VALORIZATION OF BANANA PEELS INTO 5-HYDROXYMETHYLFURFURAL

By

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Abstract

As the global population continues to increase, the accumulation of food wastes is becoming a major problem, causing resource depletion and a wide range of environmental implications, including greenhouse gas emissions. A viable way to reduce environmental pollution and achieve a sustainable bioeconomy is to convert food wastes into high-end bioproducts.

5-hydroxymethylfurfural (HMF) is a promising platform chemical that can be produced from wasted food such as fruits and vegetables. One of the potential HMF derivatives is 2,5-furandicarboxylic acid, which has applications in the synthesis of metal-organic framework materials and polymers, among others. Currently, the conversion of HMF from food wastes suffers from low production yield mainly due to a limited hydrolysis of lignocellulosic biomass and the low selectivity of the conventional catalysts. HMF conversion from food wastes can be improved by combining an appropriate pretreatment with a high-performance catalyst-solvent system.

Bananas are one of the most consumed foods in the world. Banana peel (BP), a widely discarded waste product, has a high carbohydrate content, making it an appealing feedstock for HMF production. In this study, BP was efficiently hydrolyzed under solvent-free mechanoenzymatic conditions, without the need for chemical pretreatment. Mechanoenzymatic hydrolysis is a promising environmentally friendly alternative to conventional enzyme hydrolysis of BP. Under optimal reaction conditions, mechanoenzymatic hydrolysis of BP produced higher yields of glucose (40.5 g/100 g dry BP) and fructose (17.2 g/100 g dry BP) than chemical hydrolysis (33 and 14.5 g/100 g dry BP glucose and fructose, respectively). The $AlCl_3 \times H_2O$-DMSO/H_2O system was used to transform the crude sugars generated by hydrolysis, resulting in 71.9 mol% HMF production.

Résumé

Alors que la population mondiale continue d'augmenter, l'accumulation de déchets alimentaires devient un problème majeur, entraînant l'épuisement des ressources et un large éventail d'implications environnementales, y compris les émissions de gaz à effet de serre. Un moyen viable de réduire la pollution de l'environnement et de parvenir à une bioéconomie durable est de convertir les déchets alimentaires en bioproduits haut de gamme.

L'hydroxyméthylfurfural (HMF) est un produit chimique prometteur qui peut être produit à partir de déchets alimentaires tels que des fruits et des légumes. L'un des dérivés potentiels du HMF est l'acide 2,5-furane dicarboxylique, qui a des applications tels que pour la synthèse de certains réseaux métallo-organiques, et la synthèse de polymères. Actuellement, la conversion du des résidus alimentaires en HMF n'est pas optimale due à faible rendement de production principalement en raison d'une hydrolyse limitée de la biomasse lignocellulosique, ainsi que de la faible sélectivité des catalyseurs conventionnels. La conversion du HMF à partir de déchets alimentaires peut être améliorée en combinant un prétraitement approprié avec un système catalyseur-solvant à haute performance.

Les bananes sont l'un des aliments les plus consommés au monde. La pelure de banane (BP), un déchet largement rejeté, a une teneur élevée en glucides, ce qui en fait une matière première attrayante pour la production de HMF. Dans cette étude, la BP a été efficacement hydrolysée dans des conditions mécano-enzymatiques sans solvant ni de prétraitement chimique. L'hydrolyse mécano-enzymatique est une alternative écologique prometteuse à l'hydrolyse enzymatique conventionnelle des BP. Dans des conditions de réaction optimales, l'hydrolyse mécano-enzymatique des BP a produit des rendements plus élevés en glucose (40,5% massique) et en fructose (17,2% massique) que l'hydrolyse chimique (glucose et fructose de 33 et 14,5% massique,

respectivement). Les sucres bruts générés après l’hydrolyse ont été directement transformés en HMF en utilisant le système $AlCl_3 \times H_2O$-DMSO/H_2O dans un rendement de 71,9% molaire.

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List of Abbreviations

AAO	Aryl alcohol oxidases
ACN	Acetonitrile
[BMIM]Cl	1-butyl-3-methylimidazolium chloride
BGL	β-glucosidase
BOD	Biochemical oxygen demand
BP	Banana peel
BXL	Beta-xylosidase
CA	Citric acid
CBH	Cellobiohydrolases
CBM	Cellulose binding domain
CD	Catalytic domain
CDH	Cellobiose dehydrogenase
COD	Chemical oxygen demand
DGE	3-deoxyglucos-2-ene
DGO	3-deoxyglucosone
DIW	Deionized water
DMA	Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DOE	US Department of Energy
DTG	Derivative thermogravimetry
EDTA	Ethylenediaminetetraacetic acid
EG	Endoglucanase
EU	European Union
FA	Formic acid
FAO	Food and Agriculture Organization
FDCA	2,5-furandicarboxylic acid
FFCA	5-formyl-2-furancarboxylic acid
FVW	Fruit and vegetable waste

FW	Food waste
GHG	Greenhouse gas
GVL	γ-valerolactone
HCl	Hydrochloric acid
HFIP	Hexafluoroisopropanol
HHMDHC	4-hydroxy-5-(hydroxymethyl)- 4,5-dihydrofuran-2-carbaldehyde
HMF	5-hydroxymethylfurfural
HMFCA	5-hydroxymethyl-2-furancarboxylic acid
HMHMTD	2-(hydroxymethyl)-5-(hydroxylmethylene)-tetrahydrofuran-3,4-diol
HPLC	High-performance liquid chromatography
ILs	Ionic liquids
LAG	Liquid-assisted grinding
LDA	Lignin-degrading auxiliary enzymes
LiP	Lignin peroxidases
LME	Lignin-modifying enzymes
LPMO	Lytic-polysaccharide monooxygenase
MnP	Manganese peroxidases
MPW	Meat and poultry waste
MTHF	Methyltetrahydrofuran
OSB	Oriented strand board
POX	Pyranose 2-oxidase
RAging	Reactive aging
RID	Refractive index detector
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
VFA	Volatile fatty acids
VP	Versatile peroxidases
XLN	Endoxylanases
ZrO	Zirconia

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Contribution of Authors

This thesis is submitted in the form of original papers submitted to peer-reviewed journals. The candidate, A K M Al Amin Leamon, was responsible for conducting the experiments, handling the data analysis, as well as the preparation of the first manuscript draft and the thesis. Prof Marie-Josée Dumont, supervisor of the candidate and formerly Associate Professor in the Department of Bioresource Engineering of McGill University, Prof. Valérie Orsat, co-supervisor of the candidate, Professor in the Department of Bioresource Engineering of McGill University, and Prof. Karine Auclair, Professor in the Department of Chemistry of McGill University contributed to all aspects of this research work. They provided assistance, including organizing and directing research, editing and revising the thesis and manuscripts prior to submission for publication. The details of the manuscripts that have been submitted for publication are provided below:

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Chapter 1

Introduction

General Introduction

Every year, around 30% of the food produced globally is reported as waste (Ali et al., 2022). Food waste can occur at any stage of the food production, including harvesting, storage, transportation, and consumption. The amount of waste varies depending on the country, economic growth, and level of income. As food production is a resource-intensive process, food waste has indirect negative effects on the economy and environment, leading to food insecurity, deforestation, air and water pollution, and greenhouse gas emissions (Schanes et al., 2018). To lessen the impact of food loss as waste, sustainable food waste management is required. Converting food waste into useful bioproducts is one of the most promising methods for managing food waste. The main advantages of using food waste as a raw material for alternative fuel and chemical production are that it reduces our reliance on fossil fuels and mitigates the greenhouse gas emissions and toxicity of commercial chemical products (Trivedi et al., 2020). Recently, catalytic transformation of food waste into furanic compounds has gained increasing attention. HMF is a promising platform chemical for the production of valuable compounds. The chemical structure of HMF makes it a versatile intermediate in the manufacture of high-quality fuels and chemicals, such as 2,5-furandicarboxylic acid (FDCA). FDCA serves as a building block for a variety of materials, including polyamides, polyesters, and polyurethanes (Chen et al., 2021; Yu and Tsang, 2017).

Bananas are an important food crops with excellent acceptability, easy access, low cost, and are available in large quantities, particularly in tropical and subtropical regions. Banana peel (BP), a typically discarded waste product, accounts about 35-40% of the mass of fresh fruit (Pereira et al., 2021). With the improvement of food processing technology, bananas are now utilized to make a variety of food products, including chips, flours, dried pulps, and jam. As a result, a significant amount of BP is generated as waste each year from banana processing. This type of fruit waste is either disposed of in landfills or used as fertilizer on agricultural land, neither of which is considered a highly viable proposition (Emaga et al., 2008). Since BP contains a high carbohydrate content, it can be an attractive feedstock for the manufacturing of value-added products such as HMF.

Hydrolysis is the initial step in converting plant biomass to HMF. Traditionally, chemical reagents such as acids are employed to depolymerize lignocellulosic biomass in order to generate sugars for HMF production. However, hydrolysis using chemical reagents has a number of downsides, such as high toxicity, harsh reaction conditions, and conversion of sugar into various byproducts. Microbial enzymes, on the other hand, are easier to handle, function under milder reaction conditions, and provide a cleaner and more environmentally friendly approach of hydrolyzing lignocellulosic biomass (Hammerer et al., 2018; Kaabel et al., 2020). However, enzymatic hydrolysis is traditionally carried out in diluted aqueous solvent conditions, which suffer from poor hydrolysis of insoluble fractions of lignocellulose and generate significant amounts of wastewater at the end of the hydrolysis. But recently, it has been discovered that enzymes can function very well in the absence of bulk organic or aqueous solvent using mechanochemistry-based process termed as reactive aging (RAging). The RAging process is based on alternate cycles of milling the substrate with enzymes in the presence of minuscule amounts of liquid and static incubation at a mild temperature (45–55 °C). As the hydrolysis is carried out with near-stoichiometric volumes of water, the RAging process also mimics the natural microbial hydrolysis that occurs under moist environmental conditions (Hammerer et al., 2020b, 2020a, 2018; Kaabel et al., 2020). In addition, with the application of RAging process, it is possible to obtain significantly higher sugar yields in a shorter time period than with standard enzymatic hydrolysis (Hammerer et al., 2020a).

Study Objectives

Although food waste is an appealing substrate for furanics production, their utilization for HMF production is currently challenging. Poor hydrolysis of the lignocellulosic fraction, limited selectivity of catalysts, and the formation of byproducts are the primary obstacles to HMF production from food wastes. Therefore, the primary objective of this thesis was to hydrolyze BP utilizing a novel process known as solvent-free mechanoenzymatic hydrolysis and to convert the resultant sugars into HMF. The specific objectives of this research are stated as follows:

1. To review existing literature on food waste valorization to HMF, identify the key challenges in food waste valorization, and suggest potential research directions to enhance their conversion to HMF.
2. To determine the optimum reaction conditions for BP mechanoenzymatic hydrolysis. This entailed optimizing the enzyme concentration and reaction volume, as well as assessing the influence of premilling, milling duration, and RAging cycles on BP hydrolysis under mechanochemical conditions. The conversion of sugars produced by the mechanoenzymatic hydrolysis of BP into HMF.

Chapter 2

Valorization of food wastes into furanics: A review of catalytic systems, challenges and opportunities

Abstract

Food waste (FW) has been a global environmental problem due to the massive amounts being generated each year. Converting FW into 5-hydroxymethylfurfural (HMF) is a promising option for its sustainable management. HMF is a versatile platform chemical that can be used to synthesize a wide range of value-added chemicals, including 2,5-furandicarboxylic acid (FDCA). FDCA has application in diverse fields, particularly in the synthesis of petroleum-based terephthalic acid that is used in biodegradable plastic production. This review presents an overview on the synthesis of furanic compounds from FW. In particular, the review discusses the sources of FW, their management approaches, current achievements in FW conversion to HMF along with the challenges and possible solution to improve conversion rates. The different solvent and catalytic systems for HMF and FDCA production have been reviewed including their advantages and disadvantages for large-scale and sustainable manufacturing practices.

Keywords: waste valorization, HMF, FDCA, Lewis/Brønsted acid, pretreatment

1. Introduction

Diminishing fossil fuel resources and increasing environmental crises from climate change have urged a shift towards biomass valorization as an alternative to replace fossil fuels. The concept of a ‘zero waste bioeconomy’ is now encouraging researchers to utilize waste biomass as a feedstock for renewable fuel and chemical production. FW is the most frequently generated biowaste and has been identified as a significant economic and environmental problem. Globally around 1.3 billion tonnes of food are wasted per year which amounts to one-third of the total food produced annually, with a cost of around US$ 936 billion (Sharma et al., 2021). It is reported that, on a per capita basis, developed countries generate more FW than developing countries. For example, in North America and Europe, an average person generates around 280-300 kg of FW per year whereas in sub-Saharan Africa the amount is approximately 170 kg (Gustavsson et al., 2011). The majority of the wasted food in North America and Europe is disposed in landfills which causes serious environmental deterioration. Disposing of FW in landfills releases greenhouse gases (GHGs) such as CO_2 and methane, contributing to climate change. As per a report of the Food and Agriculture Organization (FAO), FW mismanagement contributes around 8% of total greenhouse gas released in the environment per year (Sharma et al., 2021). While preventative efforts can be made to reduce FW, such as optimizing production and post-harvest processes or redistributing excess food, some amount of FW cannot be avoided due to the non-edible portions of foods. The reduction of these unavoidable FW can only be achieved with proper waste management and reuse practices and policies. To manage FW, several approaches have been taken, for instance, composting, landfill, incineration, gasification, waste to energy and extraction of value-added compounds. Among these strategies, converting waste to energy and extracting value-added compounds are the two most profitable ways to manage FW (Mak et al., 2020). FW contains around 60% carbohydrates, implying that they can be converted into a range of bio-commodity chemicals and bioenergy by applying various chemical and biological processes (Yukesh et al., 2020b). HMF is one of the valuable chemicals that can be produced utilizing FW. HMF is a furan-based platform chemical naturally found in honey, vegetables, coffee, and beverages. HMF has aldehyde, alcohol groups and a furan ring system enabling it to act as a versatile intermediate for further transformation into different value-added bioproducts, for instance, chemicals, plastic, fiber and polymers which are usually synthesized from petroleum (Mukherjee et al., 2015). Moreover, selective oxidation of HMF generates different compounds such as 5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA) and 2,5-furandicarboxylic acid (FDCA) (Chen et al., 2021). Among them, FDCA is considered as the most promising candidate in the furan family, and in 2004 it was listed among the top 12 most promising bio-based chemicals by the US Department of Energy (Werpy and Petersen, 2004). The production of FDCA is particularly appealing due to its unique properties. FDCA functions as a monomer in a range of polymeric materials such as polyamides, polyesters, and polyurethanes. However, the promising status of FDCA is undermined by the high production costs of HMF. Although HMF can be synthesized using monomeric and polymeric carbohydrates, such as fructose, glucose, sucrose, starch, inulin and cellulose, it is most commonly synthesized from high-cost fructose. Fructose is preferred because its production of HMF is more efficient and straightforward as compared to other sugars such as glucose, which first must be isomerized into fructose (Fig. 2.1). As a result, HMF cost is currently high (Menegazzo et al., 2018). Therefore, since an important fraction of FW does contain carbohydrates, replacing fructose with FW could make HMF production economically competitive.

