different solvent systems subject to reaction duration- (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (LA yield could not be quantified due to technical issue) (Reaction condition: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, temperature: 130°C, solvent ratio: 1:1)

(~19 mol%) and total product yield (~25 mol%) at 130°C in 10 min (**Figure 6.7a, b**). Apart from the improved glucose yield (~4 mol%), EC/H<sub>2</sub>O generated a higher yield of xylose (~12 mol%) and mannose (~2.5 mol%) than other solvent systems. Almost complete conversion of hemicellulose (*i.e.*, hemicellulose content is 21% of the total carbon in the substrate) was achieved in EC/H<sub>2</sub>O considering the total yield of xylose, mannose, and furfural (~19.5 mol%) at 130°C in 10 min (**Figure 6.6b**).



**Figure 6.7** (a) Total sugar yields, and (b) total product yields (LA yield could not be quantified due to technical issues, and total product yield in EC/H<sub>2</sub>O does not include the yield of LA) (Reaction condition: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, temperature: 130°C, solvent ratio: 1:1)

Characterisation of post-reaction solid residues indicated higher conversion of paper towel waste in EC/H<sub>2</sub>O solvent compared to other solvents under the same reaction conditions. Calculated *CrI* values of post-reaction solid residues (130°C, 20 min) (**Figure 6.8a**) showed a slight increase in the crystallinity ranging from ~67-69% for H<sub>2</sub>O (100%), PC/H<sub>2</sub>O, and DMC/H<sub>2</sub>O compared to untreated paper towel waste (66.4%), possibly because the decomposition of the amorphous fraction of cellulose led to a higher relative crystallinity. In contrast, a substantial decrease in *CrI* value (~47.5%) was observed in the EC/H<sub>2</sub>O system,


**Figure 6.8** (a) XRD patterns and (b) FTIR spectra of untreated paper towel waste and postreaction solid residue in different solvent systems (Reaction conditions: 5 wt% substrate loading, temperature:  $130^{\circ}$ C, duration: 20 min, 0.135 M H<sub>2</sub>SO<sub>4</sub>, solvent ratio: 1:1)

which implies an efficient breakdown of recalcitrant cellulosic fibres of paper towels. Similarly, SEM images revealed a greater reduction in the fibre sizes (**Figure 6.9**) in EC/H<sub>2</sub>O compared to other solvents. Moreover, an increase in specific surface area ( $S_{BET}$  4.01 m<sup>2</sup>g<sup>-1</sup> at 130°C, 20 min) was measured for solid residue in EC/H<sub>2</sub>O compared to untreated paper towel waste ( $S_{BET} 1.53 \text{ m}^2\text{g}^{-1}$ ) and solid residues in other solvent systems. Solid residues in PC/H<sub>2</sub>O and EC/H<sub>2</sub>O were further analysed through FTIR (**Figure 6.8b**), in which noticeable changes in transmittance were observed at 1425 cm<sup>-1</sup>, 1160 cm<sup>-1</sup>, and 848 cm<sup>-1</sup>. The observed peak at 1425 cm<sup>-1</sup> is associated with the crystalline structure of cellulose (Hospodarova et al., 2018), which was reduced to a greater extent in EC/H<sub>2</sub>O compared to PC/H<sub>2</sub>O indicating a significant alteration in the crystalline fraction of fibres. On the other hand, the observed peaks at 1160 cm<sup>-1</sup> and 848 cm<sup>-1</sup> can be attributed to the C-O-C ring vibrational stretching of  $\beta$  (1,4) linkage of cellulose (Sim et al., 2012; Khan et al., 2018), which was also significantly altered in the solid residue in the EC/H<sub>2</sub>O solvent. Analysis of soluble samples and characterisation of solid residues consistently indicate a higher conversion of paper towel waste in EC/H<sub>2</sub>O compared to other solvent systems in this study.



**Figure 6.9** Scanning electron microscope (SEM) images of untreated paper towel waste (a&f) and post-reaction solid residue in  $H_2O$  (100%) (b&g), DMC/ $H_2O$  (c&h), PC/ $H_2O$  (d&i), and EC/ $H_2O$  (e&j) at 500x (a, b, c, d, e) and 5000x (f, g, h, i, j)) magnification (Reaction conditions: 5 wt% substrate loading, 0.135 M  $H_2SO_4$ , temperature: 130°C, duration: 20 min, solvent ratio:1:1)

During the conversion of standard cellulose in PC/H<sub>2</sub>O (**Figure 6.10a**), higher total sugar yield (~40 mol%) and total product yield (~45 mol%) were observed compared to the conversion of paper towel waste (total sugar yield ~25 mol% and total product yield ~41 mol%) (**Figure 6.7a, b**) employing identical reaction conditions (130°C, 20 min). This reflects a more efficient conversion of standard cellulose than that of lignocellulosic paper towels in PC/H<sub>2</sub>O. To compare the performance of carbonate solvents with conventional solvents in biorefinery, paper towel conversion was also conducted in DMSO/H<sub>2</sub>O. It is noteworthy that only ~14 mol% of total sugar yield and ~15.4 mol% of total product yield (**Figure 6.10b**) were achieved from the conversion of paper towel waste in DMSO/H<sub>2</sub>O (130°C, 20 min), representing ~45% and ~62% lower than those of PC/H<sub>2</sub>O (total sugar yield ~25 mol% and total product yield ~41 mol%). These results clearly illustrate the significance of green carbonate solvents such as PC and EC, which could outperform DMSO and offer a potential alternative for hazardous organic solvents that are commonly used for catalytic conversion of lignocellulosic biomass.



**Figure 6.10** Total sugar yield and total product yield during the catalytic conversion of (a) standard cellulose in PC/H<sub>2</sub>O, (b) paper towel waste in DMSO/H<sub>2</sub>O (Reaction condition: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, temperature: 130°C, duration: 20 min, solvent ratio: 1:1)

#### 6.2.3 Role of carbonate solvents for effective depolymerisation

Carbonate solvents might improve depolymerisation through deconstruction and expansion/swelling of lignocellulosic fibres or their participation in the catalytic process via activation of protons/substrates, etc. To explore the potential roles of carbonate solvent, paper towel waste was treated in PC/H<sub>2</sub>O (140°C, 10 min, no acid addition) and the specific surface area of the treated substrate was compared to that of untreated paper towel waste. Untreated and PC/H<sub>2</sub>O treated paper towel waste showed similar  $S_{\text{BET}}$  values (1.03-1.5 m<sup>2</sup>g<sup>-1</sup>). Furthermore, PC/H<sub>2</sub>O treated paper towel waste was subjected to the reaction in H<sub>2</sub>O (100%) (140°C, 10 min, 0.135 M H<sub>2</sub>SO<sub>4</sub>). No significant difference in the sugar yield was observed between untreated (~11 mol%) and solvent treated (~12 mol%) substrate conversion (Figure 6.11). These results suggest that carbonate solvents on their own might not disrupt the cellulosic structure or cause swelling of the paper towel waste. The enhanced depolymerisation of paper towel waste could be related to the higher activity of protons in the presence of PC and EC as the aprotic solvents compared to that in water alone. The protons from Brønsted acid catalyst tend to be more stabilised in H<sub>2</sub>O compared to a solvent system containing an aprotic solvent due to the increased solvation of protons by H<sub>2</sub>O molecules, which leads to the lower reactivity of Brønsted acid in H<sub>2</sub>O than that of an aprotic solvent (Mellmer et al., 2014b). Alternatively, the organic solvent-water binary system can create a distinct phase near the surface of cellulose through preferential binding of organic solvent molecules to the hydrophobic surface and binding of water molecules with the hydrophilic surface. As a result, cellulose surfaces are chemically modified, and the induced bond cleavage can eventually enhance cellulose hydrolysis (Smit and Huijgen, 2017; Song et al., 2018).



**Figure 6.11** Sugar yields during the catalytic conversion of untreated and PC/H<sub>2</sub>O treated paper towel waste subject to the reaction in H<sub>2</sub>O (100%) (Reaction condition: 5 wt% substrate loading, 0.135 M H<sub>2</sub>SO<sub>4</sub>, temperature: 140°C, duration: 10 min, solvent: H<sub>2</sub>O (100%)).

Improved depolymerisation of substrates in the PC/H<sub>2</sub>O and EC/H<sub>2</sub>O solvents could also be attributed to the significant in-vessel pressure development during catalytic conversion in these solvents, which reached up to ~26 bar (130°C, 20 min), in contrast to the maximum ~5 bar recorded for H<sub>2</sub>O only (**Figure 6.12**). High *in situ* pressure during catalytic reactions was reported to accelerate the conversion of lignocellulose in previous studies (Duo et al., 2016; Yu et al., 2018b). High in-vessel pressure development in the PC/H<sub>2</sub>O and EC/H<sub>2</sub>O solvent systems might be associated with the release of CO<sub>2</sub> from solvent degradation, as PC and EC could decompose to CO<sub>2</sub> and propylene glycol (PG) and ethylene glycol (EG) respectively, under the acidic condition. As acidic degradation of PC and EC could liberate CO<sub>2</sub> (Hlavatý and Novák, 1992; Zhang et al., 2013), *in situ* pressure raised sharply during the reaction in PC/H<sub>2</sub>O and EC/H<sub>2</sub>O solvent systems (**Figure 6.12**). A noticeable amount of gas bubbles was observed in the reacted solutions of PC/H<sub>2</sub>O and EC/H<sub>2</sub>O. At the same time, solvent loss of 5-20% was recorded depending on temperature and reaction duration, suggesting that carbonate solvent was partly degraded with an irreversible production of CO<sub>2</sub> in the PC/H<sub>2</sub>O and EC/H<sub>2</sub>O solvent systems. In contrast, no solvent loss was recorded for catalytic conversion in H<sub>2</sub>O only. Maximum pressure recorded for H<sub>2</sub>O only was 5 bar, while up to ~26 bar was recorded for PC/H<sub>2</sub>O and EC/H<sub>2</sub>O (130°C, 20 min), indicating that steam generated from the water did not make a major contribution to the development of in-vessel pressure during the conversion in PC/H<sub>2</sub>O and EC/H<sub>2</sub>O. It should be remarked that the initial amount of reactants and volume of vessels were constant for all catalytic runs performed in this study.



**Figure 6.12** In-vessel record of temperature and pressure during paper towel conversion (ramping and reaction) in different solvents (a)  $H_2O$ , (b) DMC/ $H_2O$ , (c) PC/ $H_2O$ , and (d) EC/ $H_2O$  (Reaction condition: 5 wt% substrate loading, 0.135 M  $H_2SO_4$ , temperature: 130°C, duration: 20 min, solvent ratio: 1:1)

An accelerated rate of acid-catalysed reaction was reported when  $CO_2$  was applied as an additive to the reaction medium (high-temperature water) because the reaction between water and  $CO_2$  produces carbonic acid that dissociates to increase the concentration of hydronium ion in the medium (Hunter and Savage, 2003, 2008). Considering the low solubility of  $CO_2$  at temperatures of 100-200°C reported in the literature (Hunter and Savage, 2008) and effective acid-catalyzed hydrolysis for biomass depolymerisation, the catalytic effect of  $CO_2$ might not have a significant contribution to this study. By contrast, the increased reaction rates due to  $CO_2$ -derived *in situ* pressure build-up could be responsible for the improved performance achieved in PC/H<sub>2</sub>O and EC/H<sub>2</sub>O as explained earlier. Nevertheless, quantifying the catalytic effect of  $CO_2$  generated due to carbonate solvent degradation is beyond the scope of this study due to equipment and experimental limitations.

Despite higher in-vessel pressure build-up during the reaction (~12 bar at 130°C, 20 min) (Figure 6.12) compared to H<sub>2</sub>O only, DMC/H<sub>2</sub>O unexpectedly generated a lower yield of sugars (~8 mol% maximum) than that of H<sub>2</sub>O (~10 mol%). DMC has a lower polarity ( $\pi^*=$ 0.45) than H<sub>2</sub>O ( $\pi^*=1.09$ ) and PC ( $\pi^*=0.83$ ) (Jessop et al., 2012), which might influence the biomass conversion efficiency in DMC/H<sub>2</sub>O. In low-polarity solvents, the catalytic activity could be hindered due to a strong pairing between the cation and anion, and active sites of the catalyst could be blocked by counter-ion. In contrast, the cation and anion are typically separated from each other in polar solvents, leading to high solvation of ions that facilitate the catalytic activity, eliminating the interference of the counter-ion (Dyson and Jessop, 2016). DMC is considered an effective methylation agent (Fiorani et al., 2018; Tundo et al., 2018). Methylation of starch and lignin in basic conditions using DMC as the methylation agent has been reported in previous studies (Hou et al., 2011; Sen et al., 2015). Although little information exists regarding the reactions between cellulose (or its derivatives) and DMC (Fiorani et al., 2018), the methylation of cellulose might occur to some extent under the given reaction conditions in this study, which could contribute to the lower yield of sugars in the DMC solvent. Further research is required to prove this postulation.

#### 6.2.4 Tandem dehydration-rehydration reactions

A noticeable amount of sugar derivatives, *i.e.*, HMF, LA, and FA were observed after 20 min of reaction at 130°C and after 15 min at 140°C in PC/H<sub>2</sub>O (**Figure 6.2b, c**), while furfural was detected at a lower temperature (120°C, 15 min) (**Figure 6.2a**) reflecting less energy-intensive dehydration of xylose to furfural. At 150°C treatment in PC/H<sub>2</sub>O, LA yield (~23.5 mol%) surpassed glucose yield (~21.6 mol%) after 15 min of reaction (**Figure 6.2d**), suggesting that PC/H<sub>2</sub>O facilitated dehydration-rehydration reactions of sugars in parallel to hydrolysis of paper towel waste. Meanwhile, a decrease in the total detectable product yield in PC/H<sub>2</sub>O was observed at 140°C after 15 min and 150°C after 10 min (**Figure 6.3b**), this indicates the formation of insoluble humins due to polymerisation between sugars and furan derivatives during the catalytic conversion of biomass at a higher temperature (Yu et al., 2017a, 2018a).

Comparing paper towel conversion at 130°C, no dehydration product was detected in the H<sub>2</sub>O (100%) and DMC/H<sub>2</sub>O solvents. Conversely, dehydration-rehydration products were detected in the PC/H<sub>2</sub>O and EC/H<sub>2</sub>O solvents starting from 10 min of reaction time (**Figure 6.6b**), suggesting the higher potential of PC and EC for tandem biomass hydrolysis and dehydration-rehydration reactions. A notable LA yield (~6 mol%) generated in PC/H<sub>2</sub>O under mild reaction conditions (130°C, 20 min) suggests that PC might be a preferable solvent for LA synthesis from lignocellulosic biomass. The yield of LA could not be determined for EC/H<sub>2</sub>O solvent system due to technical issues (LA peak overlapped solvent peak). However, a substantial yield of FA (~6-7 mol% at 130°C, 15-20 min) was detected in the EC/H<sub>2</sub>O solvent, possibly inferring the yield of LA in the solvent system as LA and FA are coproduced during the catalytic conversion of biomass and sugars (Antonetti et al., 2016; Beh et al., 2020).

#### **6.2.5 Energy requirement for sugar production**

Energy requirement for sugar production was estimated and compared for different solvent systems (Reaction conditions: 5 wt.% substrate loading, temperature: 130°C, duration: 10 min, 0.135 M H<sub>2</sub>SO<sub>4</sub>, solvent ratio: 1:1) based on the power consumption rate recorded (Figure B.2) in the microwave reactor (**Table 6.3**). Energy requirements for ramping (up to 130°C at a ramp rate of 32°C min<sup>-1</sup>) and reaction (holding at a constant temperature) were estimated separately and then added up to determine the total energy consumption per unit of sugar produced in different solvent systems. The results revealed a lower energy requirement (~0.03 kWh) at the ramping stage for carbonate solvent-water binary systems, in contrast, H<sub>2</sub>O only required relatively higher energy (~0.05 kWh) for heating the reaction mixture. Furthermore, binary solvents exhibited a lower energy consumption per unit of sugar production than that of H<sub>2</sub>O, as low as 0.21 kWh g<sup>-1</sup> in EC/H<sub>2</sub>O, which was the most efficient solvent system in terms of energy requirement for sugar production from paper towel waste. Microwave reactor has been recognised to be more energy-efficient compared to traditional reactors that heat the reactants through convection and conduction (Yu and Tsang, 2017). Besides, higher sugar yield was reported using microwave-assisted cellulose hydrolysis compared to that of conventional heating under the same reaction conditions (Fan et al., 2013).

Table 6.3 Energy	consumption for sugar production in different solvent systems (Re	action
conditions: 5 wt%	substrate loading, temperature: 130°C, duration: 10 min, 0.135 M F	$I_2SO_4$ ,
solvent ratio: 1:1)		

Solvent	Energy consumption (kWh)			Sugar produced	Energy consumption	
	Ramp	Reaction	Total	(gg <sup>-1</sup> of	per unit of sugar production	
				paper towel waste)	$(kWh g^{-1})$	
PC/H <sub>2</sub> O	0.034	0.036	0.071	0.111	0.63	
EC/H <sub>2</sub> O	0.033	0.007	0.040	0.189	0.21	
DMC/H <sub>2</sub> O	0.037	0.035	0.073	0.060	1.22	
$H_2O$	0.05	0.062	0.110	0.081	1.35	

## 6.3 Summary

The investigated organic carbonate binary solvents, *i.e.*, PC/H<sub>2</sub>O and EC/H<sub>2</sub>O effectively facilitated the depolymerisation of lignocellulosic paper towel waste under mild reaction conditions. This chapter explored the potential roles of carbonate solvents in the catalytic system. The higher availability of reactive protons in these solvent systems and autogenous pressure development might favour the breakdown of cellulosic fibres compared to H<sub>2</sub>O only. Besides, a considerable amount of sugar derivatives was detected in PC/H<sub>2</sub>O and EC/H<sub>2</sub>O (at a higher temperature and longer duration), suggesting the suitability of solvents for tandem hydrolysis and dehydration of biomass. The study implies that PC and EC have a high potential to be considered as greener alternatives to commonly used industrial solvents for the efficient valorisation of biomass. However, these solvents have a high boiling point, which can be challenging for product separation and solvent recovery by distillation. Future research efforts can be directed to address this issue by selective adsorption for the possible implementation of these alternative solvents on an industrial scale.