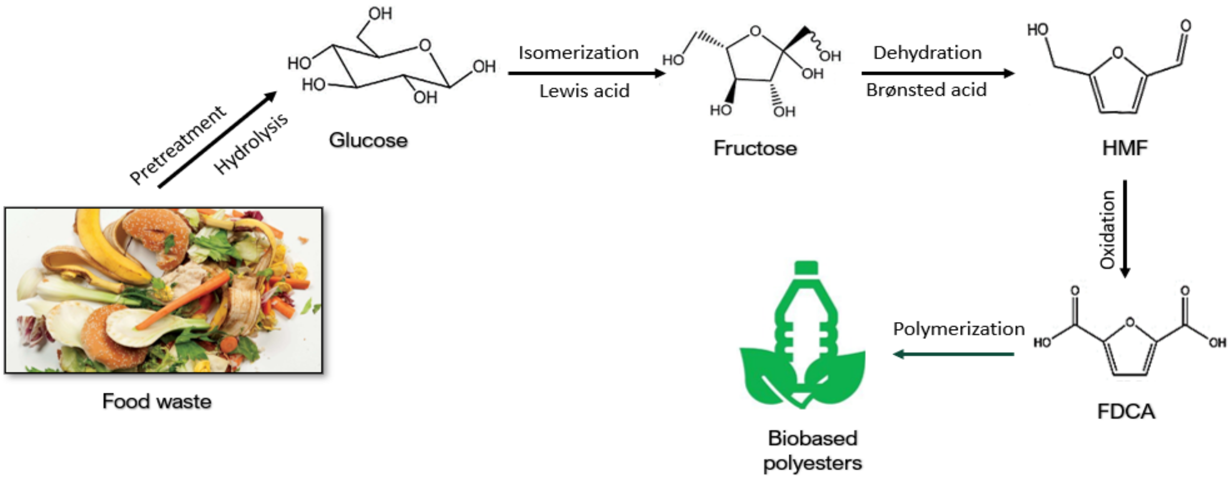

Figure 2.1: Production of HMF and FDCA from FW

The aim of this review is to discuss the catalytic conversion of FW to furanic compounds. The review presents a brief overview of the global FW generation scenario and existing FW management strategies (sections 2 and 3). Section 4 summarizes the common solvents and catalytic systems utilized in the HMF and FDCA production processes, as well as the current state of FW valorization to furanics, particularly HMF. Section 5 addresses the challenges associated with FW valorization, and section 6 suggests possible research directions to improve its conversion to HMF.

2. Different types of food waste

2.1. Fruit and vegetable waste

Fruit and vegetable waste (FVW) represents one of the major sources of municipal solid waste. The amount of FVW is increasing rapidly because of the growing demand and industrial processing of edible portions of fruits and vegetables. Around 25% to 30% of fruits and vegetables are estimated to be wasted. Food loss and waste occur at all stages from harvest to consumption, including agriculture production, post-harvest processing, distribution, and at the point of consumption in households (Sagar et al., 2018). According to an FAO report (FAO 2011), the majority of FVW is produced before reaching the consumer (Gustavsson et al., 2011). In developing countries, wastes are mostly generated during the production, post-harvesting and processing stages of crops. In addition, the absence of effective conservation techniques causes significant wastage of fruits and vegetables in these countries. However, in developed countries, food losses mainly occur due to programmed overproduction and post-harvest crop evaluation to meet the required quality standards for retailers (Plazzotta et al., 2017). Besides, FVW generating at the post-consumer phase is very significant, particularly in developed countries. Kader (2005) reported that, in the United States, on average, 12% of fresh fruits and vegetables are lost between production and consumption sites, depending on the commodity. In many countries, FVW are disposed of in landfills, resulting in environmental pollution. To enable sustainable waste management, many recycling strategies have been developed as an alternative way of FVW disposal. For example, FVW are reused as animal feed and organic fertilizer in many countries. However, the low protein content limits its effectiveness as an animal feed. In addition, FVW contains a high amount of water making it susceptible to microbial contamination. A partial drying process is required immediately prior to processing into animal feed (Van Dyk et al., 2013). FVW can be attractive sources of feedstock to extract value-added compounds such as pectin, fiber, polyphenol, oil, and dyes (Plazzotta et al., 2017; Van Dyk et al., 2013). Among the different value-added products extracted from FVW, pectin and fibers have important applications in the food industry. Pectin is commonly used in the food industry as a thickener, stabiliser and gelling agent, and fibres are supplemented in foods to help prevent diseases (Bhushan et al., 2008; Emaga et al., 2008). Phenolic compounds present in FVW also act as important sources of antioxidants, antimicrobials, anticancer and cardiovascular protective compounds (Van Dyk et al., 2013). FVW are also rich in carbohydrates. Sugars from FVW usually are processed via aerobic and anaerobic fermentation to produce bioethanol, biogas and biohydrogen. The fermentation products of FVW are used as fuel or as a source to generate heat and electricity (Van Dyk et al., 2013).

2.2. Meat and poultry waste

Meat and poultry waste (MPW) are mainly derived from slaughterhouses. Slaughterhouse waste contains mostly animal byproducts such as bones, tendons, skin, the contents of the gastrointestinal tract, blood and internal organs, which are not intended for direct human consumption (Jayathilakan et al., 2012). Waste from a slaughterhouse is commonly utilized for animal feed production through the rendering process. However, the conversion of slaughterhouse waste to animal feed is considered to be of little economic value, and there is a risk of spreading bovine spongiform encephalopathy and other diseases, making the conventional use of animal byproducts as animal feed less appealing (Adhikari et al., 2018). Therefore, alternative approaches have been taken to increase the value of animal waste. MPW are rich in organic compounds, particularly protein and fat. Because of the organic content, anaerobic digestion is frequently utilized for MPW disposal (Palatsi et al., 2011). Anaerobic digestion of MPW typically has a slow hydrolysis rate due to the presence of hardly degradable animal byproducts (Vavilin et al., 2008). Additionally, when substantial amounts of intermediate products of protein and lipid degradation accumulate, such as ammonia and long-chain fatty acids, they might hinder the anaerobic digestion. To improve digestion efficiency, MPW are now co-digested with other organic waste such as industrial, agricultural, or domestic waste (Angelidaki and Ellegaard, 2003). Proteins can be recovered from inedible tissues of MPW with the aid of heat, chemicals and enzymes. For infectious tissues, thermal or alkaline hydrolysis is needed to deactivate pathogens. The extracted proteins are used to prepare protein-based adhesives for a variety of value-added applications, including wood adhesives for the manufacture of veneer plywoods, fiberboard, blockboards, flakeboards, oriented strand board (OSB), medium as well as high density fiberboards, flooring substrates, and laminated veneer lumber (Adhikari et al., 2018).

2.3. Dairy industry waste

The number of large-scale and small-scale dairies has risen sharply throughout the world because of the high demand for milk and milk products (Kushwaha et al., 2011). According to a FAO report (FAO, 2021a), global milk production is expected to increase 1.7% per annum, reaching 1020 million tonnes by 2030. In the dairy industry, milk is processed into different food products such as butter, cheese, and yogurt. During cleaning and washing operations, dairy industries release a large amount of wastewater into drains, which is estimated to be roughly 2% of total milk processed (Kushwaha et al., 2011; Munavalli and Saler, 2009). The wastewater released from dairy industries tends to have a high Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) and contains significant quantities of minerals, proteins, fats, dissolved sugars, inorganic salt, casein, detergents and sanitizing agents (Kushwaha et al., 2011). For example, the average COD and BOD values of dairy industry effluents are 1448 and 650 mg/L, respectively (Shivsharan et al., 2013). However, the properties of dairy effluents are generally influenced by the amount of milk processed and the types of dairy products (Sinha et al., 2019). Since dairy wastewater contains high concentrations of organic compounds, these effluents can cause serious environmental pollution if discharged untreated. Nutrients and detergents present in the dairy waste can deteriorate receiving water bodies by causing eutrophication, which is damaging for aquatic life (Demirel et al., 2005; Kushwaha et al., 2011). Therefore, it is important to treat dairy wastewater using appropriate methods before discharging. Various treatment methods have been applied to treat dairy wastewater such as physicochemical and biological methods. Biological methods are usually preferred to treat dairy wastewater since the physicochemical methods are expensive and inefficient in removing soluble COD (Vidal et al., 2000). Commonly employed biological methods include aerobic treatment such as aerated lagoons, activated sludge processes, trickling filters and rotating biological contactors, and anaerobic treatments such as anaerobic sludge blanket reactors, expanded granular sludge bed and anaerobic filters (Vidal et al., 2000). Under aerobic conditions, microorganisms degrade organic substances to carbon dioxide and water. But aerobic treatment of dairy wastewater requires high energy and may suffer from bulking and excessive biomass growth. In contrast, under anaerobic conditions, the high organic content of dairy effluents can operate as a potential carbon source for bacterial growth and can easily be converted to clean energy sources like hydrogen and methane gases. Additionally, anaerobic treatments have several advantages over aerobic methods, including the absence of need for aeration, a lower area requirement, and a lower amount of excess sludge production (Demirel et al., 2005; Vidal et al., 2000).

2.4. Cereals and grains processing waste

Cereals and grains have been considered a key component of the everyday human diet for thousands of years. According to a recent report from the FAO, the total cereal production reached 2979 million tonnes and the top cereals produced, ranked on the basis of tonnage (in million tonnes), are maize (1149), wheat (766), rice (755) and barley (159) (FAOSTAT, 2019). Cereals are commonly processed by dry or wet milling. Dry milling is commonly used to remove exterior fibrous debris and germ from wheat and rye, whereas wet milling is used to produce starch and gluten from corn and wheat. In addition, pearling and malting are applied for cereal processing. Pearling, which is similar to dry milling, is an abrasive technique generally applied for rice, oat and barley processing, which intends to obtain polished grain. Malting, which consists of germinating followed by drying the grain, is applied for alcoholic beverages production with barley, wheat, and corn (Papageorgiou and Skendi, 2018). During cereal processing, byproducts such as bran, seed coats consisting of the aleurone and subaleurone layers, and germ are generated. These byproducts are rich in lignocellulosic substrates, vitamins, lipids, minerals, and phenolic compounds. The byproducts from cereal processing are traditionally utilized as animal feed because of the high nutritional content. Due to high carbohydrates contents, these byproducts are now considered as a potential feedstock for biorefineries. The polysaccharides present in grain byproducts are transformed into simple sugars such as glucose, mannose, and xylose during the biorefinery processes. The simple sugars are later converted to fuel and chemicals such as ethanol, butanol, glycerol, lactic acid, succinic acid and HMF (Uçar et al., 2018). Apart from these, cereal byproducts are also utilized in the pharmaceutical industry as growth media for microbial culture or the production of antibiotics (Papageorgiou and Skendi, 2018). Besides, cereal's brans are an important source of healthy nutrients. It is reported that bioactive compounds are mostly concentrated in the grain's outer layer, implying that cereal wholemeal contains significantly more bioactive compounds than white flour. However, some of the bioactive compounds are difficult to access using conventional milling techniques as they are trapped in strong cell wall structures in the peripheral layer. Bohm et al. (2011) developed a method for isolating the aleurone layer, which is the innermost layer of the wheat bran protein containing minerals, phytates, B vitamins such as niacin and folates, and lipidic substances such as plant sterols. The dietary fiber and bioactive compounds extracted from the cereals bran play an important role in the prevention of cardiovascular disease, obesity, diabetes, and cancer (Brouns et al., 2012; Delcour et al., 2012).

3. Current status of food waste management

The most commonly employed FW management practices are animal feeding, composting, incinerating, anaerobic digestion and landfilling.

3.1. Landfilling

Landfilling or dumping is the most widely practiced waste management process, especially in developing countries where around 90% of total FW is disposed in landfills (Thi et al., 2015). While this process is attractive for large cities, it lacks overall sustainability because it contributes to serious environmental problems such as GHG emissions, groundwater contamination, dust, smog, and odors associated with organic matter decomposition creating poor environmental conditions in surrounding areas. Additionally, landfilling can mis-use valuable resources, such as agricultural lands used for landfilling, as well as cause economic losses through incurred costs for transportation and landfill management (Adhikari et al., 2009).

3.2. Incineration

Incineration is considered a ‘quick-fix solution’ to reduce waste. This method is used in many countries for waste disposal including the United States (Thi et al., 2015). It is a thermal process that involves the burning of waste materials to 1200 °C to generate heat and combustion products such as gases and ash. Incineration can be carried out near the waste collection area and the heat generated can be applied to municipal heating systems, or to generate steam for electricity generation. Incineration is the best option to treat hazardous wastes since high temperatures can destroy pathogens and toxins. While incineration provides advantages for solid waste disposal, it is not ideal for processing wastes with a high moisture content. Since FW has a very high moisture content, the incineration method is ill-suited (Otles and Kartal, 2018).

3.3. Animal feed

The utilization of FW as animal feed is a cost-effective route for its management. FW is rich in major nutrients for animal nourishment and has been utilized as animal feed in many parts of the world for a long time. Repurposing FW to animal feed helps in alleviating food competition between humans and animals by providing alternative of cereal grains and plant protein for both monogastric and ruminant livestock species. Additionally, it contributes to mitigating the growing demand for animal feed as global demand for animal products has increased (Dou et al., 2018; Lin et al., 2013). Utilizing FW as animal feed is becoming common practice in the United States. In countries such as Japan, South Korea, and Taiwan, 33%, 81% and 72.1% of total FW is recycled for animal feed, respectively (Thi et al., 2015). However, there is a safety concern with using FW for animal feeding since the waste may include pathogenic bacteria and viruses. In 2001, feeding swine with uncooked FW caused an outbreak of mouth disease in the United Kingdom (UK). As a result, UK and the European Union (EU) banned recycling FW that contains meat, fish and other animal products. Different treatment procedures are now available to render recovered feeds safe for animals by eliminating dangerous microbes present in FW (Rajeh et al., 2021). However, it is important to determine the nutrient profile of FW by systematic sampling procedures and comprehensive nutrient analyses, because the nutrient profile of animal feed can vary depending on the source of FW, treatment method and the geographic location of the FW collection (Dou et al., 2018; Rajeh et al., 2021).