# **Chapter 7: Critical Factors for Levulinic Acid Production**

### Abstract

A considerable amount of food waste generated globally could be upcycled to synthesise platform chemicals to enhance environmental sustainability and help realise a circular economy. This chapter investigated the critical factors for catalytic production of the vital platform molecule LA from bread waste, a typical stream of starch-rich food waste generated worldwide. GVL, IPA, and PC were evaluated as bio-derived and CO<sub>2</sub>-derived green cosolvents for LA synthesis. In-vessel pressure generated in PC/H<sub>2</sub>O (1:1) solvent was conducive to rapid LA production from bread waste compared to GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O. In PC/H<sub>2</sub>O, 72 mol% total soluble product yield was observed quickly within 1 min in moderate reaction conditions (130°C, 0.5 M H<sub>2</sub>SO<sub>4</sub>), whereas ~15-20 mol% of LA could be obtained when the reaction was prolonged for 10-20 min at 130°C. The yield of LA could be significantly enhanced in GVL/H<sub>2</sub>O through phase separation using NaCl (30 wt%(aq)). LA yield increased up to a maximum of ~2.5 times in the biphasic system (28 mol%, 150°C, 15 min) (representing a theoretical yield of 66%) in  $GVL/H_2O(1:1)$  compared to the monophasic system (~11 mol%) under the same reaction conditions. The partition coefficient for LA achieved was 4.2 in the GVL/H<sub>2</sub>O (1:1) biphasic medium, indicating that the system was efficient for simultaneous production and extraction of LA. Biphasic GVL/H<sub>2</sub>O facilitated selective LA production, which could be optimised by tuning the reaction conditions. These new insights could foster the development of high-performance LA production and sustainable biorefinery.



Figure 7.1 Graphical abstract for Chapter 7

## 7.1 Research questions

Transforming food waste into platform chemicals offers a sustainable opportunity to utilise the vast waste stream for biorefinery applications and pave the way forward to realising a circular bioeconomy (Mak et al., 2020). Starch-rich foods such as rice, bread, and potatoes are commonly consumed and constitute a significant proportion of global food waste (Yu et al., 2020b), which can serve as a potential feedstock for biorefineries. Recent studies demonstrated that catalytic production of sugars and platform chemicals (*e.g.*, LA, HMF) could be an effective technique for recycling/valorising a considerable amount of starch-rich food waste generated globally (Yu et al., 2018b) However, appropriate reaction conditions and solvent selection were critical for selective and cost-effective LA production.

The selection of a suitable solvent is necessary, as it not only serves as a reaction medium but also influences the catalytic process through solvent-solute interactions, adjusting the reactivity of proton, suppressing the byproduct formation, etc. (Dyson and Jessop, 2016; Yu et al., 2018b) As the greenest and environmentally benign solvent, water was preferred as a reaction medium for LA synthesis. However, harsh reaction conditions, *i.e.*, high temperature and acidity, are required when using water as the reaction medium resulting in an energyintensive process and high byproduct (humin) formation (Xiong et al., 2021). Owing to the need for selective and high-efficiency chemical synthesis, various organic solvents as reaction mediums have been widely investigated, such as dimethylsulfoxide (DMSO) (Chen et al., 2017a), tetrahydrofurans (THF), dimethylformamide (DMF) (Antonetti et al., 2016), GVL, acetone, etc. (Lui et al., 2019) However, conventional organic solvents DMSO, DMF, THF, etc., are widely considered "non-green" due to their direct or indirect detrimental effects on the natural environment and human health and safety. Therefore, the use of alternative "green" solvents, especially those which are renewable and bio-derived (GVL, alcohols, etc.) or CO<sub>2</sub>derived (propylene carbonate (PC), dimethyl carbonate (DMC), etc.), are recommended for future applications (Prat et al., 2016; Gao et al., 2020). Furthermore, enhanced catalytic conversion of biowaste using these bio-derived and CO<sub>2</sub>-derived solvents was reported in recent studies (Yu et al., 2018b; Mellmer et al., 2018) yet their influences should be evaluated in comparable conditions to validate their efficiency and elucidate the critical factors for catalytic LA production.

Apart from using environmentally friendly and safe reaction systems, process intensification was indispensable to improve the final concentration of LA for scaling up at the industrial level (Antonetti et al., 2020b). Besides, efficient separation and purification of LA were necessary for the possible recovery of mineral acid catalysts and further conversion of LA to valuable derivatives such as GVL, which could be negatively affected by the presence of mineral acid (Wettstein et al., 2012; Lui et al., 2019). A viable strategy could be using the biphasic solvent system comprising two immiscible layers. The aqueous layer contains the acid

catalyst and serves as the reactive phase, while the organic layer acts as the extractive phase, facilitating simultaneous production and extraction of LA, which might enhance LA yield and selectivity (Wettstein et al., 2012; Wang et al., 2020). For instance, a recent study on the conversion of remnant algal biomass reported a significant enhancement of hydroxymethylfurfural (HMF) and LA yield using acidic ZSM-5 zeolite as a heterogeneous catalyst when utilising a biphasic solvent system composed of methyl isobutyl ketone (MIBK) and H<sub>2</sub>O with NaCl as the phase modifier (Rihko-Struckmann et al., 2020). Another study achieved a ~4-fold increase in LA yield from rice straw using a biphasic reaction medium containing dichloromethane (DCM) and H<sub>2</sub>O (DCM/H<sub>2</sub>O, 1:1), in which the enhanced performance was attributed to the good extraction capability of DCM solvent (Kumar et al., 2018). However, there is insufficient experimental evidence and a limited understanding of the critical impacts of the biphasic system on LA production using the recommended green solvents.

This chapter examined LA production from bread waste using PC, GVL, and isopropanol (IPA) as green co-solvent systems, *i.e.*, PC/H<sub>2</sub>O, GVL/H<sub>2</sub>O, IPA/H<sub>2</sub>O, catalysed by dilute H<sub>2</sub>SO<sub>4</sub> to investigate how and why an efficient yield of LA could be achieved at moderate reaction conditions using these bio-derived and CO<sub>2</sub>-derived green co-solvents. Water (100%) as the greenest solvent was also evaluated as a baseline for comparison. Furthermore, this study explored the application and tuning of the binary biphasic reaction medium to intensify the concentration of the target product LA considering the potential advantages of phase separation for reactive LA extraction.

## 7.2 Results and discussion

#### 7.2.1 Catalytic conversion of bread waste under bio-derived and CO<sub>2</sub>-derived solvents

Facile conversion of bread waste was achieved under moderate reaction conditions, obtaining 45-72 mol% total product yield at 130°C under bio-derived and CO<sub>2</sub>-derived co-solvent systems (**Figure 7.2a**). For H<sub>2</sub>O, PC/H<sub>2</sub>O, and GVL/H<sub>2</sub>O solvents, the maximum total sugars released from bread waste were 64-70 mol% in a short reaction duration of 1 min (**Figure 7.3a**). In contrast, using IPA/H<sub>2</sub>O, the total sugar yield after 1 min of reaction was 43.5 mol%, increasing up to 48.8 mol% when the reaction was prolonged for 20 min. Given the total sugar yield generated at 110°C (**Figure 7.2b**), hydrolysis of bread waste was faster in GVL/H<sub>2</sub>O (48.1 mol%) and PC/H<sub>2</sub>O (53.7 mol%) compared to H<sub>2</sub>O (~30 mol%) and IPA/H<sub>2</sub>O (9.4 mol%).



**Figure 7.2** Total sugar yield and LA yield during the catalytic conversion of bread waste in different solvents (a) at 130°C, 1-20 min, (b) at 110°C, 1 min (Reaction conditions: 5 wt% substrate loading, 0.5 M  $H_2SO_4$ , 130°C, 1:1 solvent ratio)



**Figure 7.3** Total product yields during the catalytic conversion of bread waste under different solvents at (a)  $130^{\circ}$ C and (b)  $130^{\circ}$ C and  $150^{\circ}$ C under GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 1-20 min, 1:1 solvent ratio).

With increasing reaction duration up to 20 min, sugar yield in H<sub>2</sub>O and IPA/H<sub>2</sub>O remained steady and generated an insignificant LA yield ~1.5 mol% after 20 min of reaction. In contrast, sugars were consumed, and LA yield increased with increasing reaction duration gradually in GVL/H<sub>2</sub>O (up to 4.8 mol%) and sharply in PC/H<sub>2</sub>O (up to 19.6 mol%) (**Figure 7.2a**). <sup>13</sup>C NMR spectra of reacted solutions (1 and 20 min reaction) (**Figure 7.4a**) provided further evidence for the disparity in catalytic conversion under different solvent systems. <sup>13</sup>C NMR chemical shift ( $\delta$ ) at 95.8 ppm, attributed to glucose (Qi et al., 2017), were observed for

all reactions. The highest intensity of glucose peak was observed for 1 min reacted solution in PC/H<sub>2</sub>O, which agrees with the maximum sugar yield measured by HPLC. In contrast, the lowest intensity of glucose peak and emerged LA peak (at 27.7, 37.6, 177 pm) along with an FA peak (at 165.45 ppm) (AIST, 2021) for 20 min reaction in PC/H<sub>2</sub>O further prove the efficient tandem catalysis in PC/H<sub>2</sub>O. The characteristic peaks for LA and FA were not detectable in IPA/H<sub>2</sub>O and H<sub>2</sub>O, while low-intensity peaks could be observed for GVL/H<sub>2</sub>O. Besides, representative solvent peaks (AIST, 2021) were detected in the reacted solutions indicated in **Figure 7.4a**.

The higher soluble product yields in PC/H<sub>2</sub>O and GVL/H<sub>2</sub>O could be related to the high reactivity of the Brønsted acid catalyst due to the availability of highly active proton in the presence of aprotic co-solvents in the reaction system (Mellmer et al., 2014b; Yu et al., 2018b) The extent of proton stabilisation influence the acid dissociation constant, and in water lowers the proton reactivity, which subsequently elevates the required energy level for acid-catalysed biomass conversion reactions such as hydrolysis and dehydration (Mellmer et al., 2014b). Therefore, reaction kinetics could be slower in H<sub>2</sub>O (100%) compared to a solvent system consisting of a polar aprotic solvent such as GVL and PC, which might enhance the reaction rates owing to reactive proton and facile glycosidic bond cleavage (Mellmer et al., 2014a). For



**Figure 7.4** (a) <sup>13</sup>C NMR spectra of soluble samples obtained after bread waste conversion in different solvents (Reaction condition: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 130°C, 1 min & 20 min, 1:1 solvent ratio), (b) <sup>13</sup>C solid-state NMR spectra of untreated bread waste and solid residues collected after reaction under different solvent systems (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 130°C, 20 min, 1:1 solvent ratio).

instance, a recent study reported a ten-fold increase in reaction rate for acid-catalysed conversion of HMF to LA using GVL with 10% H<sub>2</sub>O compared to 100% H<sub>2</sub>O as solvent (Mellmer et al., 2018). Slower conversion of bread waste was observable in the case of IPA/H<sub>2</sub>O solvent (total sugar ~10 mol%, at 110°C, 1 min) (**Figure 7.2b**), where both co-solvents are protic and probably hamper the proton reactivity during conversion.

The starch contained in the bread waste substrate represents a complex structure combining linear amylose chains and highly branched amylopectin comprising  $\alpha$  (1 $\rightarrow$ 4) and  $\alpha$  $(1\rightarrow 6)$  glycosidic bonds. <sup>13</sup>C NMR spectra of solid residues (Figure 7.4b) subjected to reaction under different solvent systems (20 min) showed differences in chemical shifts than the untreated bread waste, possibly related to the changes in starch structures (Flanagan et al., 2015). The chemical shifts observed at resonance values of 93-103, 74-85, 64-73, and 55-60 ppm can be attributed to C1, C4, C2,3,5, and C6 of glucose units, respectively (Cai et al., 2014; Yu et al., 2020b). Resonance values attributed to C1 and C4 can be helpful to understand the changes in the amorphous and highly ordered/crystalline state of starch. The C1 resonance for post-reaction solid residues shifted toward 98-103 ppm, presenting comparatively sharp peaks compared to the broad peak observed at 93-100 ppm for untreated bread waste. The broad shoulder observed around 95 ppm for untreated bread waste is characteristic of the amorphous domain of C1. In contrast, a sharp peak observed around 100 ppm (C1) for solid residues might indicate a decrease in amorphous content and a subsequent rise in relative crystallinity, which was previously reported for acid-modified starch (Atichokudomchai et al., 2004; Cai et al., 2014). In contrast, the resonance for C4 around 82 ppm was observed for solid residues, characteristic of an amorphous state (Mutungi et al., 2012). Different changes in chemical shifts in different carbon regions can reflect varied transformations between amylose and amylopectin within the starch structures. Amylose is mainly amorphous and more susceptible to acid hydrolysis than amylopectin, which comprises highly ordered/crystalline domain

building double-helical structures. However, initially during acid hydrolysis, amorphous amylose could be partially transformed into double helices resistant to acid hydrolysis, and consequently, crystalline content could be enhanced relative to amorphous content (Morrison et al., 1993; Hoover, 2000). The observed changes in solid residues compared to untreated bread waste were substantiated by XRD analysis. The XRD pattern of untreated bread waste (Figure 7.5) showed a broad crystalline peak at ~ $2\theta$ =20°, and the calculated *CrI* value was ~0.51, whereas solid residues in different solvent systems provided *CrI* values ranging from ~0.73-0.78. This also suggested the rapid decomposition of the amorphous region of starch granules during acid hydrolysis resulting in an increased relative crystallinity (Foresti et al., 2014).



**Figure 7.5** XRD pattern of untreated bread waste and solid residues collected after reaction under different solvents (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 130°C, 20 min, 1:1 solvent ratio).

#### 7.2.2 LA yield enhanced by in-vessel high pressure generated in PC/H<sub>2</sub>O

Comparing different co-solvent systems, PC/H<sub>2</sub>O was found to be the best for LA production, generating 19.6 mol% after 20 min reaction at 130°C (Figure 7.2a), which was promising considering mild reaction conditions used in this study and the reported literature results under comparable experimental conditions (Chen et al., 2017a; Lappalainen et al., 2018). Under GVL/H<sub>2</sub>O solvent, sugars depleted gradually during 3-20 min of reaction and generated 2-4.8 mol% LA. In contrast, in PC/H<sub>2</sub>O solvent, sugars started to deplete rapidly during 3-20 min of reaction, and 19.6 mol% LA yield was achieved after 20 min. A significant in-vessel pressure build-up was recorded during reaction in PC/H<sub>2</sub>O, reaching a maximum ~27 bar at 130°C, 20 min compared to reactions in other solvents (Figure 7.6a). Compared to the autogenous in-vessel pressure (~13 bar) generated in PC/H<sub>2</sub>O during 1 min reaction, the reaction pressure level almost doubled (~23-27 bar) during 3-20 min reaction (Figure 7.6b), which was analogous to rapid sugar consumption and a sharp increase in LA yield (4-19.6 mol%) during 3-20 min. In acidic conditions, PC solvent could decompose into PG and CO2 as reported in the literature (Yu et al., 2018b; Zhang et al., 2013). Noticeably, ~5-15% solvent loss was recorded for reactions in PC/H<sub>2</sub>O (1-20 min), indicating that a fraction of the PC solvent was decomposed during the reaction. Besides, <sup>13</sup>C NMR spectra (Figure 7.4a) for the reacted solutions under PC/H<sub>2</sub>O (1 and 20 min) showed peaks at 66.4 and 67.7 ppm representing PG (AIST, 2021). The PG peaks had comparatively higher intensity after 20 min reaction than 1 min, suggesting that a higher fraction of PC was decomposed to PG, which was consistent with higher CO<sub>2</sub> pressure recorded for more prolonged reactions in PC/H<sub>2</sub>O (Figure 7.6b).



**Figure 7.6** (a) Pressure profile during the catalytic conversion of bread waste in different solvents for 20 min reaction, (b) pressure profile in PC/H<sub>2</sub>O for different reaction durations (1-20 min), (c) sugar and LA yield in PC/H<sub>2</sub>O after 20 min and 5+15 min (pressure release after 5 min) reaction, (d) sugar and LA yield in PG/H<sub>2</sub>O after 5 and 20 min reaction (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 130°C, 1:1 solvent ratio).

Apart from the aprotic nature of the PC solvent, significant pressure build-up resulting from CO<sub>2</sub> generation during catalytic conversion in PC/H<sub>2</sub>O might enhance the LA production rate. Another influential factor could be the increased acidity due to carbonic acid derived from partial dissolution of CO<sub>2</sub> during the reaction, which might enhance sugar dehydration (Morais et al., 2016). Solution acidity could arise through *in situ* formation and dissociation of carbonic acid, as given in Eq. (3) (Jing et al., 2016).

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$$
$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$$
(3)

The acidity (pH) associated with CO<sub>2</sub> generated during the 3-20 min reaction in PC/H<sub>2</sub>O was estimated, following the scheme reported in the literature (Toscan et al., 2017; Van Walsum, 2001). The estimated CO<sub>2</sub>-derived pH value for specified reaction conditions was ~3.5, *i.e.*, considerably higher than the H<sub>2</sub>SO<sub>4</sub>-derived pH (~0.5) in this study. Therefore, CO<sub>2</sub>derived pH on its own might not be sufficient to catalyse tandem reactions and significantly enhance LA yield. In other words, LA yield might be improved probably by PC/H<sub>2</sub>O-generated CO<sub>2</sub> pressure more than CO<sub>2</sub>-derived acidity during the catalytic conversion of bread waste. To testify to this postulation, an additional test using PC/H<sub>2</sub>O was conducted, in which autogenous pressure developed due to PC degradation (~22 bar) was released after 5 min reaction, and then the solution underwent reaction for another 15 min (Figure 7.6c). Compared to a continuous 20 min reaction in PC/H<sub>2</sub>O (LA yield 19.6 mol%), only about half of LA was produced (LA yield 11.2 mol%) when the pressure was released prematurely during the reaction. After the pressure release, the autogenous pressure was  $\sim 4.2$  bar from the beginning till the end point of the additional 15-min reaction. Moreover, supplementary tests using PG/H<sub>2</sub>O only generated ~3 mol% LA yield (130°C, 20 min) (Figure 7.6d), which was insignificant compared to LA yield obtained in PC/H<sub>2</sub>O, therefore disproving any favourable influences by PG solvent

(decomposed from PC) on the catalytic performance. This experimental evidence confirmed the crucial enhancement of reaction pressure on catalytic LA production.

#### 7.2.3 Intensification of LA yield through phase separation

Among co-solvent systems, PC/H<sub>2</sub>O generated the highest LA yield 19.6 mol% at 130°C, and ~9 mol% soluble sugar remained after a 20 min reaction. In contrast, ~47-49 mol% soluble sugar was available after 20 min reaction in GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O (**Figure 7.2a**), which could be further converted to LA or other sugar derivatives. To improve the catalytic performance in GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O, conversion of bread waste was conducted at 150°C for a 1-20 min reaction duration (**Figure 7.7a**, **b**). As higher temperature provided more energy for the reaction, LA yield increased gradually up to 16.4 mol% in GVL/H<sub>2</sub>O (150°C, 20 min) (**Figure 7.7b**), which was more than three times higher than the maximum LA yield achieved at 130°C (4.8 mol%, 20 min). The maximum LA yield achieved in IPA/H<sub>2</sub>O was only 6.6 mol% (150°C, 20 min) (**Figure 7.7a**), notably lower than the GVL/H<sub>2</sub>O system, corroborating the positive role of aprotic GVL solvent in enhancing proton reactivity for less energy-intensive tandem catalysis (Mellmer et al., 2014b).

The biphasic solvent systems (prepared using 30 wt% NaCl<sub>(aq)</sub>) were further investigated as an intensification scheme to improve the concentration of the target product LA in this study. Promisingly, the concentration of LA at the end of the reaction ( $150^{\circ}$ C, 20 min) increased ~1.6 times in both biphasic GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O systems (**Figure 7.7c**) compared to analogous monophasic systems. Though total soluble product yields were comparable in the two biphasic systems (~33-35 mol%) (**Figure 7.3b**), the distributions of soluble products were distinctive between GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O. While biphasic GVL/H<sub>2</sub>O selectively generated LA as the main product with 26.8 mol% yields and 4.4 mol% FA as a co-product, IPA/H<sub>2</sub>O biphasic contained 10.6 mol% LA, 2.6 mol% FA, ~7 mol% HMF, and 10.2 mol% remaining



**Figure 7.7** Product yields during the catalytic conversion of bread waste at 150°C and 1-20 min reaction duration in (a) IPA/H<sub>2</sub>O (monophasic) and (b) GVL/H<sub>2</sub>O (monophasic); (c) comparative product yields in IPA/H<sub>2</sub>O and GVL/H<sub>2</sub>O monophasic and biphasic medium (30 wt% NaCl<sub>(aq)</sub>) at 150°C, 20 min (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 1:1 solvent ratio).

sugars (glucose and fructose) (**Figure 7.7c**). A considerable fraction of HMF present in both monophasic and biphasic IPA/H<sub>2</sub>O indicated that the solvent could hinder the HMF rehydration to LA. In comparison to DMSO, which is a widely recommended solvent for HMF production, IPA could create a shielding effect around HMF that helps to prevent its rehydration and suppress further conversion to byproducts such as insoluble humins (Mushrif et al., 2012). A recent study revealed that the rate constant for fructose to HMF was considerably higher than

that of HMF to degradation products when IPA was present in the solvent system (Agutaya et al., 2020), echoing the experimental observations in this study where low LA selectivity was obtained in IPA/H<sub>2</sub>O solvent system. However, it should be noted that the shielding effect of IPA is selective to HMF and not on sugars such as glucose and fructose. It might be due to the structural differences between sugar (several -OH groups contained in the molecule which can coordinate with water and IPA molecule competitively) and HMF (only one -OH group, and the competition between water and IPA to coordinate around HMF might be less intensive) that might influence the preferential coordination of IPA molecules around sugar or HMF (Mushrif et al., 2012; Agutaya et al., 2020). Considering the catalytic performance observed in this study, IPA/H<sub>2</sub>O could be considered a potential solvent for HMF production in future investigations. By contrast, in the presence of GVL solvent, H<sub>2</sub>SO<sub>4</sub> catalysed HMF production could be rapid and readily converted to LA at high acid strength (Qi et al., 2014). Considerable LA yield achieved in biphasic GVL/H<sub>2</sub>O in this study (26.8 mol%, at 150°C, 20 min) proves the high efficiency of the H<sub>2</sub>SO<sub>4</sub>/GVL/H<sub>2</sub>O system for LA production.

As GVL/H<sub>2</sub>O biphasic solvent was the most efficient for intensifying LA yield at moderate conditions, a comprehensive investigation was conducted for bread waste conversion in the co-solvent system following varied reaction conditions (150°C, 10-20 min). In biphasic GVL/H<sub>2</sub>O, LA yield increased with increasing reaction duration (~19-28 mol% in 10-15 min) (GVL/H<sub>2</sub>O, 1:1) (**Figure 7.8a**). However, a slight decrease in LA yield was observed after 20 min, suggesting that LA started to degrade with prolonged reaction duration. The major product in monophasic GVL/H<sub>2</sub>O (1:1, 15 min) was glucose (34.6 mol%), while the biphasic system selectively generated LA (~28 mol%) as the major product. The LA yield increased up to ~2.5 times in the biphasic system compared to the monophasic one (~11 mol%) (150°C, 15 min), implying that phase separation could be beneficial for intensive LA production and upscaling to an industrial scale.



**Figure 7.8** (a) Product yields during the catalytic conversion of bread waste in  $GVL/H_2O$  monophasic and biphasic medium comprising different solvent ratios; (b) LA and (c) FA distribution in the organic and aqueous phase and partition coefficients obtained for the catalytic conversion of bread waste in  $GVL/H_2O$  biphasic medium comprising different solvent ratio (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 30 wt% NaCl<sub>(aq)</sub> 150°C, 10-20 min).

Essentially, to develop an efficient biphasic reaction medium, it is necessary to understand the contribution and influences of the reaction phase (H<sub>2</sub>O) and the extraction phase (GVL) to optimise the yield of the target product. To tune the reaction and extraction phases in GVL/H<sub>2</sub>O biphasic system, catalytic tests were conducted with various ratios of GVL and H<sub>2</sub>O (1:1, 1:3, and 3:1 of GVL/H<sub>2</sub>O). The partition coefficient for LA ( $R_{LA}$ ) in the GVL/H<sub>2</sub>O biphasic solvent was calculated to evaluate the effect of the extraction phase (GVL) in the system. The  $R_{LA}$  achieved for 10-15 min reaction was 4.2 when 1:1 GVL/H<sub>2</sub>O was applied for reaction (**Figure 7.8b**), indicating a higher distribution of LA in the organic phase compared to the aqueous phase. Therefore, GVL solvent can be considered highly effective for reactive LA extraction. The partitioning of LA obtained in this study ( $R_{LA}$  4.2) was comparable to a previous study that reported  $R_{LA}$  ranging from 3.7-4 using cellulose as feedstock (Wettstein et al., 2012).

The total yield of LA increased (27.4-32 mol%) when a higher fraction of H<sub>2</sub>O (1:3, GVL/H<sub>2</sub>O) was applied during catalytic conversion, whereas the total LA yield decreased (14.5-17.1 mol%) when a lower fraction of H<sub>2</sub>O (3:1, GVL/H<sub>2</sub>O) was applied (**Figure 7.8b**). Though the total LA yield increased with a higher fraction of H<sub>2</sub>O, the extraction of LA was found to be inefficient. The partition coefficient achieved was only 1.1 (1:3, GVL/H<sub>2</sub>O), indicating a nearly even distribution of produced LA in the reaction and extraction phases due to the lower fraction of GVL applied. In comparison, ~97% of the total LA produced was extracted into the GVL phase when a higher fraction of GVL (3:1, GVL/H<sub>2</sub>O) was applied for reaction. However, a considerable decrease in total LA yield was observed, possibly due to the lack of sufficient aqueous phase available for reaction. These observations suggested the indispensable contribution of both reaction and extraction phases for an efficient biphasic system for LA production. Considering LA yield (27.4 mol%) and  $R_{LA}$  (4.2), the 1:1 GVL/H<sub>2</sub>O biphasic system (150°C, 15 min) provided the best performance for intensive LA production.



**Figure 7.9** (a) LA yield and total product yield under different reaction conditions (Reaction conditions: 5 wt% substrate loading, 150°C), (b) LA yield and other products (sugar+HMF+furfural) of consecutive runs in GVL/H<sub>2</sub>O biphasic system (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 30 wt% NaCl<sub>(aq)</sub> 150°C, 15 min, solvent ratio 1:1).

To reflect further on the mechanism and roles of catalytic species in NaCl modified  $GVL/H_2O$  biphasic system, additional tests were performed under the selected reaction conditions. In the case of reaction conducted with only NaCl (30 wt%) without acid catalyst, only marginal product yield was observed (**Figure 7.9a**). When NaCl was applied together with  $H_2SO_4$  for bread waste conversion, an increase in LA yield was observed compared to the reaction in the presence of  $H_2SO_4$  without salt addition. These observations indicated that NaCl alone could not catalyse the desired reaction yet it may act synergistically with  $H_2SO_4$ 

enhancing the LA production in the aqueous phase during biphasic conversion of bread waste. It might be because the presence of chloride salt in the polar aprotic solvent system improved the reaction rate and selectivity for LA production by stabilising the protonated transition state during the acid-catalysed conversion of bread waste (Mellmer et al., 2019). The synergistic catalysis by NaCl and  $H_2SO_4$  together with simultaneous efficient extraction of LA into GVL could account for the high LA yield obtained in the GVL/ $H_2O$  biphasic system.

Moreover, the recyclability of the aqueous phase containing H<sub>2</sub>SO<sub>4</sub> was investigated. After the catalytic run (reaction and cooling), the reacted organic phase was removed and fresh GVL and bread waste substrate were applied for another cycle of catalytic reaction (run-2) again while retaining the aqueous phase from the previous run without adding extra H<sub>2</sub>SO<sub>4</sub>. Similarly, the third cycle of catalytic reaction (run-3) was conducted. In the 2<sup>nd</sup> and 3<sup>rd</sup> run (**Figure 7.9b**), 15 mol% and 13 mol% LA was obtained, respectively, compared to the LA yield (28 mol%) obtained in the initial run, which suggested that the acid catalyst could be retained in the aqueous phase and recycled for further conversion, though a certain degree of decrease in LA yield was observed. Future studies would be required for evaluating the biphasic system in a continuous reaction mode, which may be more efficient compared to the batch reaction mode.

Apart from LA as the target product, FA yield was analysed for bread waste conversion in monophasic and biphasic GVL/H<sub>2</sub>O, as FA is often co-produced during biomass conversion (Flannelly et al., 2016). Similar to LA, the FA yield was enhanced through phase separation with the yield from ~2-3 mol% in the monophasic system to a maximum 5.4 mol% FA yield in biphasic GVL/H<sub>2</sub>O (150°C, 15 min, 1:3 solvent ratio) (**Figure 7.8c**). Using 1:1 GVL/H<sub>2</sub>O, the FA partition coefficient ( $R_{FA}$ ) obtained was ~2-3 (150°C, 10-20 min, solvent ratio 1:1), indicating that FA could also be simultaneously extracted into the GVL layer during bread waste conversion. Besides, partition coefficients for LA, FA, and HMF were evaluated in IPA/H<sub>2</sub>O solvent (150°C, 20 min, 1:1 solvent ratio), and the values were 6.6, 5.4, and 5.7, respectively (**Figure 7.10**), corroborating an effective extraction of these compounds into the organic phase. Considering the low LA selectivity and total LA yield (10.6 mol% at 150°C, 20 min), further investigation was discontinued for IPA/H<sub>2</sub>O.



**Figure 7.10** LA, FA, and HMF distribution in the organic phase and the aqueous phase, and partition coefficients obtained for the catalytic conversion of bread waste in IPA/H<sub>2</sub>O biphasic medium (Reaction conditions: 5 wt% substrate loading, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 30 wt% NaCl<sub>(aq)</sub> 150°C, 20 min).

#### 7.2.4 Perspectives on LA production and solvent recycling

To evaluate the efficiency of the catalytic system for LA production, LA yield relative to theoretical LA yield of bread waste substrate (considering total available carbohydrate and possible maximum theoretical yield (64.5%)) was calculated and compared with the reported achievements with commercially available starch substrates in the existing literature (**Table 7.1**). For PC/H<sub>2</sub>O (130°C, 20 min) and GVL/H<sub>2</sub>O biphasic solvents (150°C, 15 min), 45.7% and 66% LA yield were achieved relative to theoretical yield, respectively. This was considered promising in comparison to the reported LA yield (45.6-66.4%) from commercially available starch substrates in previous studies (Cha and Hanna, 2002; Fang and Hanna, 2002), where the conversion was conducted using comparatively harsh reaction conditions. For other recent studies where no direct comparison is possible due to the lack of data regarding relative LA yield (Vyver et al., 2011; Lui et al., 2019), it should be noted that a much longer reaction duration was required to obtain the reported LA yield.

The recyclability of GVL/H<sub>2</sub>O biphasic solvent was investigated and discussed in the previous section. For PC/H<sub>2</sub>O solvent, despite partial decomposition of PC during acid catalysis, it offers various advantages as a solvent because a high product yield can be obtained with a moderate temperature and a short duration, which play a critical role in reducing the energy consumption and reactor size. The production of PC from CO<sub>2</sub> is beneficial for process economy and environmental sustainability in terms of CO<sub>2</sub> utilisation. In the application of PC solvent, the derived CO<sub>2</sub> after reaction could be captured and recycled for PC production or other CO<sub>2</sub>-based biorefineries, which are conducive to fostering the circular economy. The spent organic solvents can be recycled after separation and purification following commonly used techniques such as fractional distillation. For instance, a comprehensive life cycle assessment (LCA) on solvent waste recovery (Raymond et al., 2010) demonstrated that implementing a solvent recovery system can reduce the environmental footprint of the total solvent manufacturing, usage, and disposal process. The energy requirements and emissions associated with the solvent recovery process have been recognised to be trivial in comparison to the emissions due to virgin solvent production and spent solvent disposal by incineration.

Substrate	<b>Reaction conditions</b>	Catalyst	LA yield based on total organic carbon (mol%)	LA yield based on the weight of substrate (%)	LA yield relative to theoretical yield (%)	Reference
Bread 1 waste 1	130 °C, 20 min, H <sub>2</sub> O	- - - 0.5 M H <sub>2</sub> SO <sub>4</sub>	1.5	1.2	3.6	- - - - This study - -
	130 °C, 20 min, IPA/H <sub>2</sub> O		1.0	0.8	2.4	
	130 °C, 20 min, GVL/H <sub>2</sub> O		4.8	3.8	11.3	
	130 °C, 20 min, PC/H <sub>2</sub> O		19.6	15.5	45.7	
	150 °C, 20 min, IPA/H <sub>2</sub> O (mono)		6.6	5.3	15.6	
	150 °C, 20 min, IPA/H <sub>2</sub> O (bi)		10.6	8.5	25.1	
	150 °C, 15 min, GVL/H2O (mono)		10.9	8.8	25.8	
	150 °C, 15 min, GVL/H <sub>2</sub> O (bi)		27.9	22.4	66.0	
	150 °C, 20 min, GVL/H2O (mono)		16.4	13.2	38.8	
	150 °C, 20 min, GVL/H <sub>2</sub> O (bi)		26.8	21.6	63.4	
Bread	130 °C, 8 h	1.5 ml 5 M H <sub>2</sub> SO <sub>4</sub> and 10 ml GVL	-	30.2	-	(Lui et al., 2019)
Starch	165 °C, 5 h	sulfonated hyperbranche d poly (arylene oxindole)s	-	31.1	-	(Vyver et al., 2011)
Starch	200 °C, 60 min	4% H <sub>2</sub> SO <sub>4</sub>	-	47.5	66.4	(Cha and Hanna, 2002)
Sorghum grain	200 °C, 40 min	8% H <sub>2</sub> SO <sub>4</sub>		32.6	45.6	(Fang and Hanna, 2002)

**Table 7.1**. Comparative LA yield obtained from bread waste in this study and from starch substrates reported in the literature

### 7.3 Summary

This chapter provided comprehensive insights into the critical factors for intensive LA production, which can be conducive to the technology scale-up. The bio-derived and CO<sub>2</sub>-derived co-solvents in this study, *i.e.*, PC/H<sub>2</sub>O, GVL/H<sub>2</sub>O, IPA/H<sub>2</sub>O, could facilitate H<sub>2</sub>SO<sub>4</sub> catalysed tandem reactions during bread waste conversion but demonstrated varied catalytic efficiency. PC/H<sub>2</sub>O solvent was the most efficient for LA production using moderate reaction conditions, which could be attributed to the CO<sub>2</sub> pressure generated *in situ* through solvent (PC) degradation. Besides, catalytic performance could be significantly enhanced in GVL/H<sub>2</sub>O and IPA/H<sub>2</sub>O using the biphasic system, facilitating reactive extraction of LA in the organic layer that intensified the final concentration of LA. GVL/H<sub>2</sub>O biphasic solvent seems promising considering LA yield (28 mol%) and LA partitioning ( $R_{LA}$  4.2) achieved in the study. The bioderived and CO<sub>2</sub>-derived solvents applied in this study could be considered emerging solvents and potential alternatives to common industrial solvents in future biorefinery applications.