3.4. Composting

Composting is a popular method for FW handling. Composting is regarded as a cost-effective and ecologically friendly solution for use on agricultural fields that is providing an alternative to chemical fertilizers (Lin et al., 2018). To transform waste into high-quality compost, specific parameters such as pH, carbon to nitrogen ratio, moisture content, aeration rate, particle size, and porosity must be properly regulated. If these parameters are not maintained appropriately, the procedure will lead to odours and gas emissions, inhibition of microbial activity, environmental pollution and production of low-quality compost. FW is a heterogeneous mixture with high moisture content and an acidic pH. Therefore, FW recycling into compost requires preprocessing of the waste and addition of bulking agents to reduce the moisture content and neutralize the pH (Cerda et al., 2018; Schaub and Leonard, 1996). When FW is co-composted with various organic substances it provides several advantages such as balanced C:N ratio, high aeration, low leachate and enhanced microbial activity (Lin et al., 2018).

3.5. Anaerobic digestion

Anaerobic digestion is widely applied for FW treatment since these wastes are widely available, biodegradable, and have a high energy potential (Xu et al., 2018). In developing countries, anaerobic digestion is commonly employed in small or domestic-scale digesters to produce gas for cooking or electricity generation. In developed countries, anaerobic digestion of FW is carried out on a commercial scale and the resulting biogas is used to co-generate heat and electricity, and it can be injected into the natural gas grid for use as transportation fuel (Scarlat et al., 2018). Compared to other food processing techniques, anaerobic digestion is a cost-effective technology to produce renewable energy. In addition, it can be employed with a broader range of substrates including those with high moisture content and containing impurities. Although anaerobic digestion is well established for the treatment of wastewater, sewage sludge, and animal manure, anaerobic digestion of FW continues to face several challenges, including rapid accumulation of volatile fatty acids (VFA) during the early stages of digestion, low buffer capacity, inhibitors, and high transportation costs (Xu et al., 2018). Several approaches have been taken to overcome the difficulties associated with anaerobic digestion of FW, including co-digestion with other organic wastes, the addition of micronutrients and antifoaming agents, and the use of various novel reactor designs. These approaches have demonstrated excellent potential for reducing VFA accumulation and inhibitors while increasing nutrient balance and buffer capacity to improve biogas generation.

However, additional research is still needed to further optimize the anaerobic digestion of FW and promote widespread adoption of this method (Hamawand, 2015; Xu et al., 2018).

4. Food waste- a sustainable raw material for the production of furanics

Recycling organic waste to produce chemicals is a promising option to overcome the challenges of resource depletion. FW is rich in different carbohydrate residues such as C5 and C6 sugars. These sugars can be considered a suitable building block for synthesizing platform chemicals. Catalytic transformation of these carbohydrates into various furanic compounds has gained increasing attention. HMF is one of the promising furanic platform chemicals that can be produced from C6 sugars. One of the reasons HMF is regarded as a top value platform chemical is its ability to be converted into FDCA via oxidation. FDCA serves as the building block of diverse commodities (such as polyesters), but its production primarily depends on the efficient production of HMF. A major drawback of the current HMF production is its high cost. HMF is currently priced between 500 to 1500 USD/kg depending on the chemical purity, which is around three times higher than fossil-based chemicals (Yu and Tsang, 2017). Current commercial HMF production mainly depends on sugar syrups extracted from energy crops, which is also contributing to its high cost (Kläusli, 2014). Therefore, more research is being carried out to find a more efficient method to utilize inexpensive renewable feedstocks for HMF production. Among different feedstocks that can be utilized for HMF production, FW represents an excellent alternative as it is inexpensive and contains 47–74% carbohydrates on a dry basis (Pleissner, Kwan and Lin, 2014; Yu et al., 2016). According to recent studies, the highest yield of HMF (71 mol%) was derived from beverage waste (Yu et al., 2018). However, the synthesis of HMF from other types of FW, such as starchy, cellulosic, and sugary wastes, remains challenging due to their complex composition (Yu et al., 2017b). Reports on yield varied between 1 to 44.6 wt% depending on the type of FW used, the catalyst used, and the reaction conditions (Menegazzo, Ghedini and Signoretto, 2018; Ji et al., 2020). To enable more efficient manufacturing of furanics from FW, further improvement of the current technology/process is needed.

4.1. HMF Production from renewable biomass

In principle, FW transformation into HMF consists broadly of three steps: (1) hydrolysis of glucose-based polysaccharides such as cellulose and starch to glucose, (2) isomerization of released glucose to fructose and (3) dehydration of fructose to HMF. These reaction steps are accelerated by employing different catalysts which are divided into two groups: (a) Brønsted acids to facilitate the hydrolysis and dehydration reactions and (b) Lewis acids for the isomerization reaction (Hu et al., 2020). An alternative mechanism for the synthesis of 5-HMF is the direct dehydration of glucose to HMF. However, the selectivity of HMF production varies depending on the type of sugar used for its synthesis. When fructose is utilized as the starting material, HMF synthesis is significantly more efficient as compared to glucose (Kong et al., 2020). Synthesis of HMF from fructose involves two reaction pathways: acyclic and cyclic pathways. The open-ring fructose undergoes three sequential dehydration steps in the acyclic pathway to generate HMF via the synthesis of 3-deoxyglucos-2-ene (DGE), 3-deoxyglucosone (DGO), and 3,4-deoxyglucosene (DGS). Cyclic pathway begins with the dehydration of ring-closure fructose at the C2–OH position, followed by the dehydration of 2-(hydroxymethyl)-5-(hydroxylmethylene)-tetrahydrofuran-3,4-diol (HMHMTD) and 4-hydroxy-5-(hydroxymethyl)-4,5-dihydrofuran-2-carbaldehyde (HHMDHC). The HMF synthesis from glucose requires an additional isomerization reaction to convert glucose into fructose via 1, 2, or 1,2-hydride shift before dehydration. The isomerization of glucose is regarded as a rate-limiting step, which complicates and slows the synthesis of HMF from glucose (Hu et al., 2020).

4.1.1. Catalytic system for HMF production

Sugars derived from biomass are usually converted into HMF using an acid catalyst reaction. Acid catalysts used in the synthesis of HMF are typically divided into two groups: homogeneous catalysts and heterogeneous catalysts.

4.1.1.1. Homogeneous Catalysts

Homogeneous catalysts are water-soluble catalysts such as organic acids, mineral acids, metal chlorides, metal triflates, and ionic liquids (ILs). Unlike heterogeneous catalysts, homogeneous catalysts can disperse uniformly to provide better catalytic performance. Commonly utilized homogeneous catalysts are mineral acids such as hydrochloric acid (HCl), sulphuric acid (H_2SO_4), and phosphoric acid (H_3PO_4). These acids are often used for HMF production due to their low cost and wide availability. Mineral acids with strong Brønsted acidities are found to be very effective to produce HMF from fructose in a variety of solvents (Hu et al., 2020). For example, dehydration of fructose in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) in presence of HCL resulted in HMF yield up to 97 wt% in 8 min (Li et al., 2010). However, mineral acids with Brønsted acidities are unable to efficiently catalyze the isomerization of glucose to fructose and are thus unsuitable to produce HMF when glucose is used as the starting material. Additionally, mineral acids are extremely corrosive and hazardous to human health and the environment, which restricts their application to a large extent (Hu et al., 2020).

Considering the high toxicity of mineral acids, researchers attempted to use organic acids as catalysts for HMF production. However, to achieve a similar conversion to mineral acid, organic acid usually requires a higher acid concentration or simultaneous use with other catalysts (Zhao et al., 2021). Different organic acids have been employed for HMF production from fructose such as formic acid (FA), malic acid (MA), citric acid (CA) and ethylenediaminetetraacetic acid (EDTA).

Among the organic acid tested for HMF production, EDTA is found promising because of its excellent catalytic activity and recyclability. EDTA is insoluble in water at room temperature, and it is also insoluble in common organic solvents such as DMSO even at high temperatures. Hence, they can be easily recovered from the reaction mixture by centrifugation or filtration following the dehydration reaction (Hu et al., 2020). However, organic acids with classic Brønsted acidities do not convert glucose to fructose and require supplementation of Lewis acid to allow glucose isomerization. When Lewis acid is supplemented with an organic acid, it exhibits better selectivity towards HMF production from glucose than mineral acids (Zhang et al., 2015). For instance, Zhang and his co-workers paired Lewis acid $AlCl_3$ with malic acid (organic acid) and HCL (mineral acid) and they observed significantly higher selectivity and yield from $AlCl_3$/ malic acid compared to $AlCl_3$/HCl combination (Zhang et al., 2016b).

Recently, metal salts, particularly transition metal chlorides with Lewis acidity, have been the research hotspots for the conversion of carbohydrates into HMF. The metal chlorides can function as bifunctional catalysts to perform the hydrolysis, isomerization and dehydration reactions for one pot conversion to HMF from glucose and glucose-based polysaccharides. During HMF production with metal chlorides, glucose isomerization is facilitated by Lewis acid, while protons generated from partial hydrolysis of metal chlorides in an aqueous medium can provide indirect Brønsted acidities for hydrolysis and dehydration reaction (Yu and Tsang, 2017; Yu et al., 2017b). For example, $SnCl_4$ possesses both Brønsted and Lewis acidities during catalytic conversion of starch and glucose to HMF (Yu et al., 2016).

4.1.1.2. Heterogeneous catalysts

HMF can be synthesized from monosaccharides or polysaccharides utilizing a range of heterogeneous catalysts, which can be broadly classified as metal oxides, zeolites, and sulfonated catalysts. In comparison to homogeneous catalysts, heterogeneous catalysts can be recovered and reused more easily, making them better candidates for the industrial synthesis of HMF from carbohydrates. However, heterogeneous catalysts having acidities derived from the Brønsted acidic group such as Amberlyst-15, Amberlyst-70, and sulfonated carbon, can be used only for the dehydration of fructose to HMF (Yu and Tsang, 2017). To convert glucose and glucose-containing polysaccharides into HMF, metal oxides and zeolites or solid base catalysts with Lewis acidity are used, which are strong enough to isomerize glucose to fructose (Hu et al., 2020). For example, in a combination with HCl, zeolite beta topology (Sn-Beta) can catalyze the HMF synthesis from glucose, starch and cellobiose, and can achieve over 70 wt% of HMF selectivity (Nikolla et al., 2011). However, heterogeneous catalysts such as H-form zeolites are often ineffective to catalyze the conversion of cellulosic polysaccharides to HMF. Besides, the preparation of conventional heterogeneous catalysts is complicated and expensive. Recently sulfonated carbon-based catalysts have gained increasing attention due to their strong acidity, high thermal stability, and low cost preparation from carbon content materials such as cellulose, starch and glucose (Cao et al., 2018; Hu et al., 2013). The sulfonated catalyst showed promising HMF yields from glucose and other carbohydrates such as cellulose and starch (Hu et al., 2013). Metal oxides are another promising heterogeneous catalyst with excellent thermostability and catalytic activity for the production of HMF from diverse complex carbohydrates, including cellulose. For example, direct conversion of pretreated cellulose to HMF in a water–THF+NMP (N-methyl-2-pyrrolidone) biphasic system using a phosphated metal oxide TiO_2, resulted in 86 wt% yield (Atanda et al., 2015).

4.1.2. Solvents system for HMF production

The reaction solvent plays important roles in the HMF synthesis process. Solvents function as both media and catalysts in the production of HMF, increasing the efficiency and thermodynamic equilibrium of the production process in order to achieve higher yields. Numerous solvents have been applied for HMF production, and the solvent effects reported vary. Commonly applied solvents for HMF production include water, organic solvents (e.g., dimethyl sulfoxide (DMSO), or water/organic solvent mixtures (e.g., water/DMSO) (Yu and Tsang, 2017; Zhao et al., 2021).

4.1.2.1. Monophasic solvent system

Water is generally considered an ideal solvent because of its widespread availability and minimal impact on the environment. Besides, carbohydrates have low solubility in organic solvents and require polar solvents such as water to dissolve (Hu et al., 2021). Apart from serving as the reaction medium, water can be dissociated into H^+ and OH^- at high temperatures, and should theoretically catalyze the hydrolysis and dehydration of biomass without any added catalyst (Zhao et al., 2021). However, HMF production from cellulose in water resulted in poor yield unless an acid catalyst was incorporated in the reaction (Asghari and Yoshida, 2010). Besides, HMF in water suffers from off-path reaction products such as levulinic acid (LA), formic acid and humins, causing a low HMF yield in aqueous media (Zhao et al., 2021).

Due to the low HMF yield in water, a number of polar organic solvents have been used for HMF production such as DMSO, dimethylformamide (DMF), dimethylacetamide (DMA), tetrahydrofuran (THF), and ethylacetate (Mukherjee et al., 2015; Zhao et al., 2021). Among the solvents used for HMF production, DMSO is considered one of the most effective solvents for HMF synthesis (Zhao et al., 2021). DMSO has a shielding effect on HMF which helps to stabilize and suppress further rehydration of HMF to LA and formic acid. DMSO also functions as a catalyst for the dehydration of fructose to HMF (Ren et al., 2017). Despite their well-known superior performance, utilizing polar organic solvents as a medium for HMF generation has numerous substantial disadvantages, including high toxicity to humans and the environment, and energy-intensive HMF recovery due to the high boiling points of the solvents (Zhang et al., 2016a).

In comparison to organic solvents, ILs are considered more environmentally friendly and can act as both a solvent and a catalyst in the manufacture of HMF, particularly from polysaccharides. ILs are strong hydrogen bond acceptors and are capable of disrupting and dissolving the polysaccharide macrostructure for hydrolysis. In addition, ILs have good thermal stability and low vapor pressure, facilitating the hydrolysis and subsequent conversion of sugars to HMF under mild conditions (Zhang et al., 2016a). The commonly utilized ILs are Lewis acid ILs (especially the imidazole-based ionic liquids), such as 1-butyl-3-methylimidazolium ($[BMIM]^+$), 1-ethyl-3-methylimidazolium ($[EMIM]^+$), 1-octyl-3-methylimidazolium ($[OMIM]^+$), etc. (Mukherjee et al., 2015). Although ILs have some advantages in HMF synthesis, including solvent recyclability, they also have some drawbacks, such as a complicated manufacturing process, low biodegradability, and high cost (Zhao et al., 2021).

4.1.2.2. Biphasic solvent system

Although water rehydrates HMF, a particular amount of water is important for HMF production since it supplies H^+ to the catalyst, helps to dissolve the reactant, and maintains a low viscosity. Therefore, biphasic solvent systems have been developed containing water-organic miscible mixtures. Using a biphasic system is particularly promising for large-scale HMF production as it improves the selectivity towards HMF production to achieve a high HMF yield. In a biphasic solvent system, sugar is converted in the aqueous phase (reaction phase), and the resulting HMF is extracted from the organic phase (extraction phase), which prevents side reactions by separating HMF from the reactant and reaction intermediates (Zhao et al., 2021). To achieve a satisfactory yield of HMF in a biphasic system, it is important to choose an extracting solvent that can provide high HMF partitioning into the organic phase. Román-Leshkov and Dumesic developed a method to measure the partition coefficient, R, by dividing the HMF concentration in the organic phase by that in the reaction phase. They determined the R values for a number of primary and secondary alcohols, ketones, and cyclic ethers in the C3–C6 range, as well as the effect of various metal salt ions on R. THF exhibited the highest R value (7.1) and reached the highest HMF selectivity (83%) (Román-Leshkov and Dumesic, 2009).