# **Chapter 8: Conclusions and Recommendations**

## 8.1 Conclusions

This thesis investigated the catalytic valorisation of polysaccharide-rich wastes for the production of value-added chemicals under green solvent systems. Considering the knowledge gap identified in existing literature, the thesis highlighted the following scientific merits: (a) developed a green and efficient system for valorising cellulosic and starchy waste substrates; (b) scrutinised feedstock characteristics and diverse catalytic systems to explore the viability of platform chemical production from paper waste with variable properties; (c) identified green and high-performance solvents for maximising conversion efficiency; (d) unravelled the role and effectiveness of organic carbonate solvents for enhancing depolymerisation, which is a bottleneck for facile hydrolysis of highly crystalline cellulosic feedstock and its subsequent conversion to chemical derivatives; (e) elucidated critical factors for optimising levulinic acid production from starchy food waste through tuning reaction conditions/system. The key findings of the thesis are summarised below.

• Binary green solvent systems, *e.g.*, GVL/H<sub>2</sub>O and acetone/H<sub>2</sub>O facilitated efficient valorisation of cellulosic paper wastes. Acetone/H<sub>2</sub>O solvent provided considerable LA yield (17 mol%) at a lower temperature yet suffered from the polymerisation of sugars and intermediates at a higher temperature, hindering further conversion to LA. The maximum ~32 mol% LA yield was generated in GVL/H<sub>2</sub>O (200°C, 5 min) considering favourable effects of GVL solvent in disrupting cellulose crystallinity and enhancing solubility of generated products and preventing humin formation during catalytic conversion. This research demonstrated that green solvents such as GVL could be a potential alternative to conventional hazardous industrial solvents for the selective production of value-added chemicals from the actual waste-based feedstock.
- The complex/recalcitrant nature of cellulosic paper wastes, their properties originated due to diverse manufacturing processes, and their influence on chemical production was scrutinised. Variable paper properties, *e.g.*, feedstock composition, cellulosic crystallinity, and thermal stability/degradability, considerably influenced the production of LA, HMF, and furfural under H<sub>2</sub>SO<sub>4</sub> and FeCl<sub>3</sub> catalysed conversion in a green solvent system (1:1 GVL/H<sub>2</sub>O). Ash contained in paper wastes negatively influenced acid hydrolysis and subsequent conversion to LA.
- Depolymerisation of highly cellulosic paper waste was accelerated by using organic carbonate solvents, *i.e.*, PC/H<sub>2</sub>O and EC/H<sub>2</sub>O and the total sugar yield was improved up to ~25 at mild reaction conditions (130°C, 20 min). However, carbonate solvents did not contribute to the disruption/swelling of cellulosic fibres. The higher performance of PC/H<sub>2</sub>O and EC/H<sub>2</sub>O was attributed to the higher availability of reactive protons in the catalytic system that facilitated efficient acid hydrolysis of recalcitrant cellulosic fibres, and substantial build-up of autogenous pressure during the catalytic reaction.
- Levulinic acid production from starchy food waste was maximised through the interplay of influential factors, *i.e.*, polar aprotic solvent, reaction pressure and phase separation. In-vessel pressure generated in PC/H<sub>2</sub>O (1:1) solvent was conducive to rapid LA production from bread waste, and ~15-20 mol% of LA could be obtained within 10-20 min at 130°C using 0.5 M H<sub>2</sub>SO<sub>4</sub>. In contrast, LA yield could be significantly enhanced in GVL/H<sub>2</sub>O through phase separation using NaCl (30 wt%<sub>(aq)</sub>) (28 mol%, 150°C, 15 min, 0.5 M H<sub>2</sub>SO<sub>4</sub>) (representing a theoretical yield of 66%). The aqueous phase containing H<sub>2</sub>SO<sub>4</sub> could be recycled for subsequent catalytic run denoting the efficiency of the biphasic solvent.

#### **8.2 Recommendations and future work**

These research efforts demonstrated the potential of polysaccharide-rich waste feedstock for value-added chemical production, which could be efficiently realised using moderate reaction conditions (*e.g.*, acidity, temperature, and duration) under microwave heating and green solvent systems. However, variability in their composition is a still major bottleneck for fostering their conversion to value-added products at an industrial scale, which must be carefully evaluated for finding suitable lignocellulosic candidates for sustainable biorefinery applications. Besides, catalytic production of chemicals is inversely related to substrate loading, and lab-scale conversion is mostly restricted to 5-10 wt% loading of substrates. To transfer the technology at an industrial scale while maintaining the catalytic yield/selectivity, more research efforts would be needed to reach beyond the current feasible substrate loading rate. Furthermore, manipulation of system components, *e.g.*, investigating the influences of reaction pressure on the catalytic valorisation of waste biomass would be highly recommended as a continuation of this research on polysaccharide-rich waste valorisation.

The selection of solvent systems is critical for platform chemical production, and a variety of bio-derived and CO<sub>2</sub>-derived green solvents were explored within the capacity and timeframe of this research. This research provided a comprehensive evaluation of various green solvents in terms of product yield and selectivity thereby demonstrating their performance, yet it could be further explored to understand interactions between substrate, catalysts, and green solvents by using mechanistic study/computational chemistry. Kinetic modelling would be helpful to quantify the energy barrier for catalytic hydrolysis and dehydration/rehydration of polysaccharide-rich wastes in diverse green solvent systems. Experimental observations supplemented with mechanistic study/simulation would be highly recommended to uncover reaction pathways and energy barriers for specific catalytic reaction steps under green co-solvent systems investigated in this research.

Green solvents such as GVL and propylene carbonate showed outstanding performances for waste valorisation yet were expensive. Nevertheless, research should be continued to find highly efficient and low-cost solvents for waste biomass valorisation. Besides, other emerging green solvents such as deep-eutectic solvents are attracting attention recently. However, their potential and efficiency are yet to be largely explored for valorising actual waste-based substrates, which should be addressed by future research efforts. In addition, considering the excellent performance achieved in this research, further exploration of biphasic solvent systems is encouraged. Finding suitable organic solvents with high partition co-efficient to target products such as HMF or LA would be beneficial in terms of process intensification. However, reactor design needs considerable attention to efficiently handle biphasic solvents in terms of product separation and recycling of catalysts. Future studies would be required for evaluating the biphasic system in a continuous reaction mode, which may be more efficient compared to the batch reaction mode.

To maximise the benefits of bio-based chemical production, the proposed biomass conversion technologies in this research should be integrated into a biorefinery, which might actualise the production of multiple chemicals/products. For instance, the generation of humin/insoluble carbonaceous solids could be minimised by using organic solvent systems for polysaccharide-rich waste conversion, however, the generation of humins could not be completely avoided during the conversion. In this case, low-value humins could be treated in the biorefinery through pyrolysis for the production of biochar that could be subsequently utilised for diverse applications, such as a fertiliser/soil amendment, functional materials for catalysis and remediation etc. (**Figure 8.1**).



**Figure 8.1** Integration of multiple processes in the biorefinery for the production of value-added chemicals, energy and functional materials from polysaccharide-rich waste biomass

Furthermore, recycling and recovery of spent organic solvents is a critical issue to ensure the sustainability of biorefinery processes. However, green solvents GVL and propylene carbonate have high boiling points, which is disadvantageous in terms of their recycling and recovery using conventional energy-intensive separation techniques such as distillation. Although a reduced environmental footprint was demonstrated by an LCA study (Raymond et al., 2010) for solvent recovery (by distillation) and recycling in comparison to virgin solvent production thereby providing environmental benefits. Therefore, research endeavours could be devoted to enhancing solvent separation/recycling through novel and efficient approaches. Besides, a comparative LCA study evaluating the environmental benefits of different green solvents could be conducted (considering their production, usage in waste biomass conversion, downstream separation, and recycling) that can provide clear evidence for the greenness of particular solvents systems for biomass/food waste valorisation. Besides, large-scale production of platform chemicals supplemented with techno-economic analysis and life cycle analysis (LCA) would be recommended to validate the upscaling feasibility of food/paper waste valorisation.

## Appendix A

	Solvent	<b>Boiling</b> point (°C)	Flash point (°C)	Safety score	Health score	Environmental score	Default ranking	Final ranking
Classical solvents	Water	100	Not applicable	1	1	1	Recommended	Recommended
	Ethanol	78	13	4	3	3	Recommended	Recommended
	Isopropanol	82	12	4	3	3	Recommended	Recommended
	Acetone	56	-18	5	3	5	Problematic	Recommended
	THF	66	-14	6	7	5	Problematic	Problematic
	DMF	153	58	3	9	5	Hazardous	Hazardous
	DMSO	189	95	1	1	5	Recommended	Problematic
Emerging solvents	Isobutanol	107	28	3	4	3	Recommended	Not available
	GVL	207	100	1	5	7	Problematic	Not available
	Dimethyl carbonate	90	16	4	1	3	Recommended	Not available
	Ethylene carbonate	248	143	1	2	7	Problematic	Not available
	Propylene carbonate	242	132	1	2	7	Problematic	Not available
	Cyrene	203	61	1	2	7	Problematic	Not available

**Table A.1** Ranking of selected 'classical' and 'emerging' solvents in the CHEM21 solvent guide (Prat et al., 2016)

## **Appendix B**



**Figure B.1** Temperature, pressure, and power consumption record in the EthosUp microwave reactor for catalytic conversion of paper towel waste in (a)  $GVL/H_2O$  and (b) acetone/H<sub>2</sub>O (reaction conditions: 5 wt% substrates, 0.135 M H<sub>2</sub>SO<sub>4</sub>, 5 min, solvent mixture 1:1)



**Figure B.2** Temperature, pressure, and power consumption record in the EthosUp microwave reactor for catalytic conversion of paper towel waste in (a)  $H_2O$ , (b)  $PC/H_2O$ , (c)  $EC/H_2O$ , and (c)  $DMC/H_2O$  (Reaction condition: 5 wt% substrate loading, 0.135 M  $H_2SO_4$ , temperature: 130°C, duration: 10 min, solvent ratio: 1:1)

# Appendix C

Paper types	Total organic carbon			
	(TOC) (%)			
Paper towel	37.7			
Rice	40.7			
Bread	40.1			
Printing paper	39.3			
Napkin	41.4			
Paper cup sugarcane	41.3			
Packaging paper	37.2			
Newspaper	43.9			
Tracing paper	39.4			
Paper mould	35.6			
Bamboo napkin	39.8			

Table C.1 Total organic carbon content of various paper substrates

### References

- Abdel-Rahman, M.A., Tashiro, Y., Sonomoto, K., 2011. Lactic acid production from lignocellulose-derived sugars using lactic acid bacteria: Overview and limits. Journal of Biotechnology, Special issue: IBS 2010 - Industrial Biotechnology 156, 286–301. https://doi.org/10.1016/j.jbiotec.2011.06.017
- Abdelrahman, O.A., Heyden, A., Bond, J.Q., 2014. Analysis of kinetics and reaction pathways in the aqueous-phase hydrogenation of levulinic acid to form γ-valerolactone over Ru/C. ACS catalysis 4, 1171–1181.
- Agrawal, R., Verma, A., Singhania, R.R., Varjani, S., Di Dong, C., Kumar Patel, A., 2021. Current understanding of the inhibition factors and their mechanism of action for the lignocellulosic biomass hydrolysis. Bioresource Technology 332, 125042. https://doi.org/10.1016/j.biortech.2021.125042
- Agutaya, J.K.C.N., Inoue, R., Vin Tsie, S.S., Quitain, A.T., de la Peña-García, J., Pérez-Sánchez, H., Sasaki, M., Kida, T., 2020. Metal-Free Synthesis of HMF from Glucose Using the Supercritical CO <sub>2</sub> –Subcritical H <sub>2</sub> O–Isopropanol System. Ind. Eng. Chem. Res. 59, 16527–16538. https://doi.org/10.1021/acs.iecr.0c03551
- AIST, 2021. AIST:Spectral Database for Organic Compounds,SDBS [WWW Document]. URL https://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre\_index.cgi (accessed 5.10.21).
- Akarsu, K., Duman, G., Yilmazer, A., Keskin, T., Azbar, N., Yanik, J., 2019. Sustainable valorization of food wastes into solid fuel by hydrothermal carbonization. Bioresource Technology 292, 121959. https://doi.org/10.1016/j.biortech.2019.121959
- Alcántara, M.Á.B., Dobruchowska, J., Azadi, P., García, B.D., Molina-Heredia, F.P., Reyes-Sosa, F.M., 2016. Recalcitrant carbohydrates after enzymatic hydrolysis of pretreated lignocellulosic biomass. Biotechnology for Biofuels 9. https://doi.org/10.1186/s13068-016-0629-4

- Alonso, D.M., Wettstein, S.G., Dumesic, J.A., 2013a. Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass. Green Chemistry 15, 584. https://doi.org/10.1039/c3gc37065h
- Alonso, D.M., Wettstein, S.G., Mellmer, M.A., Gurbuz, E.I., Dumesic, J.A., 2013b. Integrated conversion of hemicellulose and cellulose from lignocellulosic biomass. Energy Environ. Sci. 6, 76–80. https://doi.org/10.1039/C2EE23617F
- Alvarez, J.V.L., Larrucea, M.A., Bermúdez, P.A., Chicote, B.L., 2009. Biodegradation of paper waste under controlled composting conditions. Waste Management, First international conference on environmental management, engineering, planning and economics 29, 1514–1519. https://doi.org/10.1016/j.wasman.2008.11.025
- Amarasekara, A.S., Hasan, M.A., 2015. Pd/C catalyzed conversion of levulinic acid to γvalerolactone using alcohol as a hydrogen donor under microwave conditions. Catalysis Communications 60, 5–7. https://doi.org/10.1016/j.catcom.2014.11.009
- Antonetti, C., Bonari, E., Licursi, D., Nassi o Di Nasso, N., Raspolli Galletti, A.M., 2015. Hydrothermal Conversion of Giant Reed to Furfural and Levulinic Acid: Optimization of the Process under Microwave Irradiation and Investigation of Distinctive Agronomic Parameters. Molecules 20, 21232–21253. https://doi.org/10.3390/molecules201219760
- Antonetti, C., Ciorba, S., Licursi, D., Coccia, V., Cotana, F., Raspolli Galletti, A.M., 2020a.
  Production of Levulinic Acid and n-Butyl Levulinate from the Waste Biomasses Grape
  Pomace and Cynara Cardunculus L., in: Proceedings of 1st International Electronic
  Conference on Catalysis Sciences. Presented at the 1st International Electronic
  Conference on Catalysis Sciences, MDPI, Sciforum.net, p. 7549.
  https://doi.org/10.3390/ECCS2020-07549

- Antonetti, C., Licursi, D., Fulignati, S., Valentini, G., Raspolli Galletti, A., 2016. New Frontiers in the Catalytic Synthesis of Levulinic Acid: From Sugars to Raw and Waste Biomass as Starting Feedstock. Catalysts 6, 196. https://doi.org/10.3390/catal6120196
- Antonetti, C., Licursi, D., Raspolli Galletti, A.M., 2020b. New Intensification Strategies for the Direct Conversion of Real Biomass into Platform and Fine Chemicals: What Are the Main Improvable Key Aspects? Catalysts 10, 961. https://doi.org/10.3390/catal10090961
- Antoniou, N., Monlau, F., Sambusiti, C., Ficara, E., Barakat, A., Zabaniotou, A., 2019.
  Contribution to Circular Economy options of mixed agricultural wastes management:
  Coupling anaerobic digestion with gasification for enhanced energy and material
  recovery. Journal of Cleaner Production 209, 505–514.
  https://doi.org/10.1016/j.jclepro.2018.10.055
- Aricò, F., Tundo, P., 2010. Dimethyl carbonate as a modern green reagent and solvent. Russ. Chem. Rev. 79, 479–489. https://doi.org/10.1070/RC2010v079n06ABEH004113
- Atalla, R.H., VanderHart, D.L., 1999. The role of solid state 13C NMR spectroscopy in studies of the nature of native celluloses 19.
- Atichokudomchai, N., Varavinit, S., Chinachoti, P., 2004. A study of ordered structure in acidmodified tapioca starch by C CP/MAS solid-state NMR. Carbohydrate Polymers 58, 383–389. https://doi.org/10.1016/j.carbpol.2004.07.017
- Bajpai, P., 2015. Pulp and Paper Industry: Chemicals. Elsevier.
- Beh, G.K., Wang, C.T., Kim, K., Qu, J., Cairney, J., Ng, Y.H., An, A.K., Ryoo, R., Urakawa, A., Teoh, W.Y., 2020. Flame-made amorphous solid acids with tunable acidity for the aqueous conversion of glucose to levulinic acid. Green Chem. 22, 688–698. https://doi.org/10.1039/C9GC02567G

- Bengtsson, A., Bengtsson, J., Sedin, M., Sjöholm, E., 2019. Carbon Fibers from Lignin-Cellulose Precursors: Effect of Stabilization Conditions. ACS Sustainable Chem. Eng. 7, 8440–8448. https://doi.org/10.1021/acssuschemeng.9b00108
- Bereczky, Á., Lukács, K., Farkas, M., Dóbé, S., 2014. Effect of <i&gt;γ&lt;/i&gt;-Valerolactone Blending on Engine Performance, Combustion Characteristics and Exhaust Emissions in a Diesel Engine. Natural Resources 05, 177–191. https://doi.org/10.4236/nr.2014.55017
- Bernardinelli, O.D., Lima, M.A., Rezende, C.A., Polikarpov, I., deAzevedo, E.R., 2015. Quantitative 13C MultiCP solid-state NMR as a tool for evaluation of cellulose crystallinity index measured directly inside sugarcane biomass. Biotechnology for Biofuels 8. https://doi.org/10.1186/s13068-015-0292-1
- Bevilaqua, D.B., Rambo, M.K.D., Rizzetti, T.M., Cardoso, A.L., Martins, A.F., 2013. Cleaner production: levulinic acid from rice husks. Journal of Cleaner Production, Cleaner Production: initiatives and challenges for a sustainable world 47, 96–101. https://doi.org/10.1016/j.jclepro.2013.01.035
- Biermann, C.J., 1996. Handbook of Pulping and Papermaking. Elsevier.
- Boonyakarn, T., Wataniyakul, P., Boonnoun, P., Quitain, A.T., Kida, T., Sasaki, M., Laosiripojana, N., Jongsomjit, B., Shotipruk, A., 2019. Enhanced Levulinic Acid
  Production from Cellulose by Combined Brønsted Hydrothermal Carbon and Lewis
  Acid Catalysts. Ind. Eng. Chem. Res. 58, 2697–2703. https://doi.org/10.1021/acs.iecr.8b05332
- Cai, J., Cai, C., Man, J., Yang, Y., Zhang, F., Wei, C., 2014. Crystalline and structural properties of acid-modified lotus rhizome C-type starch. Carbohydrate Polymers 102, 799–807. https://doi.org/10.1016/j.carbpol.2013.10.088

- Cao, L., Yu, I.K.M., Chen, S.S., Tsang, D.C.W., Wang, L., Xiong, X., Zhang, S., Ok, Y.S., Kwon, E.E., Song, H., Poon, C.S., 2018a. Production of 5-hydroxymethylfurfural from starch-rich food waste catalyzed by sulfonated biochar. Bioresource Technology 252, 76–82. https://doi.org/10.1016/j.biortech.2017.12.098
- Cao, L., Yu, I.K.M., Tsang, D.C.W., Zhang, S., Ok, Y.S., Kwon, E.E., Song, H., Poon, C.S., 2018b. Phosphoric acid-activated wood biochar for catalytic conversion of starch-rich food waste into glucose and 5-hydroxymethylfurfural. Bioresource Technology 267, 242–248. https://doi.org/10.1016/j.biortech.2018.07.048
- Cao, Y., Chen, S.S., Tsang, D.C.W., Clark, J.H., Budarin, V.L., Hu, C., Wu, K.C.-W., Zhang,
  S., 2020. Microwave-assisted depolymerization of various types of waste lignins over two-dimensional CuO/BCN catalysts. Green Chem. 22, 725–736. https://doi.org/10.1039/C9GC03553B
- Cao, Y., He, M., Dutta, S., Luo, G., Zhang, S., Tsang, D.C.W., 2021. Hydrothermal carbonization and liquefaction for sustainable production of hydrochar and aromatics. Renewable and Sustainable Energy Reviews 152, 111722. https://doi.org/10.1016/j.rser.2021.111722
- Cerda, A., Artola, A., Font, X., Barrena, R., Gea, T., Sánchez, A., 2018. Composting of food wastes: Status and challenges. Bioresource Technology, Bioconversion of Food Wastes 248, 57–67. https://doi.org/10.1016/j.biortech.2017.06.133
- Cesaro, A., 2021. The valorization of the anaerobic digestate from the organic fractions of municipal solid waste: Challenges and perspectives. Journal of Environmental Management 280, 111742. https://doi.org/10.1016/j.jenvman.2020.111742
- Cha, J.Y., Hanna, M.A., 2002. Levulinic acid production based on extrusion and pressurized batch reaction. Industrial Crops and Products 16, 109–118. https://doi.org/10.1016/S0926-6690(02)00033-X

- Chang, C., Cen, P., Ma, X., 2007. Levulinic acid production from wheat straw. Bioresource Technology 98, 1448–1453. https://doi.org/10.1016/j.biortech.2006.03.031
- Chaudhary, R., Dhepe, P.L., 2017. Solid base catalyzed depolymerization of lignin into low molecular weight products. Green Chem. 19, 778–788. https://doi.org/10.1039/C6GC02701F
- Chen, L., Wang, L., Tsang, D.C.W., Mechtcherine, V., Poon, C.S., 2020. Efficacy of green alternatives and carbon dioxide curing in reactive magnesia cement-bonded particleboards. Journal of Cleaner Production 258, 120997. https://doi.org/10.1016/j.jclepro.2020.120997
- Chen, S.S., Cao, Y., Tsang, D.C.W., Tessonnier, J.-P., Shang, J., Hou, D., Shen, Z., Zhang, S., Ok, Y.S., Wu, K.C.-W., 2020. Effective Dispersion of MgO Nanostructure on Biochar Support as a Basic Catalyst for Glucose Isomerization. ACS Sustainable Chem. Eng. 8, 6990–7001. https://doi.org/10.1021/acssuschemeng.0c00278
- Chen, S.S., Iris, K.M., Tsang, D.C.W., Yip, A.C., Khan, E., Wang, L., Ok, Y.S., Poon, C.S., 2017a. Valorization of cellulosic food waste into levulinic acid catalyzed by heterogeneous Brønsted acids: temperature and solvent effects. Chemical Engineering Journal 327, 328–335.
- Chen, S.S., Maneerung, T., Tsang, D.C.W., Ok, Y.S., Wang, C.-H., 2017b. Valorization of biomass to hydroxymethylfurfural, levulinic acid, and fatty acid methyl ester by heterogeneous catalysts. Chemical Engineering Journal 328, 246–273. https://doi.org/10.1016/j.cej.2017.07.020
- Chen, S.S., Wang, L., Yu, I.K.M., Tsang, D.C.W., Hunt, A.J., Jérôme, F., Zhang, S., Ok, Y.S., Poon, C.S., 2018. Valorization of lignocellulosic fibres of paper waste into levulinic acid using solid and aqueous Brønsted acid. Bioresource Technology 247, 387–394. https://doi.org/10.1016/j.biortech.2017.09.110

- Chen, S.S., Yu, I.K.M., Tsang, D.C.W., Yip, A.C.K., Khan, E., Wang, L., Ok, Y.S., Poon, C.S., 2017c. Valorization of cellulosic food waste into levulinic acid catalyzed by heterogeneous Brønsted acids: Temperature and solvent effects. Chemical Engineering Journal 327, 328–335. https://doi.org/10.1016/j.cej.2017.06.108
- Chen, Z., Reznicek, W.D., Wan, C., 2018. Aqueous Choline Chloride: A Novel Solvent for Switchgrass Fractionation and Subsequent Hemicellulose Conversion into Furfural.
  ACS Sustainable Chem. Eng. 6, 6910–6919. https://doi.org/10.1021/acssuschemeng.8b00728
- Cheng, G., Varanasi, P., Li, C., Liu, H., Melnichenko, Y.B., Simmons, B.A., Kent, M.S., Singh,
  S., 2011. Transition of Cellulose Crystalline Structure and Surface Morphology of
  Biomass as a Function of Ionic Liquid Pretreatment and Its Relation to Enzymatic
  Hydrolysis. Biomacromolecules 12, 933–941. https://doi.org/10.1021/bm101240z
- Cheng, Z., Everhart, J.L., Tsilomelekis, G., Nikolakis, V., Saha, B., Vlachos, D.G., 2018. Structural analysis of humins formed in the Brønsted acid catalyzed dehydration of fructose. Green Chemistry 20, 997–1006. https://doi.org/10.1039/c7gc03054a
- Cheong, J.C., Lee, J.T.E., Lim, J.W., Song, S., Tan, J.K.N., Chiam, Z.Y., Yap, K.Y., Lim, E.Y., Zhang, J., Tan, H.T.W., Tong, Y.W., 2020. Closing the food waste loop: Food waste anaerobic digestate as fertilizer for the cultivation of the leafy vegetable, xiao bai cai (Brassica rapa). Science of The Total Environment 715, 136789. https://doi.org/10.1016/j.scitotenv.2020.136789
- Chia, M., Dumesic, J.A., 2011. Liquid-phase catalytic transfer hydrogenation and cyclization of levulinic acid and its esters to γ-valerolactone over metal oxide catalysts. Chemical Communications 47, 12233. https://doi.org/10.1039/c1cc14748j
- Chiappero, M., Norouzi, O., Hu, M., Demichelis, F., Berruti, F., Di Maria, F., Mašek, O., Fiore,S., 2020. Review of biochar role as additive in anaerobic digestion processes.

Renewable and Sustainable Energy Reviews 131, 110037. https://doi.org/10.1016/j.rser.2020.110037

- Chin, S.C., Tee, K.F., Tong, F.S., Ong, H.R., Gimbun, J., 2020. Thermal and mechanical properties of bamboo fiber reinforced composites. Materials Today Communications 23, 100876. https://doi.org/10.1016/j.mtcomm.2019.100876
- Choi, S., Song, C.W., Shin, J.H., Lee, S.Y., 2015. Biorefineries for the production of top building block chemicals and their derivatives. Metabolic Engineering 28, 223–239. https://doi.org/10.1016/j.ymben.2014.12.007
- Clark, J.H., 2019. Green biorefinery technologies based on waste biomass. Green Chemistry 21, 1168–1170. https://doi.org/10.1039/C9GC90021G
- Cozzolino, R., Lombardi, L., Tribioli, L., 2017. Use of biogas from biowaste in a solid oxide fuel cell stack: Application to an off-grid power plant. Renewable Energy 111, 781– 791. https://doi.org/10.1016/j.renene.2017.04.027
- Cui, X., Li, X., Zhang, J., Lin, Q., Xiao, H., Cheng, Z., Yan, B., Yang, X., Chen, G., 2022. Hydrothermal Treatment of the Pristine and Contaminated Cd/Zn Hyperaccumulators for Bio-Oil Production and Heavy Metal Separation. ACS Sustainable Chem. Eng. 10, 603–612. https://doi.org/10.1021/acssuschemeng.1c07151
- Dabral, S., Engel, J., Mottweiler, J., Spoehrle, S.S.M., Lahive, C.W., Bolm, C., 2018. Mechanistic studies of base-catalysed lignin depolymerisation in dimethyl carbonate. Green Chemistry 20, 170–182. https://doi.org/10.1039/C7GC03110F
- Deng, J., Wang, Y., Pan, T., Xu, Q., Guo, Q.-X., Fu, Y., 2013. Conversion of Carbohydrate Biomass to γ-Valerolactone by using Water-Soluble and Reusable Iridium Complexes in Acidic Aqueous Media. ChemSusChem 6, 1163–1167.
- Di Fidio, N., Fulignati, S., De Bari, I., Antonetti, C., Raspolli Galletti, A.M., 2020. Optimisation of glucose and levulinic acid production from the cellulose fraction of

giant reed (Arundo donax L.) performed in the presence of ferric chloride under microwave heating. Bioresource Technology 313, 123650. https://doi.org/10.1016/j.biortech.2020.123650

- Ding, D., Hu, J., Hui, L., Liu, Z., Shao, L., 2021. Valorization of Miscanthus × giganteus by γ-Valerolactone/H2O/FeCl3 system toward efficient conversion of cellulose and hemicelluloses. Carbohydrate Polymers 270, 118388. https://doi.org/10.1016/j.carbpol.2021.118388
- Du, C., Abdullah, J.J., Greetham, D., Fu, D., Yu, M., Ren, L., Li, S., Lu, D., 2018. Valorization of food waste into biofertiliser and its field application. Journal of Cleaner Production 187, 273–284. https://doi.org/10.1016/j.jclepro.2018.03.211
- Du, H., Deng, F., Kommalapati, R.R., Amarasekara, A.S., 2020. Iron based catalysts in biomass processing. Renewable and Sustainable Energy Reviews 134, 110292. https://doi.org/10.1016/j.rser.2020.110292
- Duo, J., Zhang, Z., Yao, G., Huo, Z., Jin, F., 2016. Hydrothermal conversion of glucose into lactic acid with sodium silicate as a base catalyst. Catalysis Today, Special Issue in Honour of Professor Eli Ruckenstein's Contribution to Catalysis 263, 112–116. https://doi.org/10.1016/j.cattod.2015.11.007
- Dutta, S., Yu, I.K.M., Tsang, D.C.W., Ng, Y.H., Ok, Y.S., Sherwood, J., Clark, J.H., 2019. Green synthesis of gamma-valerolactone (GVL) through hydrogenation of biomassderived levulinic acid using non-noble metal catalysts: A critical review. Chemical Engineering Journal 372, 992–1006. https://doi.org/10.1016/j.cej.2019.04.199
- Dyson, P.J., Jessop, P.G., 2016. Solvent effects in catalysis: rational improvements of catalysts via manipulation of solvent interactions. Catal. Sci. Technol. 6, 3302–3316. https://doi.org/10.1039/C5CY02197A

EDP HK, 2020. Monitoring of Solid Waste in Hong Kong - Waste Statistics for 2020 34.

- Enslow, K.R., Bell, A.T., 2015. SnCl 4-catalyzed isomerization/dehydration of xylose and glucose to furanics in water. Catalysis Science & Technology 5, 2839–2847.
- Espro, C., Paone, E., Mauriello, F., Gotti, R., Uliassi, E., Bolognesi, M.L., Rodríguez-Padrón,
  D., Luque, R., 2021. Sustainable production of pharmaceutical, nutraceutical and
  bioactive compounds from biomass and waste. Chem. Soc. Rev. 50, 11191-11207.
  https://doi.org/10.1039/D1CS00524C
- Fábos, V., Koczó, G., Mehdi, H., Boda, L., Horváth, I.T., 2009. Bio-oxygenates and the peroxide number: a safety issue alert. Energy & Environmental Science 2, 767–769.
- Fagbohungbe, M.O., Herbert, B.M.J., Hurst, L., Ibeto, C.N., Li, H., Usmani, S.Q., Semple,
  K.T., 2017. The challenges of anaerobic digestion and the role of biochar in optimizing anaerobic digestion. Waste Management 61, 236–249. https://doi.org/10.1016/j.wasman.2016.11.028
- Fan, J., De bruyn, M., Budarin, V.L., Gronnow, M.J., Shuttleworth, P.S., Breeden, S., Macquarrie, D.J., Clark, J.H., 2013. Direct Microwave-Assisted Hydrothermal Depolymerization of Cellulose. Journal of the American Chemical Society 135, 11728– 11731. https://doi.org/10.1021/ja4056273
- Fan, J., Shuttleworth, P.S., Gronnow, M., Breeden, S.W., Clark, J.H., Macquarrie, D.J., Budarin, V.L., 2018. Influence of Density on Microwave Pyrolysis of Cellulose. ACS
  Sustainable Chem. Eng. 6, 2916–2920. https://doi.org/10.1021/acssuschemeng.8b00280
- Fang, L., Li, J., Guo, M.Z., Cheeseman, C.R., Tsang, D.C.W., Donatello, S., Poon, C.S., 2018.
  Phosphorus recovery and leaching of trace elements from incinerated sewage sludge ash (ISSA). Chemosphere 193, 278–287.
  https://doi.org/10.1016/j.chemosphere.2017.11.023