Although significant progress has been made in the synthesis of HMF from different carbohydrates, there are still challenges associated with HMF manufacturing, particularly the relatively expensive cost of reaction solvents and the complexity of the post-treatment process (Kong et al., 2020). Since HMF is utilized as an intermediate compound in the manufacturing of valuable fuels and chemicals, researchers have reported that direct conversion of HMF to the final product could result in a reduction in overall production costs. Additionally, it avoids the complicated separation and purifying processes associated with HMF production (Wang et al., 2014). In recent years, HMF oxidation to FDCA attracted much attention since it is an effective substitute for terephthalic acid in a variety of polyesters, including polyethylene terephthalate (PET) (Kubota and Choi, 2018). PET is commonly utilized in the manufacturing of films, fibers, and bottles for the packaging of soft drinks, water, and fruit juices. Apart from its primary usage as a monomer in the synthesis of biobased polymers, FDCA has also application in organic synthesis, pharmacology, and the synthesis of metalorganic framework materials (Zhang and Deng, 2015).

4.2. Production of FDCA from HMF

FDCA is an organic chemical compound containing two groups of carboxylic acids connected to a central furan ring. FDCA has a high melting point of 342 °C and is insoluble in most common solvents (Haworth et al., 1945). It was first reported by Fittig and Heinzelmann in 1876, who produced it by dehydrating mucic acid under pressure using 48 % aqueous HBr (fuming hydrobromic acid) as catalyst and solvent (Fittig and Heinzelmann, 1876). Later, different dehydrating agents were applied with some modifications for FDCA production from mucic acid. However, this process is limited because the dehydration procedure required a high temperature, extremely concentrated acid, and a reaction time of more than 20 hours, and provided moderate FDCA yields (<50 wt%) with less selectivity (Zhang and Deng, 2015).

4.2.1. Thermocatalytic production of FDCA from HMF

HMF oxidation provides an alternative route to FDCA production, and the mechanism can be divided into two pathways (Fig. 2.2). The HMF can be first converted to 2,5-diformylfuran (DFF) or 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) via the oxidation of its alcohol and aldehyde groups, respectively. Thereafter, DFF or HMFCA is oxidized to 5-formyl-2-furancarboxylic acid (FFCA) and eventually to FDCA (Wang et al., 2014). Chemical oxidants or noble metal catalysts are generally used for the HMF oxidation to FDCA in presence of high temperature and O_2 pressure. The use of O_2 or air as an oxidant is considered an economical and environmentally friendly approach for catalytic oxidation of the HMF. In the past decades, homogeneous metal/bromide systems such as Co/Mn/Zr/Br catalysts have been studied for the oxidation of HMF to FDCA using molecular oxygen as an oxidant and water/acetic acid as a solvent. However, homogeneous catalytic systems have some major drawbacks, including a low yield of FDCA, formation of byproducts, and difficulties in separating and recycling homogeneous catalysts (Zhang and Deng, 2015).

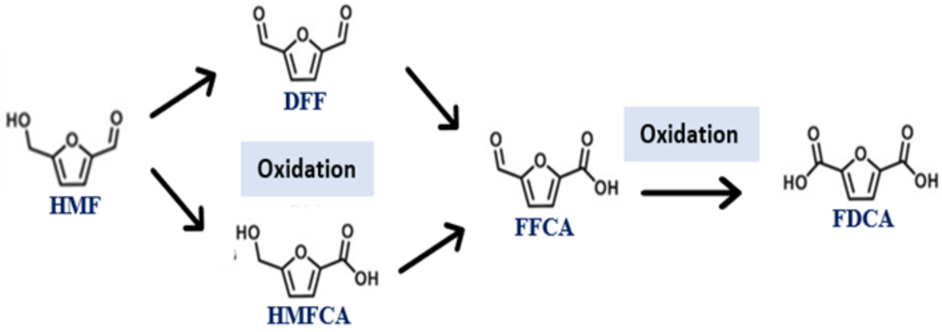

Figure 2.2: Reaction pathway for the oxidation of HMF to FDCA

To overcome these challenges, researchers focused on developing heterogeneous catalytic systems with higher and better catalytic activity for FDCA production. Noble metal catalysts such as platinum (Pt), gold (Au), palladium (Pd), or ruthenium (Ru) are typically used as heterogeneous catalysts for the thermochemical oxidation of HMF due to their remarkable ability to activate O_2. According to the literature, Au catalysts are more active in aldehyde oxidation during HMF oxidation, while Pt and Pd are more active in oxidation of alcohol groups (Chen et al., 2021). Under optimal thermochemical oxidation conditions, more than 99 wt% yield of FDCA could be achieved using these metals as novel heterogeneous catalysts (Cai et al., 2013; Zhang and Deng, 2015). It was found that Pt catalysts are the most active of all metal catalysts, particularly at low temperatures (Chen et al., 2021). Verdeguer and co-workers used a Pt/C catalyst to catalyze the oxidation of HMF in the presence of air and were able to produce FDCA with a yield of 81 wt% with 100% conversion of HMF in two hours. Additionally, they discovered that supporting the Pt catalyst with Pb significantly improves the catalytic activity of the Pt/C catalyst, resulting in 99 wt% FDCA production and 100% HMF conversion under the same reaction conditions (Verdeguer et al., 1993). Carbon-supported Pd catalysts also exhibited outstanding catalytic activity for the aerobic oxidation of HMF to FDCA under low-temperature conditions (Table 2.1). In 2011, Davis et al. compared the catalytic activity of Pd/C and Pt/C catalysts and demonstrated that the catalytic activities of both catalysts were roughly equivalent, with selectivity toward FDCA conversion of

71% and 79%, respectively (Davis et al., 2011). Later, Yang et al. investigated the aerobic oxidation of HMF over a variety of Ca–Mn oxides, and observed that Pd/$CaMn_2O_4$ had the highest catalytic performance, yielding 96.8 wt% FDCA after 12 hours (Yang et al., 2019). Contrarily, Au catalysts require higher temperatures for the oxidation of HMF. When compared to Pt and Pb catalysts, Au catalysts can catalyze the initial conversion of HMF to HMFCA at a significantly faster rate, but the subsequent oxidation of HMFCA to FDCA requires higher O_2 pressures and base concentrations to achieve the same FDCA selectivity as Pt and Pd catalysts (Davis et al., 2011). Ru catalysts are economically appealing due to their low cost, but they exhibit low reaction rates for HMF conversion and FDCA synthesis (Chen et al., 2021).

To achieve a high yield of FDCA, aerobic oxidation of HMF to FDCA typically requires a certain concentration of a base (e.g. NaOH, $NaHCO_3$, K_2CO_3), which provides a kinetically favorable environment for HMF conversion to FDCA. Gorbanev et al. (2009) carried out the oxidation of HMF using an Au catalyst and observed that the selectivity of the catalyst toward the FDCA and intermediate oxidation product formation HMFCA is dependent on the amount of base given to the reaction during the experiment. When the amount of NaOH in the reaction was low, the yield of HMFCA was higher as compared to FDCA (13 wt% vs 1 wt%) with a low conversion of HMF (13 wt%), whereas under optimal basic conditions (20 equiv NaOH, 20 bar O_2, 30 °C, 18 h), the yields of HMFCA and FDCA were approximately 25 wt% and 70 wt%, respectively. They came to the conclusion that in the absence of a base, the catalyst can be deactivated by the initially formed acids (HMFCA), as similar situation was observed by Klitgaard et al. (2008) during alcohol oxidation in a methanol solution (Gorbanev et al., 2009). They reported that, in the absence of a base, free benzoic acid generated during aerobic oxidation of benzyl alcohol to methyl benzoate inhibited the Au catalyst (Au/$K_2Ti_6O_{13}$), but the activity of the catalyst can be restored immediately by adding a base (Klitgaard et al., 2008). Davis et al., (2011) reported that under the same base concentration, a carbon-supported Au catalyst produces HMFCA as the major product, whereas supported Pt and Pd catalysts produce FDCA as the final reaction product. The selectivity of Au catalysts towards FDCA increased when the base concentration was raised, indicating that OH is essential to activate the alcohol side chain of HFCA to produce FDCA over Au catalyst (Davis et al., 2011). However, adding bases to produce FDCA has a number of disadvantages, including the need to neutralize the product solutions with a substantial amount of inorganic acids such as hydrochloric acid or sulfuric acid, and the resultant salts must be separated to obtain the FDCA in its pure form. Therefore, attempts have been made to produce environmentally friendly base-free oxidation catalytic systems. Gupta et al. (2011) reported base-free oxidation of HMF to FDCA using hydrotalcite-supported gold nanoparticle catalyst (Au/HT). The catalyst exhibited an excellent FDCA yield of up to 99 wt% in water after 7h at 95 °C under 1 bar oxygen pressure (Gupta et al. 2011). Very recently, Kandasamy et al. (2021) reported a very effective Ru-assisted NaY zeolite catalyst for HMF to FDCA oxidation. The study showed that in a base-free environment, a 3 wt% Ru-NaY catalyst could completely convert HMF in 2 hours. The FDCA yield was of 94 mol% after 8 hours at 120°C and 10 bar O_2 pressure. Importantly, the catalyst could be reused up to four times with just a slight reduction in FDCA production (Kandasamy et al., 2021).

Table 2.1: Oxidative production of FDCA using different catalytic systems

Feedstock	Catalyst	Solvent	Condition	Gas source	Yield%	Reference
FDCA production with base						
HMF	Pt/C	Water	23°C, 6 h, 2 equiv. NaOH, 6.9 bar	O_2	79	(Davis et al., 2011)
HMF	Pd/C	Water	23°C, 6 h, 2 equiv. NaOH, 6.9 bar	O_2	71	
HMF	Au/C	Water	23°C, 6 h, 2 equiv. NaOH, 6.9 bar	O_2	7	
HMF	Au/C	Water	30°C, 22 h, 20 equiv. NaOH, 20 bar	O_2	72	
HMF	Ru/C	DMSO/water	130 °C, 12 h, 2 equiv. $NaHCO_3$, 40 bar	O_2	93	(Liu et al., 2019)
HMF	Pt/C	NMP/water	80 °C, 0.5 h, 2 equiv. NaOH, 22 bar	O_2	73.8	(Tekautz et al., 2012)
HMF	Pt-Pb/C	water	25°C, 2 h, 4 equiv. NaOH, 1 bar	O_2	99	(Verdeguer et al., 1993)
HMF	Pt/Beta	Water	90 °C, 24 h, 6 equiv. Na_2CO_3, 1 bar	O_2	99	(Liu et al., 2021)
HMF	Au/CeO_2	water	130°C, 5 h, 4 equiv. NaOH, 10 bar	air	96	(Casanova et al., 2009)
HMF	Au/TiO_2	water	30°C, 18 h, 20 equiv. NaOH, 20 bar	O_2	71	(Gorbanev et al., 2009)
HMF	Au-Cu/TiO_2	water	95°C, 4 h, 10 equiv. NaOH, 10 bar	O_2	99	(Pasini et al., 2011)
HMF	Au/HY	water	60°C, 6 h, 4 equiv. NaOH, 3 bar	O_2	>99	(Cai et al., 2013)
HMF	Pd/PVP	water	90°C, 5 h, 4 equiv. NaOH, 1 bar	O_2	90	(Siyo et al., 2014)
FDCA production without Base						
HMF	Au/HT	water	95 °C, 7 h, 1 bar	O_2	>99	(Gupta et al., 2011)
HMF	Pt/Fe3O4/rGO	water	95 °C, 9 h, 5 bar	O_2	99	(Zhou et al., 2019)
HMF	Pt/CNT	water	100 °C, 12 h, 30 bar	O_2	97.8	(Sharma et al., 2019)
HMF	Pd/CNT	water	100 °C, 12 h, 30 bar	O_2	95.6	
HMF	Pd/CNT	water	100 °C, 12 h, 30 bar	O_2	92.4	
HMF	Ru-NaY	water	120 °C, 8 h, 10 bar	O_2	94	(Kandasamy et al., 2021)
FDCA from lignocellulosic biomass						
Rice straw	MnO_2	DMSO/water	192 °C, 0.57 h, Ultrasound, 0.57 M HCL	-	52.1	(Chai et al., 2021)
Rice straw	Cr-Mn/USY	DMSO/water	180 °C, 4 h, 0.5 mM $KHCO_3$	-	67	(Chai et al., 2022)
Electrocatalytic production of FDCA						
HMF	NiOOH	1 M NaOH	0.6 V vs SCE, 4 h	-	71	(Grabowski et al., 1991)
HMF	NiBx/NF	1 M KOH	0.6 V vs standard hydrogen electrode, 1.7 h	-	99.8	(Zhang et al., 2019)
HMF	NiSe@NiOx	1 M KOH	1.423 V vs reversible hydrogen electrode	-	99	(Gao et al., 2020)
Biocatalytic production of FDCA						
HMF	HMF oxidase	0.1 M KH_2PO_4	25 °C, 15 h, 1 bar	air/ O_2	95	(Dijkman et al., 2014)
HMF	Laccase/TEMPO	0.05 M $C_2H_3NaO_2$	35 °C, 150 rpm, 96 h, air bubbling	air	90.2	(Wang et al., 2018)
HMF	PaoABC/ GOaseM$_{3–5}$/ HRP /Catalase	0.2 M KH_2PO_4	37 °C, 6 h	air	100	(McKenna et al., 2017)

4.2.2. Direct production of FDCA from lignocellulosic biomass

Besides production from HMF, direct conversion of lignocellulose biomass to FDCA has also been studied in recent years. Although utilization of abundant lignocellulose biomass is undoubtedly an attractive option for FDCA production, the complex recalcitrant structure of lignocellulose makes it challenging to obtain a high yield of FDCA. Chai and co-workers (2021) explored the feasibility of direct production of FDCA from rice straw using a combination of ultrasonic-assisted dilute acid pretreatment and MnO_2 catalyst. The response surface method was used to optimize different parameters of FDCA production, and the maximum yield reached was 52.1 wt% under optimal conditions. Analysis of the reaction mechanism indicated that the heavy metals present in the rice straw could migrate into the solution during the thermochemical conversion process, where they act as Lewis acids to improve the FDCA production to some extent (Chai et al., 2021). Later, the same authors utilized Cr-Mn bimetallic supported Ultra-stabilized Y (USY) zeolite monolithic catalyst for direct production of FDCA from rice straw. The FDCA yield could reach 67 wt% yield under the optimal reaction conditions and the catalyst showed stable recovery performance. They reported that the combination of Cr and Mn increased oxygen mobility and synergistically improved the catalytic activity for efficient FDCA production from lignocellulosic biomass (Chai et al., 2022).

4.2.3. Electrocatalytic and biocatalytic production of FDCA from HMF

Due to growing environmental concerns, considerable effort has also been made to develop clean and green technologies for the production of FDCA. Electrochemical oxidation of HMF to create FDCA is regarded as a promising clean synthetic process that is driven by the electrochemical potential of electrodes (Sajid et al., 2018). Since electrochemical catalysis is based on electron migration, it does not require O_2 as an oxidant or inefficient stoichiometric chemical oxidants

(Kubota and Choi, 2018). Grabowski et al., (1991) first demonstrated the electrochemical oxidation of HMF to FDCA with the nickel oxide/hydroxide anode in NaOH solution using H-shaped electrochemical cells. The electrolysis of HMF yielded 71 mol% FDCA after 4 hours (Grabowski et al., 1991). Recently, electrochemical oxidation of HMF has received increasing interest considering the overall profitability of the system. Like most heterogeneous catalysis, a surface reaction occurs at the interface between the active electrode and the electrified electrolyte in electrocatalysis. Therefore, thermochemically active noble metal catalysts such Au, Pt and Pd have been shown to be active in the electrocatalytic reaction (Chen et al., 2021). Chadderdon et al. (2014) studied the electrocatalytic oxidation of HMF to FDCA on monometallic Au/C and Pd/C, and bimetallic Pd-Au catalysts under alkaline conditions. They found that the formation of FDCA over electrocatalytic oxidation of HMF using novel metals depends on the electrode potential and catalyst surface composition. On Au/C catalyst, oxidation of HMF to HMFCA was faster and required a lower electrode potential than Pd/C catalyst. During HMF oxidation to FDCA, Pd/C catalysts followed two competitive pathways and were dependent on the electrode potential. The oxidation potential Pd/C catalyst could be improved by coupling it with Au. The bimetallic Pd–Au catalysts achieved much higher FDCA yield (83 wt%) at lower potentials than the two monometallic catalysts (Chadderdon et al., 2014). Recently, some inexpensive transition-metal catalysts based on Ni, Co, Cu, and Mn were developed, and they demonstrated greater efficiency at oxidizing HMF and increasing conversion yield than noble metal catalysts (Chen et al., 2021). Gao et al. (2020) synthesized a non-precious electrocatalyst, NiSe@NiO_x core-shell nanowires. The catalyst achieved remarkable efficiency in electro-oxidizing HMF to FDCA (around 99 mol% yield) and showed robust stability for successive electrolysis (Gao et al., 2020). Aside from electrochemical catalysis, the biocatalytic transformation of HMF to FDCA has received extensive attention as a possible greener alternative. The enzymatic approach has several advantages over other methods, including gentle reaction conditions, increased selectivity, and environment amity. Several enzymes such as aryl-alcohol oxidase, Laccase, HMF oxidase, galactose oxidase, catalase, horseradish peroxidase and unspecific peroxygenase have been used for HMF oxidation to FDCA (Rajesh et al., 2019). So far, the most promising results have been obtained using a continuous one-pot reaction with a multienzyme cascade combining periplasmic aldehyde oxidase, galactose oxidase, catalase, and horseradish peroxidase, which resulted in 100% FDCA conversion after only 6 hours (McKenna et al., 2017). Besides, reaction containing single oxidase enzymes also yielded a high FDCA. For example, HMF oxidase produced 95 mol% FDCA in 15 h at ambient temperature and pressure (Dijkman et al., 2014). Although significant and promising achievements were obtained in the biotransformation of HMF to FDCA, the method is not up to the mark for industrial production. The biotransformation of FDCA requires lower substrate concentration (HMF) with a long processing time and precise control (Rajesh et al., 2019). Further research in this field is needed for the cost-effective and large-scale industrial manufacturing of FDCA.

4.3. Current status of HMF production from food waste

Food waste (FW) is a promising feedstock for the production of furanics and numerous studies have been conducted recently on FW to develop a viable technology for its valorization to furanics, particularly HMF, which are summarized in Table 2.2. To date, there has been no literature on FDCA production from FW.

Table 2.2: HMF production from food waste

Feedstock	Catalyst	Solvent	Condition	Yield%	Reference
Cooked food waste	ZrP	Water	160 °C, 6 h	4.3	(Parshetti et al., 2015)
Cooked rice Bread crust	$SnCl_4$	DMSO/water	140 °C, 20 min	8.1 9.5	(Yu et al., 2016)
Bread waste	$SnCl_4$ $AlCl_3$ $Fecl_3$	DMSO/water	160 °C, 20 min	30 27 10	(Yu et al., 2017a)
Bread waste	$SnCl_4$	ACN or Acetone /water ACN or Acetone /water DMSO/water THF/water	140 °C, 10 min 140 °C, 10 min 140 °C, 1 h 140 °C, 2 h	26 26 27.4 8	(Yu et al., 2017c)
Cooked rice	$SnCl_4$ $AlCl_3$ $Zr(o)Cl_2$	DMSO/water	140 °C, 40 min	25 23 12	(Yu et al., 2017b)
	$FeCl_3$ $CrCl_3$		160 °C, 20 min	20 15	
Raw mixed vegetables	$SnCl_4$ $Zr(o)Cl_2$	DMSO/water	140 °C, 20 min	5.2 2	
	$FeCl_3$ $CrCl_3$ $AlCl_3$		140 °C, 40 min	1 2 3	
Bread waste	Sulfonated biochar	DMSO/water	180 °C, 20 min	30.4	(Cao et al., 2018)
Food and beverage waste	Glucoamylase, sucrase, glucose isomerase, Amberlyst 36	DMSO/water	140 °C, 40 min	71.3	(Yu et al., 2018)
Orange waste Apple wastes	D001-cc resin	[Bmim]Cl	Ultrasound-[Bmim]Cl pretreatment; 160 °C, 40 min	42.15 44.66	(Ji et al., 2020)

In 2015, Parshetti and his co-workers established a thermochemical system for the conversion of FW to HMF by utilizing a heterogeneous catalyst, zirconium phosphate (ZrP). Even though the catalyst could reach a maximum HMF yield of 4.3 wt% under optimal reaction conditions, preliminary cost estimations suggested that thermochemical treatment is a promising option for industrial production of HMF from FW (Parshetti et al., 2015). Later, Yu and co-workers studied the influence of dual roles of metal chloride in the conversion of starch-rich FW (cooked rice and bread crust) to HMF using a variety of Lewis acid catalysts in a DMSO/water solvent system. The maximum glucose conversion (44–65% yield) and HMF production (8–9.5 mol% yield) were achieved over the $SnCl_4$ catalyst. They observed that the Lewis acid sites on metal chlorides and the Brønsted acidity derived via partial hydrolysis of metal ions functioned synergistically in the hydrolysis of glycosidic bonds, glucose isomerization, and fructose dehydration to HMF. Besides that, metal chlorides also promoted undesirable polymerization leading to humin formation (Yu et al., 2016). Using $SnCl_4$ as a catalyst, the same group later studied the effects of several binary combinations of polar aprotic solvents (DMSO, THF, ACN, and acetone) and water on HMF production from bread waste. While HMF synthesis was significantly faster in ACN/H_2O and acetone/H_2O due to faster glucose isomerization, approximately similar HMF yields (26-27 mol%) were obtained in water/ DMSO, ACN or acetone, indicating that these mediums have identical selectivity for HMF synthesis (Yu et al., 2017c). In another study, HMF yield of 30 mol% was achieved from bread wastes using $SnCl_4$ catalyst and DMSO/water as solvent (Yu et al., 2017a). According to the authors, an optimal kinetics balance between Lewis and Brønsted acidities of metal chlorides is important to enhance the catalyst's selectivity towards desirable reactions over undesirable side reactions to achieve high HMF productivity from FW. Besides, the preliminary economic analysis indicated that the valorization of starch-rich FW to HMF is a financially viable approach. The same authors further investigated trivalent and tetravalent metal catalysts such as $AlCl_3$, $CrCl_3$, $FeCl_3$, $Zr(O)Cl_2$, and $SnCl_4$ for a one-pot conversion of starchy, sugary, and cellulosic FW to HMF. Under microwave heating at 140 °C for 20 min, starchy and sugary FW yielded up to 22.7 and 13 wt% HMF respectively over tetravalent catalyst $SnCl_4$, while the conversion of cellulosic wastes was limited by marginal hydrolysis of crystalline cellulose. Isomerization of glucose to fructose was reported to be a kinetically limited step during HMF production which was predicted due to interference from non-carbohydrate components present in the wastes (Yu et al., 2017b).

In another experiment, Cao et al. (2018) utilized sulfonated biochar for catalytic conversion of bread waste into HMF. Sulfonated biochar is a heterogeneous Brønsted acid that exhibits high acidity and thermal stability, making it ideal for esterification, acetylation, hydrolysis, and dehydration. The sulfonated biochar was prepared utilizing forest wood residues, and the catalyst could achieve a maximum HMF yield of 30.4 Cmol% in 20 min at 180 °C in DMSO/ deionized-water (DIW) solvent. It was reported that the effectiveness of sulfonated biochar catalyst was correlated to the density of strong/weak Brønsted acidity (-SO3H, -COOH, and -OH groups), which decreases with the increase in humins' content. The recyclability of the biochar catalyst can be increased by a regeneration process using sulphuric acid (Cao et al., 2018).

Very recently the transformation of sugary FW such as orange and apple wastes into HMF using ultrasound-[Bmim]Cl pretreatment in ionic liquids (ILs)-ion exchange resin system was reported by (Ji et al., 2020). Ultrasound is considered as a green technology for pretreatment of plant biomass. It helps to separate the lignin and enhance the dissolution of cellulosic biomass to improve the mass transfer rates between biomass and catalysts, which eventually increases the hydrolysis yield. The kinetics studies showed that under optimum ultrasonic frequencies, the ultrasound-[Bmim]Cl pretreatment improved the cellulose hydrolysis in fruit wastes, with maximum HMF yields of 42 and 45 mol% achieved for orange and apple wastes, respectively, over D001-cc cation exchange resin. They observed that when the temperature was low, the early stage of the reaction was dominated by hydrolysis, with isomerization and dehydration occurring at a later stage as the reaction time progressed. At high temperatures, hydrolysis, isomerization, and dehydration occurred simultaneously in the early stage, and the late stage was primarily HMF rehydration (Ji et al., 2020).

Besides cellulosic FW, beverage wastes are utilized as a feedstock for HMF production. Beverage wastes constitute a large portion of industrial FW and are rich in simple carbohydrates including glucose, fructose, and sucrose. The simple composition of these wastes makes it a more attractive starting material than cellulose or starch in terms of energy requirements for macrostructure breakdown. Yu et al. (2018) recently worked on the HMF production from mixed food and beverage wastes using a combination of biological and chemical catalytic methods. The study showed that a 70% solid-to-liquid ratio of food and beverage wastes is economically advantageous for the production of glucose and fructose hydrolysates using glucoamylase and sucrase enzymes. After purifying the hydrolysate using chromatographic columns, the isomerization process was performed by using glucose isomerase with a fructose-to-glucose ratio of 1:1. The glucose-fructose syrup was separated using a Simulated Moving Bed (SMB) system to produce high-fructose syrup with 89.0 g/L fructose concentration, which was used as feedstock for HMF production over a commercial solid acid catalyst (Amberlyst 36). A maximum HMF yield of 71 mol% with a selectivity of 77% was produced under microwave heating at 140°C for 40 min. The catalyst was recovered and reused for four runs with consistent HMF production. To maximize the economic viability of the process, the authors suggested that further optimization is required (Yu et al., 2018).

5. Challenges in food wastes valorization to HMF

Although FW presents itself as an attractive alternative for the production of furanic compounds, there are several challenges associated with their valorization including low yield, low catalytic efficiency, inefficient hydrolysis of cellulose and formation of byproducts. Major challenges in FW valorization are further discussed below.

5.1. Heterogenous composition of food wastes

FW are a heterogeneous mixture of carbohydrates, fats and oils, proteins, vitamins and minerals, and their composition can vary significantly depending on the cooking methods, food materials, eating habits, and local cultures. Therefore, finding accurate statistics for the exact content in FW is difficult. Besides, the majority of polysaccharides and proteins in FW exist in the solid phase, which can affect the catalytic conversion of FW depending on their properties, particles size, and solid content (Ma et al., 2018). For example, insoluble FW macromolecules such as lipids and proteins form solid-solid interactions with solid acid catalysts, reducing their catalytic efficacy. Thus, heterogeneous FW conversion over solid acid catalysts often has limited catalytic activity (Lin et al., 2012; Parshetti et al., 2015). Furthermore, the presence of noncarbohydrate impurities such as organic acids and heavy metals can potentially interfere with the FW catalytic system and can affect the synthesis of HMF. For example, inorganic metals, such as calcium, magnesium present in FW can act as catalysts to transform the FW valorization into an autocatalytic process, whereas organic acids have a high affinity for metal ions and can inhibit the catalytic activity during HMF production (Yu et al., 2017b; Kim et al., 2020). Although it is possible to obtain high-quality feedstocks by removing impurities from wastes, this increases the manufacturing costs. Besides, FW contains large volume of water, which fluctuates according to the type of food and season, and may require an additional pretreatment step to remove the excess water (Yukesh et al., 2020a).

5.2. Ineffective dissolution of polysaccharides

FW, particularly fruit and vegetable wastes, are rich in lignocellulosic biomass, which acts as an important source of glucose for HMF production. Lignocellulose is a complex polymer made of cellulose, hemicellulose and lignin. However, the content of the different components in lignocellulose differs based on plant types and species (H. Isikgor and Remzi Becer, 2015). However, cellulose is the major polysaccharides present in lignocellulose, and its efficient hydrolysis is important for a higher glucose yield. In cellulose, the greater proportion of glucose chains are arranged in highly ordered crystalline form, which is considered to be one of the most critical factors in cellulose hydrolysis Additionally, hemicellulose and lignin are crosslinked with cellulose to form a rigid structure, which further increases lignocellulose's resistance towards hydrolysis (Rytioja et al., 2014). Yu and colleagues observed a poor HMF yield from raw mixed vegetables due to poor cellulose hydrolysis. They suggested that the highly dense crystalline structure of cellulose hinders its breakdown in water and organic solvents, subsequently inhibiting catalyst diffusion into the cellulose polymeric chain (Yu et al., 2017b).