- Fang, Q., Hanna, M.A., 2002. Experimental studies for levulinic acid production from whole kernel grain sorghum. Bioresource Technology 81, 187–192. https://doi.org/10.1016/S0960-8524(01)00144-4
- Fang, W., Sixta, H., 2015. Advanced Biorefinery based on the Fractionation of Biomass in γ-Valerolactone and Water. ChemSusChem 8, 73–76. https://doi.org/10.1002/cssc.201402821
- Filiciotto, L., Balu, A.M., Romero, A.A., Angelici, C., van der Waal, J.C., Luque, R., 2019.
  Reconstruction of humins formation mechanism from decomposition products: A GC-MS study based on catalytic continuous flow depolymerizations. Molecular Catalysis 479, 110564. https://doi.org/10.1016/j.mcat.2019.110564
- Fiorani, G., Perosa, A., Selva, M., 2018. Dimethyl carbonate: a versatile reagent for a sustainable valorization of renewables. Green Chem. 20, 288–322. https://doi.org/10.1039/C7GC02118F
- Flanagan, B.M., Gidley, M.J., Warren, F.J., 2015. Rapid quantification of starch molecular order through multivariate modelling of <sup>13</sup> C CP/MAS NMR spectra. Chem. Commun. 51, 14856–14858. https://doi.org/10.1039/C5CC06144J
- Flannelly, T., Lopes, M., Kupiainen, L., Dooley, S., Leahy, J.J., 2016. Non-stoichiometric formation of formic and levulinic acids from the hydrolysis of biomass derived hexose carbohydrates. RSC Advances 6, 5797–5804. https://doi.org/10.1039/C5RA25172A
- Foresti, M.L., Williams, M. del P., Martínez-García, R., Vázquez, A., 2014. Analysis of a preferential action of α-amylase from B. licheniformis towards amorphous regions of waxy maize starch. Carbohydrate Polymers 102, 80–87. https://doi.org/10.1016/j.carbpol.2013.11.013
- Foston, M., 2014. Advances in solid-state NMR of cellulose. Current Opinion in Biotechnology 27, 176–184. https://doi.org/10.1016/j.copbio.2014.02.002

- Galletti, A.M.R., Antonetti, C., De Luise, V., Licursi, D., Nassi, N., 2012. LEVULINIC ACID
  PRODUCTION FROM WASTE BIOMASS. BioResources 7.
  https://doi.org/10.15376/biores.7.2.1824-1835
- Gallo, J.M.R., Alonso, D.M., Mellmer, M.A., Dumesic, J.A., 2013. Production and upgrading of 5-hydroxymethylfurfural using heterogeneous catalysts and biomass-derived solvents. Green Chem. 15, 85–90. https://doi.org/10.1039/C2GC36536G
- Gao, F., Bai, R., Ferlin, F., Vaccaro, L., Li, M., Gu, Y., 2020. Replacement strategies for nongreen dipolar aprotic solvents. Green Chem. 22, 6240–6257. https://doi.org/10.1039/D0GC02149K
- Giwa, A.S., Xu, H., Chang, F., Wu, J., Li, Y., Ali, N., Ding, S., Wang, K., 2019. Effect of biochar on reactor performance and methane generation during the anaerobic digestion of food waste treatment at long-run operations. Journal of Environmental Chemical Engineering 7, 103067. https://doi.org/10.1016/j.jece.2019.103067
- Grigatti, M., Barbanti, L., Hassan, M.U., Ciavatta, C., 2020. Fertilizing potential and CO<sub>2</sub> emissions following the utilization of fresh and composted food-waste anaerobic digestates. Science of The Total Environment 698, 134198. https://doi.org/10.1016/j.scitotenv.2019.134198
- Gu, X., Martinez-Fernandez, J.S., Pang, N., Fu, X., Chen, S., 2020. Recent development of hydrothermal liquefaction for algal biorefinery. Renewable and Sustainable Energy Reviews 121, 109707. https://doi.org/10.1016/j.rser.2020.109707
- Guan, C.-Y., Chen, S.S., Lee, T.-H., Yu, C.-P., Tsang, D.C.W., 2020. Valorization of biomass from plant microbial fuel cells into levulinic acid by using liquid/solid acids and green solvents. Journal of Cleaner Production 260, 121097. https://doi.org/10.1016/j.jclepro.2020.121097

- Gunny, A.A.N., Arbain, D., Nashef, E.M., Jamal, P., 2015. Applicability evaluation of Deep Eutectic Solvents–Cellulase system for lignocellulose hydrolysis. Bioresource Technology 6.
- Gupta, S.S.R., Kantam, M.L., 2018. Selective hydrogenation of levulinic acid into γvalerolactone over Cu/Ni hydrotalcite-derived catalyst. Catalysis Today 309, 189–194. https://doi.org/10.1016/j.cattod.2017.08.007
- Gürbüz, E.I., Gallo, J.M.R., Alonso, D.M., Wettstein, S.G., Lim, W.Y., Dumesic, J.A., 2013.
  Conversion of Hemicellulose into Furfural Using Solid Acid Catalysts in γValerolactone. Angewandte Chemie International Edition 52, 1270–1274.
  https://doi.org/10.1002/anie.201207334
- Hayes, G.C., Becer, C.R., 2020. Levulinic acid: a sustainable platform chemical for novel polymer architectures. Polym. Chem. 11, 4068–4077. https://doi.org/10.1039/D0PY00705F
- He, M., Zhu, X., Dutta, S., Khanal, S.K., Lee, K.T., Masek, O., Tsang, D.C.W., 2022. Catalytic co-hydrothermal carbonization of food waste digestate and yard waste for energy application and nutrient recovery. Bioresource Technology 344, 126395. https://doi.org/10.1016/j.biortech.2021.126395
- Hlavatý, J., Novák, P., 1992. The influence of H+ ions liberated by electropolymerization on the decomposition of propylene carbonate. Electrochimica Acta 37, 2595–2597. https://doi.org/10.1016/0013-4686(92)87058-8
- Hoover, R., 2000. ACID-TREATED STARCHES. Food Reviews International 16, 369–392. https://doi.org/10.1081/FRI-100100292
- Hospodarova, V., Singovszka, E., Stevulova, N., 2018. Characterization of Cellulosic Fibers by FTIR Spectroscopy for Their Further Implementation to Building Materials. AJAC 09, 303–310. https://doi.org/10.4236/ajac.2018.96023

- Hou, C., Chen, Y., Chen, W., Li, W., 2011. Microwave-assisted methylation of cassava starch with dimethyl carbonate. Carbohydrate Research 346, 1178–1181. https://doi.org/10.1016/j.carres.2011.04.001
- Hu, X., Wu, L., Wang, Y., Mourant, D., Lievens, C., Gunawan, R., Li, C.-Z., 2012. Mediating acid-catalyzed conversion of levoglucosan into platform chemicals with various solvents. Green Chemistry 14, 3087–3098. https://doi.org/10.1039/C2GC35961H
- Hubbe, M.A., Gill, R.A., 2016. Fillers for Papermaking: A Review of their Properties, Usage Practices, and their Mechanistic Role. BioResources 11, 2886–2963. https://doi.org/10.15376/biores.11.1.2886-2963
- Hunter, S.E., Savage, P.E., 2008. Quantifying rate enhancements for acid catalysis in CO2enriched high-temperature water. AIChE Journal 54, 516–528. https://doi.org/10.1002/aic.11392
- Hunter, S.E., Savage, P.E., 2003. Acid-Catalyzed Reactions in Carbon Dioxide-Enriched High-Temperature Liquid Water. Ind. Eng. Chem. Res. 42, 290–294. https://doi.org/10.1021/ie020565z
- Jahan, M.S., Rahman, M.M., Ni, Y., 2021. Alternative initiatives for non-wood chemical pulping and integration with the biorefinery concept: A review. Biofuels, Bioproducts and Biorefining 15, 100–118. https://doi.org/10.1002/bbb.2143
- Jessop, P.G., Jessop, D.A., Fu, D., Phan, L., 2012. Solvatochromic parameters for solvents of interest in green chemistry. Green Chem. 14, 1245. https://doi.org/10.1039/c2gc16670d
- Jiang, Z., Remón, J., Li, T., Budarin, V.L., Fan, J., Hu, C., Clark, J.H., 2019. A one-pot microwave-assisted NaCl–H2O/GVL solvent system for cellulose conversion to 5hydroxymethylfurfural and saccharides with in situ separation of the products. Cellulose 26, 8383–8400. https://doi.org/10.1007/s10570-019-02362-8

- Jing, S., Cao, X., Zhong, L., Peng, X., Zhang, X., Wang, S., Sun, R., 2016. In Situ Carbonic Acid from CO 2: A Green Acid for Highly Effective Conversion of Cellulose in the Presence of Lewis acid. ACS Sustainable Chem. Eng. 4, 4146–4155. https://doi.org/10.1021/acssuschemeng.6b00623
- Joshi, P., Visvanathan, C., 2019. Sustainable management practices of food waste in Asia: Technological and policy drivers. Journal of Environmental Management 247, 538– 550. https://doi.org/10.1016/j.jenvman.2019.06.079
- Kaza, S., Yao, L., Bhada-Tata, P., Woerden, F.V., 2018. What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050. World Bank Publications.
- Khan, A.S., Man, Z., Bustam, M.A., Nasrullah, A., Ullah, Z., Sarwono, A., Shah, F.U., Muhammad, N., 2018. Efficient conversion of lignocellulosic biomass to levulinic acid using acidic ionic liquids. Carbohydrate Polymers 181, 208–214. https://doi.org/10.1016/j.carbpol.2017.10.064
- Kono, H., Erata, T., Takai, M., 2002. CP/MAS <sup>13</sup> C NMR Study of Cellulose and Cellulose Derivatives. 2. Complete Assignment of the <sup>13</sup> C Resonance for the Ring Carbons of Cellulose Triacetate Polymorphs. Journal of the American Chemical Society 124, 7512–7518. https://doi.org/10.1021/ja010705g
- Kumar, S., Ahluwalia, V., Kundu, P., Sangwan, R.S., Kansal, S.K., Runge, T.M., Elumalai, S., 2018. Improved levulinic acid production from agri-residue biomass in biphasic solvent system through synergistic catalytic effect of acid and products. Bioresource Technology 251, 143–150. https://doi.org/10.1016/j.biortech.2017.12.033
- Lai, D., Deng, L., Guo, Q., Fu, Y., 2011. Hydrolysis of biomass by magnetic solid acid. Energy Environ. Sci. 4, 3552–3557. https://doi.org/10.1039/C1EE01526E

- Lange, J.-P., Price, R., Ayoub, P.M., Louis, J., Petrus, L., Clarke, L., Gosselink, H., 2010. Valeric Biofuels: A Platform of Cellulosic Transportation Fuels. Angewandte Chemie International Edition 49, 4479–4483. https://doi.org/10.1002/anie.201000655
- Lappalainen, K., Vogeler, N., Kärkkäinen, J., Dong, Y., Niemelä, M., Rusanen, A., Ruotsalainen, A.L., Wäli, P., Markkola, A., Lassi, U., 2018. Microwave-assisted conversion of novel biomass materials into levulinic acid. Biomass Conv. Bioref. 8, 965–970. https://doi.org/10.1007/s13399-018-0334-6
- Lê, H.Q., Ma, Y., Borrega, M., Sixta, H., 2016a. Wood biorefinery based on γvalerolactone/water fractionation. Green Chemistry 18, 5466–5476. https://doi.org/10.1039/C6GC01692H
- Lê, H.Q., Zaitseva, A., Pokki, J.-P., Ståhl, M., Alopaeus, V., Sixta, H., 2016b. Solubility of Organosolv Lignin in γ-Valerolactone/Water Binary Mixtures. ChemSusChem 9, 2939–2947. https://doi.org/10.1002/cssc.201600655
- Lenihan, P., Orozco, A., O'Neill, E., Ahmad, M.N.M., Rooney, D.W., Walker, G.M., 2010. Dilute acid hydrolysis of lignocellulosic biomass. Chemical Engineering Journal 156, 395–403. https://doi.org/10.1016/j.cej.2009.10.061
- Li, C., Aston, J.E., Lacey, J.A., Thompson, V.S., Thompson, D.N., 2016. Impact of feedstock quality and variation on biochemical and thermochemical conversion. Renewable and Sustainable Energy Reviews 65, 525–536. https://doi.org/10.1016/j.rser.2016.06.063
- Li, J., Ding, D.-J., Deng, L., Guo, Q.-X., Fu, Y., 2012. Catalytic Air Oxidation of Biomass-Derived Carbohydrates to Formic Acid. ChemSusChem 5, 1313–1318. https://doi.org/10.1002/cssc.201100466
- Li, Y., Jin, Y., Borrion, A., Li, H., 2019. Current status of food waste generation and management in China. Bioresource Technology 273, 654–665. https://doi.org/10.1016/j.biortech.2018.10.083

- Licursi D., Antonetti C., Fulignati S., Corsini A., Boschi N., Raspolli Galletti A.M., 2018. Smart valorization of waste biomass: exhausted lemon peels, coffee silverskins and paper wastes for the production of levulinic acid. Chemical Engineering Transactions 65, 637–642. https://doi.org/10.3303/CET1865107
- Liu, C.-G., Xiao, Y., Xia, X.-X., Zhao, X.-Q., Peng, L., Srinophakun, P., Bai, F.-W., 2019.
  Cellulosic ethanol production: Progress, challenges and strategies for solutions.
  Biotechnology Advances 37, 491–504.
  https://doi.org/10.1016/j.biotechadv.2019.03.002
- Liu, W., Du, H., Liu, H., Xie, H., Xu, T., Zhao, X., Liu, Y., Zhang, X., Si, C., 2020a. Highly Efficient and Sustainable Preparation of Carboxylic and Thermostable Cellulose Nanocrystals via FeCl3-Catalyzed Innocuous Citric Acid Hydrolysis. ACS Sustainable Chem. Eng. 8, 16691–16700. https://doi.org/10.1021/acssuschemeng.0c06561
- Liu, W., You, W., Sun, W., Yang, W., Korde, A., Gong, Y., Deng, Y., 2020b. Ambientpressure and low-temperature upgrading of lignin bio-oil to hydrocarbons using a hydrogen buffer catalytic system. Nat Energy 5, 759–767. https://doi.org/10.1038/s41560-020-00680-x
- Liu, X., Bouxin, F.P., Fan, J., Budarin, V.L., Hu, C., Clark, J.H., 2021. Microwave-assisted catalytic depolymerization of lignin from birch sawdust to produce phenolic monomers utilizing a hydrogen-free strategy. Journal of Hazardous Materials 402, 123490. https://doi.org/10.1016/j.jhazmat.2020.123490
- Lu, Q., Li, X., Tang, L., Lu, B., Huang, B., 2015. One-pot tandem reactions for the preparation of esterified cellulose nanocrystals with 4-dimethylaminopyridine as a catalyst. RSC Adv. 5, 56198–56204. https://doi.org/10.1039/C5RA08690F
- Lui, M.Y., Wong, C.Y.Y., Choi, A.W.-T., Mui, Y.F., Qi, L., Horváth, I.T., 2019. Valorization of Carbohydrates of Agricultural Residues and Food Wastes: A Key Strategy for

Carbon Conservation. ACS Sustainable Chem. Eng. 7, 17799–17807. https://doi.org/10.1021/acssuschemeng.9b04242

- Luterbacher, J.S., Rand, J.M., Alonso, D.M., Han, J., Youngquist, J.T., Maravelias, C.T., Pfleger, B.F., Dumesic, J.A., 2014. Nonenzymatic Sugar Production from Biomass Using Biomass-Derived g-Valerolactone 343, 5.
- Maina, S., Kachrimanidou, V., Koutinas, A., 2017. A roadmap towards a circular and sustainable bioeconomy through waste valorization. Current Opinion in Green and Sustainable Chemistry, New Business Models, Ethic, Legislation and Economics 2017 8, 18–23. https://doi.org/10.1016/j.cogsc.2017.07.007
- Mak, T.M.W., Xiong, X., Tsang, D.C.W., Yu, I.K.M., Poon, C.S., 2020. Sustainable food waste management towards circular bioeconomy: Policy review, limitations and opportunities. Bioresource Technology 297, 122497. https://doi.org/10.1016/j.biortech.2019.122497
- Mellmer, M.A., Alonso, D.M., Luterbacher, J.S., Gallo, J.M.R., Dumesic, J.A., 2014a. Effects of γ-valerolactone in hydrolysis of lignocellulosic biomass to monosaccharides. Green Chem. 16, 4659–4662. https://doi.org/10.1039/C4GC01768D
- Mellmer, M.A., Sanpitakseree, C., Demir, B., Bai, P., Ma, K., Neurock, M., Dumesic, J.A., 2018. Solvent-enabled control of reactivity for liquid-phase reactions of biomassderived compounds. Nat Catal 1, 199–207. https://doi.org/10.1038/s41929-018-0027-3
- Mellmer, M.A., Sanpitakseree, C., Demir, B., Ma, K., Elliott, W.A., Bai, P., Johnson, R.L., Walker, T.W., Shanks, B.H., Rioux, R.M., Neurock, M., Dumesic, J.A., 2019. Effects of chloride ions in acid-catalyzed biomass dehydration reactions in polar aprotic solvents. Nature Communications 10, 1132. https://doi.org/10.1038/s41467-019-09090-4