5.3. Rate-limiting transformation of glucose to fructose

The key step in the catalytic conversion of cellulosic substrate to HMF is the isomerization of glucose to fructose (Parshetti et al., 2015). Compared to fructose, HMF production from glucose is limited due to the low enolization rate of glucose (Kuster, 1990). Therefore, during the production of HMF from FW, glucose isomerization to fructose was found kinetically limited (Yu et al., 2016; Yu et al., 2017b; Yu et al., 2017c; Cao et al., 2018). Yu et al., (2017b) reported that the rate of FW hydrolysis was faster than the rate of glucose conversion to fructose over metal catalysts. Since glucose is the most abundant monosaccharide in FW, the lack of fructose generated by isomerization limited its subsequent dehydration to HMF, resulting in a poor HMF yield. Later, the same authors investigated the effect of various polar aprotic solvents on HMF synthesis from FW and found that, with the majority of solvents, inadequate glucose isomerization was a key limiting factor for poor HMF production (Yu et al., 2017c). They predicted that insufficient glucose isomerization could be due to interference with the isomerization reaction by non-carbohydrate components in FW, such as lipid, protein, recalcitrant fibre and ash, because tests with standard glucose provided a high fructose yield under similar experimental conditions. However, the isomerization step can be accelerated by increasing the reaction temperature and time, but this would also accelerate the formation of byproducts (Yu et al., 2017b).

5.4. Undesirable off-path reactions

The key to enhance HMF production is to promote desired reactions while suppressing unwanted ones. However, HMF production is severely limited by the pronounced off-path reactions such as isomerization, fragmentation, and condensate formation (Thoma et al., 2020). Byproducts of HMF formation include glycolaldehyde, glyceraldehyde, and lactic acid, which can be generated concurrently with HMF from glucose and fructose during hydrothermal conversion of biomass, while HMF rehydration may result in the co-generation of other chemicals such as levulinic acid and formic acid (Aida et al., 2007). Excessive acidity given by Brønsted and Lewis acids promotes these undesirable side reactions to various extents (Li et al., 2017). In addition, prolonged reaction time and high temperature favor side reactions of HMF. Depending on the system components, the reaction temperature for HMF synthesis typically ranges from 80 to 300 °C. Kinetic studies on HMF production revealed that high energy input helps to speed up HMF production by improving the rates of desirable reactions, but it also accelerates undesirable reactions to a similar extent due to their comparable activation energies. Besides, the presence of off-path reaction products not only affects the HMF yield but also makes HMF separation and purification complex (Thoma et al., 2020; Yu and Tsang, 2017). To improve the HMF production, biphasic systems containing organic solvent and water were developed, which demonstrated a promising yield by shielding HMF from unwanted side reactions. Despite their well-established superior performance, there are a number of challenges associated with the use of organic solvents that may limit its upscale application, including environmental toxicity and difficult product purification process from the high-boiling point of organic solvents (Yu et al., 2017c).

6. Strategies to improve food waste valorization to HMF

6.1. Pretreatment

Cellulose is a significant component of FW and can be utilized to produce bio-based fuels and chemicals, such as furanic compounds (Menegazzo et al., 2018). However, the conversion of cellulose to chemicals and fuels is limited by their highly compact structure. In crystalline regions, compact packing of cellulose chains does not even allow small molecules like water to penetrate these structural entities. This greatly reduces the accessibility of catalysts attacks and results in lower degradation as compared to amorphous cellulose (Arantes and Saddler, 2010). Therefore, to get maximum FW hydrolysis, a pretreatment step preceding hydrolysis is important. Pretreatments enhance the rate of FW hydrolysis by increasing the surface area, reducing particle size, and decreasing the degree of cellulose crystallinity. Although there are different pretreatment methods available, for instance, physical, chemical and biological methods, a proper method needs to be selected considering certain factors such as biomass type, energy requirement, cost, and eco-friendliness (Alvira et al., 2010; Yukesh et al., 2020b).

6.1.1. Physico-mechanical pretreatment

Physico-mechanical pretreatments usually require higher energy input than other pretreatment methods (Yukesh et al., 2020a). The common treatment methods include thermal, microwave, ultrasonic, high-pressure homogenizer, and ball milling. These types of treatment do not usually affect the original substrate composition. Temperature-based pretreatments, such as microwave irradiation, improve the solubilization of FW by breaking down the crystalline cellulose and partially liberating and breaking down hemicellulose and lignin (Kumari and Singh, 2018). High-temperature treatment also degrades organic molecules such as lipids and proteins, which could enhance the catalytic activity during HMF production (Krishna and Kalamdhad, 2014). In addition, thermal treatments also sterilize the FW, minimizing carbohydrate loss due to microbial consumption (Ma et al., 2018). However, excess heat or radiation may depolymerize the reduced sugars, affecting further the FW conversion (Yukesh et al., 2020b).

Mechanical pretreatments such as ultrasonic treatments offer a convenient and green technique for pretreating lignocellulosic biomass. Ultrasonication disrupts cell walls by numerous physical and chemical changes in liquid solutions, including radiation forces and the formation of free radicals, which are induced by the monolithic cavitation generated by the ultrasound (Kumari and Singh, 2018; Mason and Peters, 2002). Ultrasonic treatment can separate the lignin from plant biomass and promote cellulose solubilization, resulting in higher mass transfer rates between the biomass and catalysts for effective conversion (Ji et al., 2020). Ji et al. (2020) found that multi-frequency ultrasound could significantly promote cellulose disintegration in sugary FW and improved the HMF yield compared to the untreated substrate.

6.1.2. Chemical pretreatment

Chemical pretreatment methods are widely utilized for biomass pretreatment as the procedures are simple and quick. Chemical pretreatments are usually carried out using acid and alkali compounds such as sulphuric acid (H_2SO_4), hydrochloric acid (HCl), sodium hydroxide (NaOH) and lime (Ca $(OH)_2$). Acid pretreatment improves the solubilization of polysaccharides, while alkali pretreatment is efficient in separating lignin from the carbohydrate fraction, solubilizing proteins and catalyzing lipid saponification (Kumari and Singh, 2018; Ma et al., 2018). However, during chemical pretreatment of FW, a severe acidic condition should be avoided to minimize byproducts formation such as aliphatic carboxylic acids and phenolic compounds that can reduce the final product yield (Jönsson and Martín, 2016). Besides, pretreatment with strong acids has certain drawbacks, including toxicity, corrosiveness, and the demand for expensive non-metallic reactor vessels (Kumari and Singh, 2018).

In recent years, pretreatment with ILs has attracted much attention owing to their unique properties such as low vapor pressures and low viscosity, high dissolution ability, high thermal stabilities, and relative nontoxicity (Ji et al., 2020; Socha et al., 2014). ILs provide benefits of selectively extracting lignin and hemicellulose from FW, delivering pure cellulose for hydrolysis and subsequent furanics conversion (Socha et al., 2014). Ji et al. (2020) reported that anions and cations of ILs could effectively dissolve and disintegrate cellulose from sugary FW. During the ILs treatment, anions deprotonate the hydroxyl group of cellulose, while cations attack the hydroxyl oxygen atoms, breaking hydrogen bonds in cellulose and subsequently causing cellulose dissolution (Ji et al., 2020). Although ILs pretreatment provides considerable improvement in biomass structure for efficient hydrolysis, the high cost associated with the manufacturing of ILs makes it less attractive for industrial usage (Kumari and Singh, 2018).

6.1.3. Biological pretreatment

Biological pretreatment is an environmentally friendly method that uses biological agents, for instance, microbes or enzymes without chemical additives. Thus, biological pretreatment would be the most sustainable way to pretreat FW. Biological pretreatment is usually performed by incubating the biomass with microbes, where the microbes secrete enzymes based on the different FW components such as amylases, cellulases, hemicellulases, ligninases, proteases and lipases enzymes to degrade starch, cellulose, hemicellulose, lignin, proteins and lipids. Different fungi and yeast from the genus Phanerochaete, Aspergillus, Candida, and porcine intestinal yeast are used for biological pretreatment (Yukesh et al., 2020b). White-rot fungi are generally preferred for pretreating substrates containing lignin because they can secrete all the essential enzymes for complete lignocellulose breakdown (Kumari and Singh, 2018). Commercial enzymes are also used for biological pretreatment. Enzymes can act immediately, which makes the pretreatment faster (Kumari and Singh, 2018; Ma et al., 2018). FW can be incubated with preferred enzymes which helps to solubilize both the lignocellulosic biomass and impurities present in the FW such as proteins and lipids. Compared to the chemical and physical pretreatment methods, biological pretreatments do not require high energy input or corrosive chemicals and do not cause major environmental pollution. Operational conditions, such as pH and temperature are not severe for biological pretreatment, and they can be easily integrated into the HMF production process from FW. However, biological treatments have limitations. For example, microbiological treatments are slow and require a longer residence period, whereas an enzymatic pretreatment is expensive for large-scale applications (Yu et al., 2019; Amin et al., 2017; Ma et al., 2018).

6.1.4. Combination of pretreatment methods

Although a single pretreatment approach can provide a significant improvement in biomass hydrolysis, there are still some drawbacks associated with each treatment method. Therefore, to overcome the limitations of an individual pretreatment method, a combination of two or more methods can improve the overall pretreatment efficiency due to their synergistic effects. For example, when a combination of pretreatment techniques is applied, the efficiency of sugar production is increased while process time and inhibitor formation are reduced. Physical and chemical pretreatments are commonly applied as a combined pretreatment method (Kumari and Singh, 2018; Yu et al., 2019). HMF synthesis from FW was reported to improve when ultrasonic pretreatment was combined with ILs. ILs promoted the destruction of the hydrogen bonds in crystalline cellulose, whereas ultrasound accelerated the reaction, leading to enhanced cellulose dissolution in FW (Ji et al., 2020). Moreover, a combination of biological pretreatment with other chemical/physical pretreatments has demonstrated the potential for considerable improvements in regards to energy requirement, pretreatment times, and environmental friendliness (Kumari and Singh, 2018; Shirkavand et al., 2016). Ma et al. (2010) reported that combined pretreatment with white-rot fungus and mild acid significantly improved the lignocellulose hydrolysis as compared to the sole acid pretreatment under the same conditions. Nonetheless, to obtain optimal efficacy of combined pretreatments, the pretreatment methods and order of pretreatments should be selected based on the biomass characteristics and mechanism of action of each pretreatment method.

6.2. Optimization of process parameters

6.2.1. Catalyst use

Furanics' production from renewable biomass suffers from the low selectivity of catalysts. A high-performance conversion system demands a balance between desirable reactions and undesirable reactions, which depends on different factors such as catalyst characteristics, solvent properties and reaction conditions (Yu and Tsang, 2017; Yu et al., 2017a). Catalyst characteristics, such as active species, active sites, pore size, and surface area, are vital factors that affect the hydrothermal conversion of biomass and control the selectivity towards the desirable intermediates and product (Yu and Tsang, 2017). Catalytic conversion of FW to furanics is acid-catalyzed and usually requires both Brønsted and Lewis acids. Homogeneous catalysts are usually inexpensive and have good catalytic performance, but there are concerns regarding equipment corrosion, environmental pollution and recyclability of the catalysts. In addition, homogeneous catalysts such as mineral acids and organic acids lack Lewis acidity, so achieving the highly efficient conversion of biomass into furans is challenging. On the other hand, heterogeneous catalysts offer superior selectivity and recyclability and are becoming increasingly appealing for furan production. Bifunctional solid acid catalysts possessing both Lewis and Brønsted acid sites are promising for the cost-effective production of furanics (Yu and Tsang, 2017). Metal chlorides as Lewis acid catalysts showed distinctive performance in the conversion of standard carbohydrates. Protons released from partial hydrolysis of metals could facilitate both the hydrolysis and dehydration reactions. Studies on FW valorization to HMF using metal chlorides showed that the catalyst could effectively catalyze starch rich FW but successive glucose isomerization was rate-limited due to insufficient Lewis acid activity (Yu et al., 2017b). Lewis acids are important for promoting the isomerization via 1,2-hydride shift, however, excessive Lewis acid sites have a higher tendency to be unfavorable to polymerization than Brønsted acids (Yu et al., 2016; Yu and Tsang, 2017; Yu et al., 2017a). Therefore, it is important to determine an optimal Lewis-to-Brønsted acid (L: B) ratio that can promote faster kinetics of the desirable reactions over the undesirable ones (Yu and Tsang, 2017; Yu et al., 2017a). Also, metal chlorides have been shown to increase glucose isomerization and dehydration when used in combination with solid acids or mineral acids. For instance, in conjunction with an isomerization catalyst ($CrCl_3$), Amberlyst 38 could achieve 74% and 40% HMF yield from glucose and cellulose respectively (Wrigstedt et al., 2016). Yu and co-workers (2016) also studied a binary catalytic system to improve the rates of isomerization and dehydration reactions by sequentially adding metal catalysts $AlCl_3$ and $FeCl_3$ to the reaction. $AlCl_3$ was reported to be more efficient at glucose isomerization than fructose dehydration, while $FeCl_3$ was found to be more efficient at fructose dehydration. The binary catalytic system accelerated both the isomerization and dehydration reactions, resulting in an increase in HMF yield (Yu et al., 2016).

6.2.2. Solvent use

The characteristics of the solvent system also have a great influence on the production of furan products from FW. Solvents perform a variety of functions during hydrothermal conversion of biomass, including dissolving substrate and catalysts, improving thermodynamic equilibrium of production process by stabilizing substrate, intermediate and products, acting as a catalysts to improve the reaction kinetics, and preventing product consumption by inhibiting side reactions (Yu and Tsang, 2017). Therefore, the selection of an appropriate solvent system is important for greater conversion efficiency and process economy. From an environmental perspective, water is considered a green solvent, but it lowers the HMF yield by inducing side reactions. In contrast to water, organic solvents can reduce the occurrence of side reactions and greatly promote the conversion of biomass and yield of HMF. High boiling point polar solvents, particularly DMSO, provide a high yield of HMF by improving reaction kinetics and suppressing side reactions, but they also make HMF separation and purification complicated (Teong et al., 2014). The use of low-boiling-point solvents such as diethyl ether (35 °C) and Hexafluoroisopropanol (HFIP) (58 °C) enables easy separation of HMF while also reducing the total cost of the process (Tschirner et al., 2018; Yu and Tsang, 2017). The biomass-derived γ-valerolactone (GVL) and methyltetrahydrofuran (MTHF) are promising green solvents for HMF production (Yu and Tsang, 2017). GVL shows remarkable promotion effects on biomass conversion by achieving faster hydrolysis with lower activation energy than water. In addition, it also limits the undesirable hydration, and humins formation during HMF production, resulting in a significant increase in yield (Pandey et al., 2021). Luterbacher and co-workers (2014) reported up to 60% of HMF yield from corn stover using a water-GVL solvent mixture. Besides the satisfactory HMF yield, GVL promotes complete biomass solubilization and also contributes to the disruption of cellulose crystallinity, resulting in a more efficient thermocatalytic saccharification of biomass (Luterbacher et al., 2014).Recently, biphasic systems have become more attractive for furan production from biomass. Biphasic systems provide better recycling of catalysts and purification of targeted furanic products, resulting in improved process efficiency and economy. Different biphasic systems, such as water/GVL, MIBK, THF, MTHF, or DMSO, show promising results for the production of HMF from renewable biomass. Nevertheless, biphasic systems require further optimizations in terms of extraction efficiency and solvent recyclability to achieve an economically viable manufacturing method (Teong et al., 2014; Yu and Tsang, 2017).

6.3. Development of green synthesis process

In addition to improving furanics production from biomass, through the use of catalysts and solvents with high selectivity, it is also necessary to develop an environmentally friendly HMF production process. Despite the well-recognized high performance, the solvent and catalysts used for the biomass conversion process often arouse environmental considerations. For example, $AlCl_3$ may induce neurological damage, while Cr^{6+}, a carcinogenic agent produced by the oxidation of Cr^{2+} and Cr^{3+}, must be handled with caution (Yu and Tsang, 2017). Therefore, it is important to develop an efficient, environmentally friendly catalytic system for the production of furanics. Enzymes present a promising alternative to develop 'green' synthetic routes to chemical products since enzymes are of biological origin and allow for mild working conditions as compared to traditional chemical catalysts. Besides, enzymes offer advantages such as high stereoselectivity, regioselectivity, and chemoselectivity, and such exceptional selectivity limits the formation of side reactions and allows easier separation of the product (Dev et al., 2018). Enzymatic conversion of glucose to fructose has been performed for HMF production. The biochemical conversion of glucose to fructose has several advantages, including the use of a single enzyme for simultaneous isomerization of two aldose sugars (i.e., glucose and xylose) and the ability to dehydrate fructose to HMF at low process temperatures (i.e., 110–120 °C), thereby minimizing side reactions (Wang et al., 2019). Besides that, lignocellulolytic enzymes offer a promising approach for the depolymerization of plant biomass. Enzymes require a milder reaction condition and provide a safer production process, but traditional enzymatic hydrolysis of lignocellulosic material suffers from low conversion rates and substrate or product inhibition. Recently, Hammerer et al. (2018) studied the solvent-free mechanoenzymatic hydrolysis of lignocellulose. The method is also called Reactive Aging (RAging), which is based on alternate cycles of milling (ball milling) and longer periods of static incubation (aging). The application of RAging led to higher yields and/or faster conversion rates than traditional enzymatic hydrolysis. Furthermore, mechanoenzymatic hydrolysis can be performed without pretreatment and allows for solid loading up to 100% w/v, making it more cost-effective for large-scale industrial applications (Hammerer et al., 2018; Hammerer et al., 2020; Kaabel, Friščić and Auclair, 2020).

7. Conclusion

FW is considered a major global environmental issue as the amount of waste generated around the world has increased substantially in recent decades. While conventional FW management practices are environmentally unsafe and produce low-value products, much research is being conducted to develop an efficient and environmentally sustainable system for transforming FW into high-value products. Recently, the valorization of FW to HMF and its derivative, FDCA, has received a lot of attention as a promising green solution for alternative fuel and chemical production. Although researchers have made several efforts to generate HMF from FW, as outlined in this study, there are still a number of challenges associated with HMF production from FW, such as low yield, high cost, and formation of byproducts. FW conversion to furanic compounds can be enhanced by using an appropriate pretreatment method that promotes hydrolysis and by adopting a high-performance catalyst-solvent system that increases HMF selectivity and yield. Different pretreatment methods can be applied to pretreat FW, including physical, chemical, biological and combined pretreatments. Among the different pretreatment strategies, a combined pretreatment method is more advantageous than a single pretreatment method in terms of saving time and reducing formation of inhibitors. In the conversion of sugars to HMF, heterogeneous catalysts, particularly bifunctional catalysts with an optimum proportion of Lewis and Brønsted acids, are promising choices since they have been demonstrated to enhance selectivity toward desirable reactions. Biphasic solvent systems containing an aqueous-organic phase are particularly attractive to minimize side reactions and enhance HMF recovery for subsequent conversion to FDCA. Nevertheless, it is important to develop a production system that is not just efficient but also economically and environmentally sustainable. Consideration should be given to the recyclability of the catalysts and solvents. In addition, efforts should also be made to convert FW directly to FDCA, which can lower the production costs by eliminating the need to separate HMF.

Connecting Statement

The literature review (Chapter 2) discussed the current state of food waste valorization to furanics, specifically HMF, as well as challenges associated with converting food wastes to HMF and possible research directions to improve their conversion. In Chapter 3, a typical food waste, banana peel, was hydrolyzed using a mechanoenzymatic method, and the resultant sugars were used as a feedstock for the synthesis of HMF utilizing a bifunctional metal catalyst.

Chapter 3 has been submitted for publication.

Chapter 3

Semisynthetic transformation of banana peel to enhance the conversion of sugars to 5-hydroxymethylfurfural

Abstract

Bananas are one of the most popular fruits in the world, and their peels are rich in different carbohydrates, making them an appealing resource for alternative fuel/chemical production. This study aimed to efficiently convert banana peels into the value-added chemical 5-hydroxymethylfurfural (HMF) by using an integrated mechanoenzymatic/catalytic approach. The effects of the reaction volume, milling time, and reactive aging cycles (RAging) on the mechanoenzymatic hydrolysis of banana peels (BP) were studied. The solvent-free enzymatic hydrolysis of BP under RAging conditions was found to provide higher glucose (40.5 g/100 g dry BP) and fructose (17.2 g/100 g dry BP) yields than chemical hydrolysis (33 and 14.5 g/100 g dry BP glucose and fructose, respectively) without the need for chemical pre-treatment or high temperatures. Next, conversion of the resulting monosaccharides into HMF in the presence of the $AlCl_3 \times H_2O$-DMSO/H_2O system resulted in 71.9 mol% yield, which is so far the highest HMF yield obtained from cellulosic food waste. Under identical reaction conditions, one-pot conversion of untreated BP to HMF using $AlCl_3 \times H_2O$ as catalyst and DMSO/water as solvent system yielded 22.7 mol% HMF, suggesting that mechanoenzymatic hydrolysis greatly promotes the release of sugars from BP to improve HMF yield.

Keywords: Cellulase; Mechanoenzymology; Reactive aging; Banana peel; HMF.

1. Introduction

The global supply of fossil fuels is progressively decreasing, while the worldwide energy demand is anticipated to rise by 2% annually. As a consequence, the predicted energy consumption for 2050 is expected to be twice that of 2001 (Ji et al., 2020). The growing energy demand creates an urgent need to harness plant biomass as an alternative feedstock to substitute for fossil fuels. Moreover, the concept of "circular bioeconomy" is encouraging researchers and industries to utilize food wastes as a potential raw material for chemical and energy production (Sharma et al., 2021). Among the various types of food wastes, fruits and vegetables account for 36% of total food wastes (Lin et al., 2013). These refuses are rich in carbohydrates, proteins and fibers, making them attractive feedstock for the production of value-added products (Kumar et al., 2020).

Bananas are one of the most widely consumed fruits and are currently the second most produced fruit in the world (Khawas et al., 2016; Palacios et al., 2017). According to the Food and Agriculture Organization of the United Nations, the global banana exports (excluding plantains) reached a record high of 22 million tons in 2020 (FAO, 2021b). Usually, the banana peel (BP) is discarded as waste after consumption, which contributes to environmental pollution. The BP represents 30-40% of the overall fruit mass, and acts as an important source of cellulose, hemicellulose, pectin, and lignin (Oberoi et al., 2012). Therefore, reusing BP to produce chemicals is a promising option to overcome the challenges of resource depletion and to minimize environmental pollution.

This research aimed to convert BP into the furan-based chemical 5-hydroxymethylfurfural (HMF), which is regarded as one of the most promising platform compounds by the US Department of Energy (DOE) (Bozell and Petersen, 2010). HMF is a furanic molecule comprising of an aldehyde and an alcohol group, making this compound a versatile intermediate for further transformation into a vast array of chemicals that function as building blocks for the synthesis of fibers and polymers, which are otherwise generated from petroleum (Mukherjee et al., 2015). In principle, HMF production from lignocellulosic biomass requires three steps, i.e. hydrolysis of glucose-based polysaccharides, isomerization of glucose to fructose, and the dehydration of fructose to HMF. In the traditional HMF production process, these reaction steps are accelerated by employing different acid-base catalysts. For example, Brønsted acids are used to facilitate the hydrolysis and the dehydration reactions, and Lewis acids are used to catalyze the isomerization steps (Yu et al., 2017). However, according to recent studies, HMF synthesis from cellulosic food wastes is still challenging due to their complex composition, the low selectivity of the catalytic systems, the inefficient hydrolysis of crystalline cellulose, and the formation of byproducts (Menegazzo et al., 2018). Therefore, to improve the HMF yield from cellulosic food wastes, a more efficient production system needs to be developed.

Enzymes are promising catalysts to develop ‘green’ synthetic routes to chemical products. Compared to chemical catalysts, enzymes offer several advantages, including milder reaction conditions, higher selectivity, and allow easier separation of the targeted product (Dev et al., 2018). Recently, mechanoenzymatic reactions in moist-solid reaction mixtures have received a lot of attention as a low-waste and efficient method for hydrolyzing lignocellulosic substrates (Hammerer et al., 2020a, 2020b, 2018; Kaabel et al., 2020; Ostadjoo et al., 2019; Pérez-Venegas et al., 2020). Enzymatic hydrolysis can be performed in a single step without bulk solvent while allowing significantly higher substrate loadings than traditional dilute aqueous reactions. In particular, Hammerer et al. developed a mechanoenzymatic technique, called Reactive Aging (RAging), which consists of alternate cycles of short milling and longer incubation time (aging) (Hammerer et al., 2018). The application of the RAging method can provide a high conversion of the plant biomass in a shorter period of time without the need for any prior pretreatment of the biomass (Hammerer et al., 2020a).

Herein, the mechanoenzymatic hydrolysis of BP using the commercial cellulases blend Cellic CTec2, and the subsequent conversion of the sugars into HMF using $AlCl_3$ in a DMSO/water solvent system was explored. To the best of the authors' knowledge, this study is the first to provide a semisynthetic route to HMF from BP.

2. Materials and methods

2.1. Materials

The water used for all sample preparation was MilliQ water quality with a specific resistance of 18.2 MΩ cm at 25 °C. Mechanoenzymatic reactions were conducted in a FormTech Scientific FTS1000 shaker mill using SmartSnap stainless steel or Teflon milling jars (15 ml), containing stainless steel or zirconia balls (7 mm in diameter). Aging of reaction mixtures was performed in an IsoTemp vented oven from Fischer Scientific at 55 °C. A VWR Incubating Microplate Shaker was used for in-solution enzymatic hydrolysis. Cellic CTec2 cellulase blend (SAE0020) and the Coomassie Plus (Bradford) Assay Reagent (23238) were purchased from Sigma-Aldrich and Thermo scientific, respectively. Vortexing was performed with a VWR Mini Vortexer set to level 10. High-performance liquid chromatography (HPLC) was performed using mobile phases comprising of HPLC-grade acetonitrile (ACN) (≥ 99.9%), HPLC-grade methanol (≥ 99.9%), and HPLC-grade water purchased from Sigma-Aldrich. Glucose (99.5%), fructose (≥99%), mannose (99%), galactose (99%), xylose (99%), and arabinose (99%), were purchased from Sigma Aldrich to calibrate the HPLC. Additional reagents including HCl, formic acid, and AlCl3$^{\times}$H2O were purchased from Sigma-Aldrich. All experiments were conducted in triplicate and the results were reported as the average with standard deviation.

2.2. Biomass preparation

Ripe yellow bananas were purchased from a nearby supermarket and the peels were removed, chopped, and dried for 48 hours at 60 °C in a hot-air oven. The dried BP was pulverized to a fine powder using a blender. The resultant powder was collected and stored in a closed vial at room temperature.

2.3. Chemical composition of BP

The cellulose and hemicellulose content of the dry BP powder were determined through the ANKOM filter bag technique using an ANKOM 200i fiber analyzer (ANKOM Technologies, Inc., Fairport, NY, USA), following the protocol described by Musule et al. (Musule et al., 2016). Powdered BP (0.5 g) was taken from each sample unit and placed in ANKOM fiber bags for digestion in the fiber analyzer. The estimated parameters were the neutral detergent fiber (NDF), the acid detergent fiber (ADF), and the acid detergent lignin (ADL). The content of cellulose and hemicellulose was measured by subtracting ADL and ADF from NDF, respectively.

The thermal behavior of the dry BP powder was studied using a thermogravimetric analyzer (TGA; Q50, TA Instruments, New Castle, USA). For the analysis, around 30 mg of dry BP was used. The analyses were conducted in the presence of a stream of nitrogen flowing at a rate of 60 ml/min. The sample was heated at a rate of 5 °C/min over a temperature range of 20-600 °C.

2.4. Influence of enzyme loading on BP hydrolysis in aqueous solution

Dry BP powder (25 mg) was added to the enzyme preparation (15, 30, 45 or 60 mg of Cellic CTec2 enzyme per gram of BP) and water (for a total of 1000 µl, i.e. $\eta = 40$ µl/mg) in a 2 ml Eppendorf tube. The reaction mixtures were incubated for 24 h at 55 °C and 1000 rpm in a shaking incubator. The samples were analyzed using HPLC.

2.5. Influence of the milling vessel type and reaction volume on mechanoenzymatic hydrolysis

BP (100 mg) was combined with 4.5 mg Cellic CTec2 enzyme in a 15 ml Teflon or stainless steel milling jar containing two 7 mm zirconia or stainless steel balls. The total water volume added was 150 µl (η= 1.5 µl/mg). The samples were milled at 30 Hz for 30 min and aged for 30 min at 55 °C in a vented oven. As needed, aliquots (~ 20 mg) were collected in an Eppendorf tube and stored at -20 °C for later analysis by HPLC. To determine the optimal reaction volume of mechanoenzymatic hydrolysis, 4.5 mg Cellic CTec2 enzyme was diluted in an appropriate volume of water to obtain a final η value of 1, 1.5, or 2.5 µl/mg BP, before addition to 100 mg BP in a 15 ml Teflon milling vessel containing two 7 mm zirconia balls. The samples were treated as described above and subsequently analyzed using HPLC.

2.6. Influence of pre-milling BP on the yield of mechanoenzymatic reactions

BP (800 mg) was milled at 30 Hz for 60 min in a 15 ml stainless steel jar with two 7 mm stainless steel balls. Native or pre-milled BP (150 mg) was added to 6.8 mg of Cellic CTec2 enzyme in a 15 ml Teflon milling vessel containing two 7 mm zirconia balls. The total water volume was 225 µl (η = 1.5 µl/mg). The sample was milled for 30 min at 30 Hz, and aliquots (~ 20 mg) were collected in an Eppendorf tube and stored at -20 °C until analysis. The remaining samples were aged for 3 days at 55 °C in a vented oven. Aliquots (~ 20 mg) were collected and kept at -20 °C in an Eppendorf tube. The samples were analyzed using HPLC.