- Mellmer, M.A., Sener, C., Gallo, J.M.R., Luterbacher, J.S., Alonso, D.M., Dumesic, J.A., 2014b. Solvent Effects in Acid-Catalyzed Biomass Conversion Reactions. Angewandte Chemie International Edition 53, 11872–11875. https://doi.org/10.1002/anie.201408359
- Mika, L.T., Cséfalvay, E., Németh, Á., 2018. Catalytic Conversion of Carbohydrates to Initial Platform Chemicals: Chemistry and Sustainability. Chem. Rev. 118, 505–613. https://doi.org/10.1021/acs.chemrev.7b00395
- Mohan, S.V., Dahiya, S., Amulya, K., Katakojwala, R., Vanitha, T.K., 2019. Can circular bioeconomy be fueled by waste biorefineries — A closer look. Bioresource Technology Reports 7, 100277. https://doi.org/10.1016/j.biteb.2019.100277
- Moity, L., Durand, M., Benazzouz, A., Pierlot, C., Molinier, V., Aubry, J.-M., 2012. Panorama of sustainable solvents using the COSMO-RS approach. Green Chemistry 14, 1132. https://doi.org/10.1039/c2gc16515e
- Molleti, J., Tiwari, M.S., Yadav, G.D., 2018. Novel synthesis of Ru/OMS catalyst by solventfree method: Selective hydrogenation of levulinic acid to γ-valerolactone in aqueous medium and kinetic modelling. Chemical Engineering Journal 334, 2488–2499. https://doi.org/10.1016/j.cej.2017.11.125
- Morais, A.R.C., Matuchaki, M.D.D.J., Andreaus, J., Bogel-Lukasik, R., 2016. A green and efficient approach to selective conversion of xylose and biomass hemicellulose into furfural in aqueous media using high-pressure CO <sub>2</sub> as a sustainable catalyst. Green Chem. 18, 2985–2994. https://doi.org/10.1039/C6GC00043F
- Morais, E.S., Freire, M.G., Freire, C.S.R., Coutinho, J.A.P., Silvestre, A.J.D., 2020. Enhanced Conversion of Xylan into Furfural using Acidic Deep Eutectic Solvents with Dual Solvent and Catalyst Behavior. ChemSusChem 13, 784–790. https://doi.org/10.1002/cssc.201902848

- Moret, S., Dyson, P.J., Laurenczy, G., 2014. Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media. Nat Commun 5, 4017. https://doi.org/10.1038/ncomms5017
- Morone, P., Koutinas, A., Gathergood, N., Arshadi, M., Matharu, A., 2019. Food waste: Challenges and opportunities for enhancing the emerging bio-economy. Journal of Cleaner Production 221, 10–16. https://doi.org/10.1016/j.jclepro.2019.02.258
- Morrison, W.R., Tester, R.F., Gidley, M.J., Karkalas, J., 1993. Resistance to acid hydrolysis of lipid-complexed amylose and lipid-free amylose in lintnerised waxy and non-waxy barley starches. Carbohydrate Research 245, 289–302. https://doi.org/10.1016/0008-6215(93)80078-S
- Motagamwala, A.H., Huang, K., Maravelias, C.T., Dumesic, J.A., 2019. Solvent system for effective near-term production of hydroxymethylfurfural (HMF) with potential for long-term process improvement. Energy Environ. Sci. 12, 2212–2222. https://doi.org/10.1039/C9EE00447E
- Mukherjee, A., Dumont, M.-J., Raghavan, V., 2015. Review: Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities. Biomass and Bioenergy 72, 143–183. https://doi.org/10.1016/j.biombioe.2014.11.007
- Mushrif, S.H., Caratzoulas, S., Vlachos, D.G., 2012. Understanding solvent effects in the selective conversion of fructose to 5-hydroxymethyl-furfural: a molecular dynamics investigation. Phys. Chem. Chem. Phys. 14, 2637. https://doi.org/10.1039/c2cp22694d
- Mutungi, C., Passauer, L., Onyango, C., Jaros, D., Rohm, H., 2012. Debranched cassava starch crystallinity determination by Raman spectroscopy: Correlation of features in Raman spectra with X-ray diffraction and 13C CP/MAS NMR spectroscopy. Carbohydrate Polymers 87, 598–606. https://doi.org/10.1016/j.carbpol.2011.08.032

- Nguyen, C.M., Kim, J.-S., Nguyen, T.N., Kim, S.K., Choi, G.J., Choi, Y.H., Jang, K.S., Kim, J.-C., 2013. Production of 1- and d-lactic acid from waste Curcuma longa biomass through simultaneous saccharification and cofermentation. Bioresource Technology 146, 35–43. https://doi.org/10.1016/j.biortech.2013.07.035
- Nzediegwu, E., Portillo-Perez, G., Dumont, M.-J., 2021. Valorization of decationized newsprint to levulinic acid. Cellulose 28, 8581–8599. https://doi.org/10.1007/s10570-021-04061-9
- Obregón, I., Corro, E., Izquierdo, U., Requies, J., Arias, P.L., 2014. Levulinic acid hydrogenolysis on Al2O3-based Ni-Cu bimetallic catalysts. Chinese Journal of Catalysis 35, 656–662. https://doi.org/10.1016/S1872-2067(14)60051-6
- Oladejo, J., Shi, K., Luo, X., Yang, G., Wu, T., 2019. A Review of Sludge-to-Energy Recovery Methods. Energies 12, 60. https://doi.org/10.3390/en12010060
- Oliveira, F.R., Patel, A.K., Jaisi, D.P., Adhikari, S., Lu, H., Khanal, S.K., 2017. Environmental application of biochar: Current status and perspectives. Bioresource Technology, Special Issue on Biochar: Production, Characterization and Applications – Beyond Soil Applications 246, 110–122. https://doi.org/10.1016/j.biortech.2017.08.122
- Opatokun, S.A., Yousef, L.F., Strezov, V., 2017. Agronomic assessment of pyrolysed food waste digestate for sandy soil management. Journal of Environmental Management 187, 24–30. https://doi.org/10.1016/j.jenvman.2016.11.030
- Pan, J., Ma, J., Zhai, L., Luo, T., Mei, Z., Liu, H., 2019. Achievements of biochar application for enhanced anaerobic digestion: A review. Bioresource Technology 292, 122058. https://doi.org/10.1016/j.biortech.2019.122058
- Pandey, R., Shrivastava, S.L., 2018. Comparative evaluation of rice bran oil obtained with twostep microwave assisted extraction and conventional solvent extraction. Journal of Food Engineering 218, 106–114. https://doi.org/10.1016/j.jfoodeng.2017.09.009

- Parker, H.L., Sherwood, J., Hunt, A.J., Clark, J.H., 2014. Cyclic Carbonates as Green Alternative Solvents for the Heck Reaction. ACS Sustainable Chem. Eng. 2, 1739– 1742. https://doi.org/10.1021/sc5002287
- Peng, W., Pivato, A., 2019. Sustainable Management of Digestate from the Organic Fraction of Municipal Solid Waste and Food Waste Under the Concepts of Back to Earth Alternatives and Circular Economy. Waste Biomass Valor 10, 465–481. https://doi.org/10.1007/s12649-017-0071-2
- Petridis, L., Smith, J.C., 2018. Molecular-level driving forces in lignocellulosic biomass deconstruction for bioenergy. Nat Rev Chem 2, 382–389. https://doi.org/10.1038/s41570-018-0050-6
- Pileidis, F.D., Titirici, M.-M., 2016. Levulinic Acid Biorefineries: New Challenges for Efficient Utilization of Biomass. ChemSusChem 9, 562–582. https://doi.org/10.1002/cssc.201501405
- Ponnusamy, V.K., Nagappan, S., Bhosale, R.R., Lay, C.-H., Duc Nguyen, D., Pugazhendhi, A., Chang, S.W., Kumar, G., 2020. Review on sustainable production of biochar through hydrothermal liquefaction: Physico-chemical properties and applications. Bioresource Technology 310, 123414. https://doi.org/10.1016/j.biortech.2020.123414
- Prat, D., Wells, A., Hayler, J., Sneddon, H., McElroy, C.R., Abou-Shehada, S., Dunn, P.J., 2016. CHEM21 selection guide of classical- and less classical-solvents. Green Chemistry 18, 288–296. https://doi.org/10.1039/C5GC01008J
- Pratama, A.P., Rahayu, D.U.C., Krisnandi, Y.K., 2020. Levulinic Acid Production from Delignified Rice Husk Waste over Manganese Catalysts: Heterogeneous Versus Homogeneous. Catalysts 10, 327. https://doi.org/10.3390/catal10030327
- Putro, J.N., Kurniawan, A., Soetaredjo, F.E., Lin, S.-Y., Ju, Y.-H., Ismadji, S., 2015. Production of gamma-valerolactone from sugarcane bagasse over TiO <sub>2</sub> -supported

platinum and acid-activated bentonite as a co-catalyst. RSC Advances 5, 41285–41299. https://doi.org/10.1039/C5RA06180F

- Qi, L., Alamillo, R., Elliott, W.A., Andersen, A., Hoyt, D.W., Walter, E.D., Han, K.S., Washton, N.M., Rioux, R.M., Dumesic, J.A., Scott, S.L., 2017. Operando Solid-State NMR Observation of Solvent-Mediated Adsorption-Reaction of Carbohydrates in Zeolites. ACS Catal. 7, 3489–3500. https://doi.org/10.1021/acscatal.7b01045
- Qi, L., Mui, Y.F., Lo, S.W., Lui, M.Y., Akien, G.R., Horváth, I.T., 2014. Catalytic Conversion of Fructose, Glucose, and Sucrose to 5-(Hydroxymethyl)furfural and Levulinic and Formic Acids in γ-Valerolactone As a Green Solvent. ACS Catalysis 4, 1470–1477. https://doi.org/10.1021/cs401160y
- Rasapoor, M., Young, B., Asadov, A., Brar, R., Sarmah, A.K., Zhuang, W.-Q., Baroutian, S., 2020. Effects of biochar and activated carbon on biogas generation: A thermogravimetric and chemical analysis approach. Energy Conversion and Management 203, 112221. https://doi.org/10.1016/j.enconman.2019.112221
- Raymond, M.J., Slater, C.S., Savelski, M.J., 2010. LCA approach to the analysis of solvent waste issues in the pharmaceutical industry. Green Chem. 12, 1826–1834. https://doi.org/10.1039/C003666H
- Rihko-Struckmann, L.K., Oluyinka, O., Sahni, A., McBride, K., Fachet, M., Ludwig, K., Sundmacher, K., 2020. Transformation of remnant algal biomass to 5-HMF and levulinic acid: influence of a biphasic solvent system. RSC Adv. 10, 24753–24763. https://doi.org/10.1039/D0RA02784G
- Rinaldi, R., Schüth, F., 2009. Acid Hydrolysis of Cellulose as the Entry Point into Biorefinery Schemes. ChemSusChem 2, 1096–1107. https://doi.org/10.1002/cssc.200900188

- Rivas, S., Raspolli-Galletti, A.M., Antonetti, C., Santos, V., Parajó, J.C., 2016. Sustainable conversion of Pinus pinaster wood into biofuel precursors: A biorefinery approach. Fuel 164, 51–58. https://doi.org/10.1016/j.fuel.2015.09.085
- Saffari, N., Hajabbasi, M.A., Shirani, H., Mosaddeghi, M.R., Mamedov, A.I., 2020. Biochar type and pyrolysis temperature effects on soil quality indicators and structural stability.
  Journal of Environmental Management 261, 110190. https://doi.org/10.1016/j.jenvman.2020.110190
- Samuel, R., Pu, Y., Foston, M., Ragauskas, A.J., 2010. Solid-state NMR characterization of switchgrass cellulose after dilute acid pretreatment. Biofuels 1, 85–90. https://doi.org/10.4155/bfs.09.17
- Sanchez-Monedero, M.A., Cayuela, M.L., Roig, A., Jindo, K., Mondini, C., Bolan, N., 2018. Role of biochar as an additive in organic waste composting. Bioresource Technology 247, 1155–1164. https://doi.org/10.1016/j.biortech.2017.09.193
- Savage, N., 2011. Fuel options: The ideal biofuel. Nature 474, S9–S11. https://doi.org/10.1038/474S09a
- Schäffner, B., Holz, J., Verevkin, S.P., Börner, A., 2008. Organic Carbonates as Alternative Solvents for Palladium-Catalyzed Substitution Reactions. ChemSusChem 1, 249–253. https://doi.org/10.1002/cssc.200700142
- Sen, S., Patil, S., Argyropoulos, D.S., 2015. Methylation of softwood kraft lignin with dimethyl carbonate. Green Chem. 17, 1077–1087. https://doi.org/10.1039/C4GC01759E
- Serrano-Ruiz, J.C., Luque, R., Sepúlveda-Escribano, A., 2011. Transformations of biomassderived platform molecules: from high added-value chemicals to fuels via aqueousphase processing. Chemical Society Reviews 40, 5266. https://doi.org/10.1039/c1cs15131b

- Sewsynker-Sukai, Y., Naomi David, A., Gueguim Kana, E.B., 2020. Recent developments in the application of kraft pulping alkaline chemicals for lignocellulosic pretreatment: Potential beneficiation of green liquor dregs waste. Bioresource Technology 306, 123225. https://doi.org/10.1016/j.biortech.2020.123225
- Sharma, H.B., Sarmah, A.K., Dubey, B., 2020. Hydrothermal carbonization of renewable waste biomass for solid biofuel production: A discussion on process mechanism, the influence of process parameters, environmental performance and fuel properties of hydrochar.
  Renewable and Sustainable Energy Reviews 123, 109761. https://doi.org/10.1016/j.rser.2020.109761
- Sharma, P., Gaur, V.K., Kim, S.-H., Pandey, A., 2020. Microbial strategies for biotransforming food waste into resources. Bioresource Technology 299, 122580. https://doi.org/10.1016/j.biortech.2019.122580
- Shen, J., Song, Z., Qian, X., Ni, Y., 2011. A Review on Use of Fillers in Cellulosic Paper for Functional Applications. Ind. Eng. Chem. Res. 50, 661–666. https://doi.org/10.1021/ie1021078
- Shin, H.J., Kim, C.-J., Kim, S.B., 2009. Kinetic study of recycled newspaper liquefaction in polyol solvent. Biotechnology and Bioprocess Engineering 14, 349–353. https://doi.org/10.1007/s12257-008-0246-6
- Shuai, L., Luterbacher, J., 2016. Organic Solvent Effects in Biomass Conversion Reactions. ChemSusChem 9, 133–155. https://doi.org/10.1002/cssc.201501148
- Shuai, L., M. Questell-Santiago, Y., S. Luterbacher, J., 2016. A mild biomass pretreatment using γ-valerolactone for concentrated sugar production. Green Chemistry 18, 937– 943. https://doi.org/10.1039/C5GC02489G
- Sim, S.F., Mohamed, M., Mohd Irwan Lu, N.A.L., P. Sarman, N.S., Samsudin, S.N.S., 2012. COMPUTER-ASSISTED ANALYSIS OF FOURIER TRANSFORM INFRARED

(FTIR) SPECTRA FOR CHARACTERIZATION OF VARIOUS TREATED AND UNTREATED AGRICULTURE BIOMASS. BioResources 7, 5367–5380. https://doi.org/10.15376/biores.7.4.5367-5380

- Sluiter, A., 2008. Determination of Ash in Biomass: Laboratory Analytical Procedure (LAP); Issue Date: 7/17/2005. Technical Report 8.
- Smit, A., Huijgen, W., 2017. Effective fractionation of lignocellulose in herbaceous biomass and hardwood using a mild acetone organosolv process. Green Chemistry 19, 5505– 5514. https://doi.org/10.1039/C7GC02379K
- Smith, E.L., Abbott, A.P., Ryder, K.S., 2014. Deep Eutectic Solvents (DESs) and Their Applications. Chem. Rev. 114, 11060–11082. https://doi.org/10.1021/cr300162p
- Smith, M.D., Cheng, X., Petridis, L., Mostofian, B., Smith, J.C., 2017. Organosolv-Water Cosolvent Phase Separation on Cellulose and its Influence on the Physical Deconstruction of Cellulose: A Molecular Dynamics Analysis. Sci Rep 7, 14494. https://doi.org/10.1038/s41598-017-15048-7
- Soh, L., Eckelman, M.J., 2016. Green Solvents in Biomass Processing. ACS Sustainable Chem. Eng. 4, 5821–5837. https://doi.org/10.1021/acssuschemeng.6b01635
- Song, B., Yu, Y., Wu, H., 2018. Solvent effect of gamma-valerolactone (GVL) on cellulose and biomass hydrolysis in hot-compressed GVL/water mixtures. Fuel 232, 317–322. https://doi.org/10.1016/j.fuel.2018.05.154
- Song, J., Zhou, B., Liu, H., Xie, C., Meng, Q., Zhang, Z., Han, B., 2016. Biomass-derived γvalerolactone as an efficient solvent and catalyst for the transformation of CO 2 to formamides. Green Chemistry 18, 3956–3961. https://doi.org/10.1039/C6GC01455K
- Taherzadeh, M., Bolton, K., Wong, J., Pandey, A., 2019. Sustainable Resource Recovery and Zero Waste Approaches. Elsevier.

- Tang, X., Zeng, X., Li, Z., Hu, L., Sun, Y., Liu, S., Lei, T., Lin, L., 2014. Production of γ-valerolactone from lignocellulosic biomass for sustainable fuels and chemicals supply.
  Renewable and Sustainable Energy Reviews 40, 608–620. https://doi.org/10.1016/j.rser.2014.07.209
- Tanger, P., Field, J., Jahn, C., DeFoort, M., Leach, J., 2013. Biomass for thermochemical conversion: targets and challenges. Frontiers in Plant Science 4.
- Tekin, K., Karagöz, S., Bektaş, S., 2014. A review of hydrothermal biomass processing. Renewable and Sustainable Energy Reviews 40, 673–687. https://doi.org/10.1016/j.rser.2014.07.216
- T. Horváth, I., Mehdi, H., Fábos, V., Boda, L., T. Mika, L., 2008. γ-Valerolactone—a sustainable liquid for energy and carbon-based chemicals. Green Chemistry 10, 238–242. https://doi.org/10.1039/B712863K
- Timokhin, V.I., Regner, M., Motagamwala, A.H., Sener, C., Karlen, S.D., Dumesic, J.A., Ralph, J., 2020. Production of p-Coumaric Acid from Corn GVL-Lignin. ACS Sustainable Chem. Eng. 8, 17427–17438. https://doi.org/10.1021/acssuschemeng.0c05651
- Toscan, A., Morais, A.R.C., Paixão, S.M., Alves, L., Andreaus, J., Camassola, M., Dillon,
  A.J.P., Lukasik, R.M., 2017. High-pressure carbon dioxide/water pre-treatment of sugarcane bagasse and elephant grass: Assessment of the effect of biomass composition on process efficiency. Bioresource Technology 224, 639–647. https://doi.org/10.1016/j.biortech.2016.11.101
- Tuck, C.O., Perez, E., Horvath, I.T., Sheldon, R.A., Poliakoff, M., 2012. Valorization of Biomass: Deriving More Value from Waste. Science 337, 695–699. https://doi.org/10.1126/science.1218930
- Tundo, P., Musolino, M., Aricò, F., 2018. The reactions of dimethyl carbonate and its derivatives. Green Chemistry 20, 28–85. https://doi.org/10.1039/C7GC01764B
- UNEP, 2021. Food Waste Index Report 2021 [WWW Document]. UNEP UN Environment Programme. URL http://www.unep.org/resources/report/unep-food-waste-indexreport-2021 (accessed 4.14.21).
- Unger, N., Razza, F., 2018. Food Waste Management (Sector) in a Circular Economy, in: Benetto, E., Gericke, K., Guiton, M. (Eds.), Designing Sustainable Technologies, Products and Policies: From Science to Innovation. Springer International Publishing, Cham, pp. 127–132. https://doi.org/10.1007/978-3-319-66981-6\_15
- Usmani, Z., Sharma, M., Karpichev, Y., Pandey, A., Chander Kuhad, R., Bhat, R., Punia, R., Aghbashlo, M., Tabatabaei, M., Gupta, V.K., 2020. Advancement in valorization technologies to improve utilization of bio-based waste in bioeconomy context.
  Renewable and Sustainable Energy Reviews 131, 109965. https://doi.org/10.1016/j.rser.2020.109965
- Van Ewijk, S., Park, J.Y., Chertow, M.R., 2018. Quantifying the system-wide recovery potential of waste in the global paper life cycle. Resources, Conservation and Recycling 134, 48–60. https://doi.org/10.1016/j.resconrec.2018.02.026
- Van Walsum, G.P., 2001. Severity Function Describing the Hydrolysis of Xylan Using Carbonic Acid, in: Davison, B.H., McMillan, J., Finkelstein, M. (Eds.), Twenty-Second Symposium on Biotechnology for Fuels and Chemicals, ABAB Symposium. Humana Press, Totowa, NJ, pp. 317–329. https://doi.org/10.1007/978-1-4612-0217-2\_27
- Varkolu, M., Velpula, V., Burri, D.R., Kamaraju, S.R.R., 2016. Gas phase hydrogenation of levulinic acid to γ-valerolactone over supported Ni catalysts with formic acid as hydrogen source. New J. Chem. 40, 3261–3267. https://doi.org/10.1039/C5NJ02655E

- Vyver, S.V. de, Thomas, J., Geboers, J., Keyzer, S., Smet, M., Dehaen, W., A. Jacobs, P.,
  F. Sels, B., 2011. Catalytic production of levulinic acid from cellulose and other biomass-derived carbohydrates with sulfonated hyperbranched poly(arylene oxindole)s. Energy & Environmental Science 4, 3601–3610. https://doi.org/10.1039/C1EE01418H
- Wambugu, C.W., Rene, E.R., van de Vossenberg, J., Dupont, C., van Hullebusch, E.D., 2019.Role of Biochar in Anaerobic Digestion Based Biorefinery for Food Waste. Frontiers in Energy Research 7.
- Wan, Z., Sun, Y., W. Tsang, D.C.W., Hou, D., Cao, X., Zhang, S., Gao, B., Sik Ok, Y., 2020. Sustainable remediation with an electroactive biochar system: mechanisms and perspectives. Green Chemistry 22, 2688–2711. https://doi.org/10.1039/D0GC00717J
- Wang, C., Zhang, Q., Chen, Y., Zhang, X., Xu, F., 2018. Highly Efficient Conversion of Xylose Residues to Levulinic Acid over FeCl <sub>3</sub> Catalyst in Green Salt Solutions. ACS Sustainable Chem. Eng. 6, 3154–3161. https://doi.org/10.1021/acssuschemeng.7b03183
- Wang, J., Cui, H., Wang, Y., Zhao, R., Xie, Y., Wang, M., Yi, W., 2020. Efficient catalytic conversion of cellulose to levulinic acid in the biphasic system of molten salt hydrate and methyl isobutyl ketone. Green Chem. 22, 4240–4251. https://doi.org/10.1039/D0GC00897D
- Wang, Q.-N., Weng, X.-F., Zhou, B.-C., Lv, S.-P., Miao, S., Zhang, D., Han, Y., Scott, S.L., Schüth, F., Lu, A.-H., 2019. Direct, Selective Production of Aromatic Alcohols from Ethanol Using a Tailored Bifunctional Cobalt–Hydroxyapatite Catalyst. ACS Catal. 9, 7204–7216. https://doi.org/10.1021/acscatal.9b02566
- Wang, R., Xie, X., Liu, Y., Liu, Z., Xie, G., Ji, N., Ma, L., Tang, M., 2015. Facile and Low-Cost Preparation of Nb/Al Oxide Catalyst with High Performance for the Conversion

of Kiwifruit Waste Residue to Levulinic Acid. Catalysts 5, 1636–1648. https://doi.org/10.3390/catal5041636

- Wettstein, S.G., Alonso, D.M., Chong, Y., Dumesic, J.A., 2012. Production of levulinic acid and gamma-valerolactone (GVL) from cellulose using GVL as a solvent in biphasic systems. Energy Environ. Sci. 5, 8199. https://doi.org/10.1039/c2ee22111j
- Wolfaardt, F.J., Fernandes, L.G.L., Oliveira, S.K.C., Duret, X., Görgens, J.F. and Lavoie, J.M., 2021. Recovery approaches for sulfuric acid from the concentrated acid hydrolysis of lignocellulosic feedstocks: A mini-review. Energy Convers. Manag.: X, 10, 100074. https://doi.org/10.1016/j.ecmx.2020.100074
- Xiong, X., Yu, I.K.M., Cao, L., Tsang, D.C.W., Zhang, S., Ok, Y.S., 2017. A review of biocharbased catalysts for chemical synthesis, biofuel production, and pollution control. Bioresource Technology 246, 254–270. https://doi.org/10.1016/j.biortech.2017.06.163
- Xiong, X., Yu, I.K.M., Chen, S.S., Tsang, D.C.W., Cao, L., Song, H., Kwon, E.E., Ok, Y.S.,
  Zhang, S., Poon, C.S., 2018. Sulfonated biochar as acid catalyst for sugar hydrolysis
  and dehydration. Catalysis Today 314, 52–61.
  https://doi.org/10.1016/j.cattod.2018.02.034
- Xiong, X., Yu, I.K.M., Dutta, S., Mašek, O., Tsang, D.C.W., 2021. Valorization of humins from food waste biorefinery for synthesis of biochar-supported Lewis acid catalysts.
  Science of The Total Environment 775, 145851. https://doi.org/10.1016/j.scitotenv.2021.145851
- Xiong, X., Yu, I.K.M., Tsang, D.C.W., Bolan, N.S., Sik Ok, Y., Igalavithana, A.D., Kirkham, M.B., Kim, K.-H., Vikrant, K., 2019. Value-added chemicals from food supply chain wastes: State-of-the-art review and future prospects. Chemical Engineering Journal 375, 121983. https://doi.org/10.1016/j.cej.2019.121983

- Xu, H., Feng, L., Wu, G., Zhang, Q., 2021. Evolution of structural properties and its determinants of global waste paper trade network based on temporal exponential random graph models. Renewable and Sustainable Energy Reviews 149, 111402. https://doi.org/10.1016/j.rser.2021.111402
- Xu, Z., Huang, F., 2014. Pretreatment methods for bioethanol production. Applied biochemistry and biotechnology 174, 43–62. https://doi.org/10.1007/s12010-014-1015-y
- Yabushita, M., Kobayashi, H., Fukuoka, A., 2014. Catalytic transformation of cellulose into platform chemicals. Applied Catalysis B: Environmental, Advances in Catalysis for Biomass Valorization 145, 1–9. https://doi.org/10.1016/j.apcatb.2013.01.052
- Yamada, T., Aratani, M., Kubo, S., Ono, H., 2007. Chemical analysis of the product in acidcatalyzed solvolysis of cellulose using polyethylene glycol and ethylene carbonate. Journal of Wood Science 53, 487–493. https://doi.org/10.1007/s10086-007-0886-8
- Yan, L., Yang, N., Pang, H., Liao, B., 2008. Production of Levulinic Acid from Bagasse and Paddy Straw by Liquefaction in the Presence of Hydrochloride Acid. CLEAN – Soil, Air, Water 36, 158–163. https://doi.org/10.1002/clen.200700100
- Yang, C., Wang, S., Yang, J., Xu, D., Li, Y., Li, J., Zhang, Y., 2020. Hydrothermal liquefaction and gasification of biomass and model compounds: a review. Green Chem. 22, 8210– 8232. https://doi.org/10.1039/D0GC02802A
- Yang, L., Tsilomelekis, G., Caratzoulas, S., Vlachos, D.G., 2015. Mechanism of Brønsted Acid-Catalyzed Glucose Dehydration. ChemSusChem 8, 1334–1341. https://doi.org/10.1002/cssc.201403264
- Yang, Y., Tilman, D., 2020. Soil and root carbon storage is key to climate benefits of bioenergy crops. Biofuel Research Journal 7, 1143–1148. https://doi.org/10.18331/BRJ2020.7.2.2

- Yao, J., Xie, X., Shi, Q., 2021. Improving enzymatic saccharification of Chinese silvergrass by FeCl<sub>3</sub>-catalyzed γ-valerolactone/water pretreatment system. Renewable Energy 177, 853–858. https://doi.org/10.1016/j.renene.2021.06.009
- Yoo, C.G., Meng, X., Pu, Y., Ragauskas, A.J., 2020. The critical role of lignin in lignocellulosic biomass conversion and recent pretreatment strategies: A comprehensive review. Bioresource Technology 301, 122784. https://doi.org/10.1016/j.biortech.2020.122784
- Yu, I.K.M., Chen, H., Abeln, F., Auta, H., Fan, J., Budarin, V.L., Clark, J.H., Parsons, S., Chuck, C.J., Zhang, S., Luo, G., Tsang, D.C.W., 2020a. Chemicals from lignocellulosic biomass: A critical comparison between biochemical, microwave and thermochemical conversion methods. Critical Reviews in Environmental Science and Technology 1–54. https://doi.org/10.1080/10643389.2020.1753632
- Yu, I.K.M., Fan, J., Budarin, V.L., Bouxin, F.P., Clark, J.H., Tsang, D.C.W., 2020b. NaClpromoted phase transition and glycosidic bond cleavage under microwave heating for energy-efficient biorefinery of rice starch. Green Chem. 22, 7355–7365. https://doi.org/10.1039/D0GC01761B
- Yu, I.K.M., Fan, J., L. Budarin, V., P. Bouxin, F., H. Clark, J., W. Tsang, D.C.W., 2020c. Evidences of starch–microwave interactions under hydrolytic and pyrolytic conditions. Green Chemistry 22, 7109–7118. https://doi.org/10.1039/D0GC02644A
- Yu, I.K.M., Tsang, D.C.W., 2017. Conversion of biomass to hydroxymethylfurfural: A review of catalytic systems and underlying mechanisms. Bioresource Technology 238, 716–732. https://doi.org/10.1016/j.biortech.2017.04.026
- Yu, I.K.M., Tsang, D.C.W., Chen, S.S., Wang, L., Hunt, A.J., Sherwood, J., De Oliveira Vigier,K., Jérôme, F., Ok, Y.S., Poon, C.S., 2017a. Polar aprotic solvent-water mixture as the

medium for catalytic production of hydroxymethylfurfural (HMF) from bread waste. Bioresource Technology 245, 456–462. https://doi.org/10.1016/j.biortech.2017.08.170

- Yu, I.K.M., Tsang, D.C.W., Su, Z., Yip, A.C.K., Shang, J., Ok, Y.S., Kim, K.-H., Poon, C.S., 2018a. Contrasting Roles of Maleic Acid in Controlling Kinetics and Selectivity of Sn(IV)- and Cr(III)-Catalyzed Hydroxymethylfurfural Synthesis. ACS Sustainable Chemistry & Engineering 6, 14264–14274. https://doi.org/10.1021/acssuschemeng.8b02931
- Yu, I.K.M., Tsang, D.C.W., Yip, A.C.K., Chen, S.S., Ok, Y.S., Poon, C.S., 2017b. Valorization of starchy, cellulosic, and sugary food waste into hydroxymethylfurfural by one-pot catalysis. Chemosphere 184, 1099–1107. https://doi.org/10.1016/j.chemosphere.2017.06.095
- Yu, I.K.M., Tsang, D.C.W., Yip, A.C.K., Chen, S.S., Ok, Y.S., Poon, C.S., 2016. Valorization of food waste into hydroxymethylfurfural: Dual role of metal ions in successive conversion steps. Bioresource Technology 219, 338–347. https://doi.org/10.1016/j.biortech.2016.08.002
- Yu, I.K.M., Tsang, D.C.W., Yip, A.C.K., Hunt, A.J., Sherwood, J., Shang, J., Song, H., Ok, Y.S., Poon, C.S., 2018b. Propylene carbonate and γ-valerolactone as green solvents enhance Sn(IV)-catalysed hydroxymethylfurfural (HMF) production from bread waste. Green Chemistry 20, 2064–2074. https://doi.org/10.1039/C8GC00358K
- Yu, I.K.M., Xiong, X., Tsang, D.C.W., Wang, L., Hunt, A.J., Song, H., Shang, J., Ok, Y.S., Poon, C.S., 2019. Aluminium-biochar composites as sustainable heterogeneous catalysts for glucose isomerisation in a biorefinery. Green Chem. 21, 1267–1281. https://doi.org/10.1039/C8GC02466A

- Zhang, C., Su, H., Baeyens, J., Tan, T., 2014. Reviewing the anaerobic digestion of food waste for biogas production. Renewable and Sustainable Energy Reviews 38, 383–392. https://doi.org/10.1016/j.rser.2014.05.038
- Zhang, L., Yu, H., Wang, P., Li, Y., 2014. Production of furfural from xylose, xylan and corncob in gamma-valerolactone using FeCl3·6H2O as catalyst. Bioresource Technology 151, 355–360. https://doi.org/10.1016/j.biortech.2013.10.099
- Zhang, T., Li, W., Xu, Z., Liu, Q., Ma, Q., Jameel, H., Chang, H., Ma, L., 2016. Catalytic conversion of xylose and corn stalk into furfural over carbon solid acid catalyst in γ-valerolactone. Bioresource Technology 209, 108–114. https://doi.org/10.1016/j.biortech.2016.02.108
- Zhang, Z., O'Hara, I.M., Rackemann, D.W., Doherty, W.O.S., 2013. Low temperature pretreatment of sugarcane bagasse at atmospheric pressure using mixtures of ethylene carbonate and ethylene glycol. Green Chem. 15, 255–264. https://doi.org/10.1039/C2GC36323B
- Zhao, Z., Bababrik, R., Xue, W., Li, Y., Briggs, N.M., Nguyen, D.-T., Nguyen, U., Crossley, S.P., Wang, S., Wang, B., Resasco, D.E., 2019. Solvent-mediated charge separation drives alternative hydrogenation path of furanics in liquid water. Nat Catal 2, 431–436. https://doi.org/10.1038/s41929-019-0257-z
- Zheng, M., Pang, J., Sun, R., Wang, A., Zhang, T., 2017. Selectivity Control for Cellulose to Diols: Dancing on Eggs. ACS Catal. 7, 1939–1954. https://doi.org/10.1021/acscatal.6b03469
- Zhi, Z., Li, N., Qiao, Y., Zheng, X., Wang, H., Lu, X., 2015. Kinetic study of levulinic acid production from corn stalk at relatively high temperature using FeCl<sub>3</sub> as catalyst: A simplified model evaluated. Industrial Crops and Products 76, 672–680. https://doi.org/10.1016/j.indcrop.2015.07.058

- Zhou, X., Li, W., Mabon, R., J. Broadbelt, L., 2018. A mechanistic model of fast pyrolysis of hemicellulose. Energy & Environmental Science 11, 1240–1260. https://doi.org/10.1039/C7EE03208K
- Zhou, Z., Liu, D., Zhao, X., 2021. Conversion of lignocellulose to biofuels and chemicals via sugar platform: An updated review on chemistry and mechanisms of acid hydrolysis of lignocellulose. Renewable and Sustainable Energy Reviews 146, 111169. https://doi.org/10.1016/j.rser.2021.111169
- Zhu, Z., Rezende, C.A., Simister, R., McQueen-Mason, S.J., Macquarrie, D.J., Polikarpov, I., Gomez, L.D., 2016. Efficient sugar production from sugarcane bagasse by microwave assisted acid and alkali pretreatment. Biomass and Bioenergy 93, 269–278. https://doi.org/10.1016/j.biombioe.2016.06.017
- Zimmerman, J.B., Anastas, P.T., Erythropel, H.C., Leitner, W., 2020. Designing for a green chemistry future. Science 367, 397–400. https://doi.org/10.1126/science.aay3060