2.7. Enzymatic reactions under milling and aging conditions

BP (300 mg) was added to 13.5 mg Cellic CTec2 enzyme in a 15 ml Teflon milling vessel containing two zirconia balls of 7 mm in diameter. The final water volume was 450 µl (η = 1.5 µl/mg) and the samples were milled in a shaker mill for 90 min at 30 Hz. Aliquots (~ 20 mg) were collected at 5, 15, 30, 45, 60 and 90 min intervals, and immediately stored at -20 °C. For aging the reactions, ~ 20 mg aliquots were transferred to a 1.5 ml Eppendorf tube and incubated in a vented oven at 55 °C for 3 days. Samples were analyzed using HPLC.

2.8. Enzymatic reactions under RAging conditions

Samples for RAging were prepared as described above (section 2.7). The samples were milled at 30 Hz for 5 min and transferred to a vented oven set to 55 °C for 55 min with the jar kept closed. The samples were subjected to 7 cycles of milling 5 min + aging 55 min. Aliquots (~ 20 mg) were collected after 1, 2, 3, 4, 5, 6 and 7 h, and immediately stored at -20 °C until analysis.

2.9. Chemical hydrolysis of BP

Chemical hydrolysis of BP was performed following the protocol described by Nzediegwu et al. (Nzediegwu et al., 2021). Thus, BP (25 mg) was added to 0.2 or 0.5 M HCl (2 ml) in a Pyrex tube fitted with high-temperature seals, and the samples were incubated at 180 °C for 10 min in a Fisher Scientific High Temp Oil Bath 160-A. Additional hydrolysis reactions were carried out using 0.2 M HCl for 5, 15 and 30 min under similar reaction conditions. The reactions were quenched by immersion in an ice bath and neutralization with CaCO3 to a pH 5–6, before centrifugation for 5 min at 21,100 ×g. Samples were analyzed by HPLC.

2.10. Conversion of mechanoenzymatically hydrolyzed BP to HMF

BP was mechanoenzymatically hydrolyzed as described above (milled at 30 Hz for 30 min and then aged in a ventilated oven at 55 °C for 30 min). Following aging, the samples were suspended in chilled water to obtain a 10 mg/ml suspension. The enzymes were inactivated by heating the suspension for 10 min at 100 °C. The suspension was then vortexed for 5 s, sonicated for 10 min and centrifuged for 5 min at 21,100 ×g. The supernatant was transferred to a fresh tube, and the concentration of sugars was measured by HPLC. The conversion of these sugars to HMF was performed following the manuscripts of Jia et al. (Jia et al., 2017). Thus, the supernatant (0.5 ml) was combined with DMSO/water (9:1 v/v) in a 10 ml Pyrex tube, and 20 mol% $AlCl_3 \times H_2O$ (based on the monosaccharides present in the samples) was added to the sample. The total reaction volume was 5 ml, and the sample was incubated in an oil bath with a magnetic stirrer (Thermo Fisher Scientific) for 1 hour at 140 °C and 600 rpm. The temperature of the oil bath was monitored using a K-type thermocouple with a deviation of roughly 1 °C. The reaction was by immersion of the Pyrex tube in an ice bath. The HMF yield was obtained by HPLC.

The conversion of sugars to HMF was also performed with $AlCl_3 \times H_2O$ by lowering the pH to 2.5 using HCl, according to an earlier method (Pagán-Torres et al., 2012). As a control, a reaction involving only HCl (pH = 2.5) was included. The reactions were performed and analyzed under similar conditions as described above.

For direct conversion of BP to HMF, 5 wt/v% of untreated BP was combined with 55.5 mM $AlCl_3 \times H_2O$ in accordance with a previous study (Yu et al., 2017). HCl was used to bring the pH of the reaction mixture down to 2.5. A combination of DMSO/water (5 ml of 9:1 v/v) was used as the solvent. The samples were incubated, quenched, and analyzed as described above.

2.11. Analysis of sugars and HMF

2.11.1. HPLC analysis

To analyze the sugar concentration by HPLC, the frozen samples (~20 mg) were lyophilized, weighted precisely, and suspended in 500 µl of water. The enzymes were inactivated by heating aliquots (1 ml) at 100 °C for 10 min. The suspension was vortexed for 5 s, sonicated 10 min and centrifuged for 5 min at 21,100 ×g. The supernatants were mixed with ACN to reach 50% (v/v). The solution was then filtered and analyzed using an Agilent 1100 HPLC system, equipped with a refractive index detector (RID). Separation was achieved using a Zorbax Carbohydrate analysis column (4.6 × 150 mm, 5 μL). The column and the RID were both set at 30 °C, and the mobile phase consisted of a blend of HPLC grade acetonitrile (ACN) and water (85:15) applied in an isocratic mode. The injection volume and flow rate were 5 μL and 1.4 ml/min, respectively. The retention times of glucose and fructose were 7.4 and 8.4 min, respectively. The glucose and fructose yields were calculated from a calibration curve (concentration of pure analytes in H_2O against the areas displayed on the chromatogram).

To determine the HMF yield using HPLC, the samples were filtered and analyzed using a Phenomenex C18 column (4.6×150 mm). The mobile phase was an isocratic 90:10 (v/v) blend of HPLC grade water and methanol, both containing 0.1% (v/v) formic acid. Detection was achieved using a variable wavelength detector (VWD) set at 267 nm. The injection volume and flow rate were 5 μl and 0.6 ml/min, respectively. The retention time of HMF was 6.07 min. The HMF yield was calculated using equation (1)

$$HMF\ yield\ (mol\%) = \frac{Weight\ of\ HMF\ produced\ (mg)}{Weight\ of\ Glucose\ \&\ Fructose\ (from\ hydrolysis)\ fed\ \ (mg)} \times \frac{180\ g/mol}{126\ g/mol} \times 100\% \quad (1)$$

3. Results and discussion

3.1. Compositional analysis of the BP samples

The fiber analysis of BP revealed that the cellulose and hemicellulose contents were 10.5 and 10.1 dry wt%, respectively. Apart from cellulose and hemicellulose, BP is also reported to be rich in pectin, starch, and simple sugars like sucrose, glucose, and fructose (Khawas et al., 2016; Oberoi et al., 2012). TGA and derivative thermogravimetric (DTG) techniques are frequently used to determine the thermal behavior of biomass, such as moisture loss and residual ash content, as well as for quantifying the content of lignocellulose components based on the material decomposition at a certain temperature (Díez et al., 2020). According to Figure 3.1, BP lost 5.2 dry wt% of its initial mass before reaching 100 °C, which is attributable to the elimination of moisture from the

BP (Shahedifar and Rezadoust, 2013). At temperatures exceeding 150 °C, the degradation of lignocellulosic compounds began (Díez et al., 2020). The TGA and DTG curves of BP showed two significant mass losses that were related to two distinct thermal events. The first major mass loss occurred at 190 °C, which corresponds to pectin decomposition, according to the findings of Orozco et. al (Sánchez Orozco et al., 2014). Mass loss for pectin is estimated at 15.1 dry wt%, which is in agreement with the pectin content reported by Oberoy et al. for BP (15.9 dry wt%.) (Oberoi et al., 2012). The second major mass loss corresponds to holocellulose decomposition. Holocellulose is a combination of cellulose and hemicellulose which starts to degrade between 200 and 410 °C (Nzediegwu et al., 2021). For BP, the degradation of holocellulose happened in the range of 250–315 °C, with a maximum decomposition rate at around 285 °C. The mass loss for the holocellulose fraction was calculated to be 23.1 dry wt %, which is very close to the value of 20.6 dry wt% obtained from the fiber analysis. Lignin, on the other hand, has the widest decomposition range, starting from 200 °C onward. In some cases, lignin degradation is indicated by a small peak that overlaps with the end of the cellulose degradation (Díez et al., 2020). For BP, a small peak at 330 °C suggests lignin degradation with a mass loss of 6.6 dry wt%. The overall mass loss at the end of the decomposition process was calculated at 66.5 dry wt%, suggesting an ash content of 33.5 dry wt%.

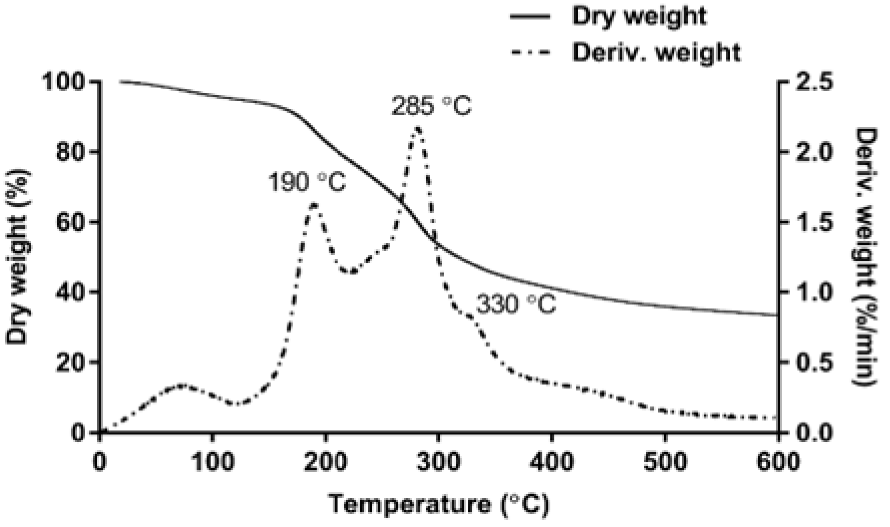

Figure 3.1: Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of BP

3.2. Enzymatic hydrolysis of BP

3.2.1. BP saccharification under classical hydrolysis condition

The activity of the Cellic CTec2 enzyme blend towards BP under classical hydrolysis conditions was assessed in order to determine the optimum enzyme loading, which is defined as the mass of protein per mass of BP (mg g^{-1}). The Cellic CTec2 blend is reported to contain several cellulases, including exoglucanases, endoglucanases, β-glucosidases, hemicellulases, as well as oxidative enzymes, lytic-polysaccharide monooxygenases (LPMOs) (Müller et al., 2015). The protein concentration of the Cellic CTec2 blend was measured using the Bradford assay. Figure 3.2 illustrates the sugar yields from BP hydrolysis with various enzyme loadings following 24 h of incubation at 55 °C and 1000 rpm. The reaction with 45 mg Cellic CTec2 enzyme per gram of BP produced the highest glucose and fructose yields after 24 hours (36.2 and 12.8 g of glucose and fructose per 100 g of dry BP, respectively). Increasing the enzyme loading to 60 mg/g of BP had little effect on the sugar yields (30.5 and 11.3 g of glucose and fructose per 100 g of dry BP, respectively). The lower sugar yields are probably due to the overcrowding of enzymes on the substrate's surface (Hammerer et al., 2018; Igarashi et al., 2011).

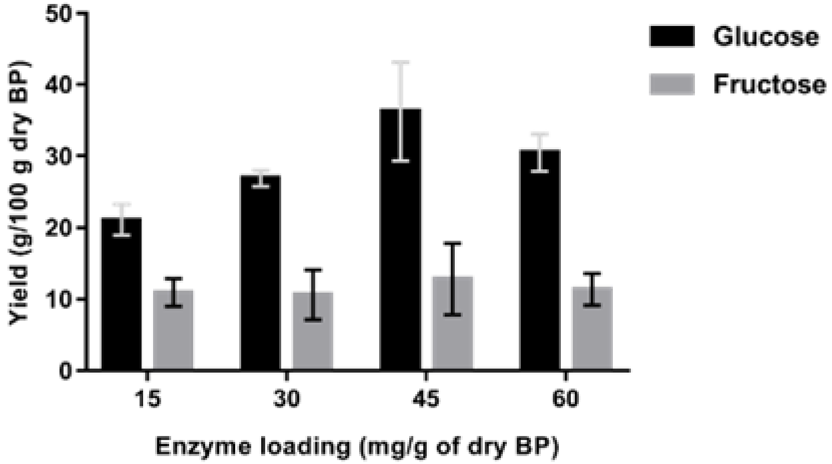

Figure 3.2: Influence of enzyme loading on the hydrolysis of BP. BP (25 mg) was suspended in water (1 ml) with various Cellic CTec2 enzyme loadings and incubated for 24 hours at 55 °C and 1000 rpm. Sugar concentrations were determined by HPLC

3.2.2. BP saccharification under mechanoenzymatic conditions

For enzymatic lignocellulose hydrolysis under conventional dilute aqueous conditions, the biomass must be chemically pretreated to improve the accessibility of the enzymes to the polysaccharides chain. In moist-solid mixtures, no chemical pre-treatment is needed (Hammerer et al., 2020a). To analyze the BP hydrolysis under mechanoenzymatic conditions, the impact of ball milling and liquid volume on BP hydrolysis was investigated. The choice of milling jar and ball material can influence the hydrolysis of a substrate (Hammerer et al., 2018). To evaluate the effect of this parameter on the reaction efficiency, both stainless steel and Teflon milling jars, containing either stainless steel or zirconia milling balls were tested. After 30 min of milling and 30 min of aging, the fructose and glucose yields were comparable for both types milling jars (Fig. 3.3a) and for both types of milling balls, implying that hydrolysis of BP might be less sensitive to the environment than biomass saccharification.

Another important parameter in mechanoenzymatic transformations is the total volume of liquid added. Water is an essential substrate for the Cellic CTec2 enzyme and can also serve as an additive in liquid-assisted grinding (LAG) to accelerate, direct, or optimize mechanoenzymatic reactivity while avoiding solubility limitations (Hammerer et al., 2018; Therien et al., 2019). The amount of water used in mechanoenzymatic reactions is often defined by the parameter η, which is a ratio of liquid volume to the weight of substrate (µL mg^{-1}) (Hammerer et al., 2018). To be within the LAG regime, the generally accepted η value is between 0.5 to 2 µL mg^{-1} (Arciszewski and Auclair, 2022; Hammerer et al., 2020a). Interestingly, it has been reported that effective hydrolysis of biomass requires a higher η value (η = 1.34 µL ml^{-1}) than pure cellulose such as microcrystalline cellulose (MCC) (η= 0.9 µL ml^{-1}) (Hammerer et al., 2020a, 2018). Herein, three different η values were tested (1.0, 1.5 and 2.5 µL mg^{-1}). As shown in Figure 3.3b, the glucose and fructose yields were within error for all η values tested, and η = 1.5 µL mg^{-1} (150 µl/100 mg BP, which gave 23 and 8.4 g of glucose and fructose per 100 g of dry BP, respectively) was selected for all subsequent experiments.

The influence of substrate pre-milling on BP hydrolysis was also investigated. Hammerer et al. (2020a) had reported that pre-milling lignocellulosic biomass prior to enzymatic hydrolysis significantly improved the reaction yield (Hammerer et al., 2020a). Thus, BP was pre-milled for 60 min before being milled in the presence of Cellic CTec2 enzyme (30 min) with or without subsequent aging for 3 days. As depicted in Figure 3.3c, pre-milling of BP did not have a significant effect on the glucose and fructose yields. Furthermore, the reaction was mostly complete after 30 min of milling, with little yield increase following aging.

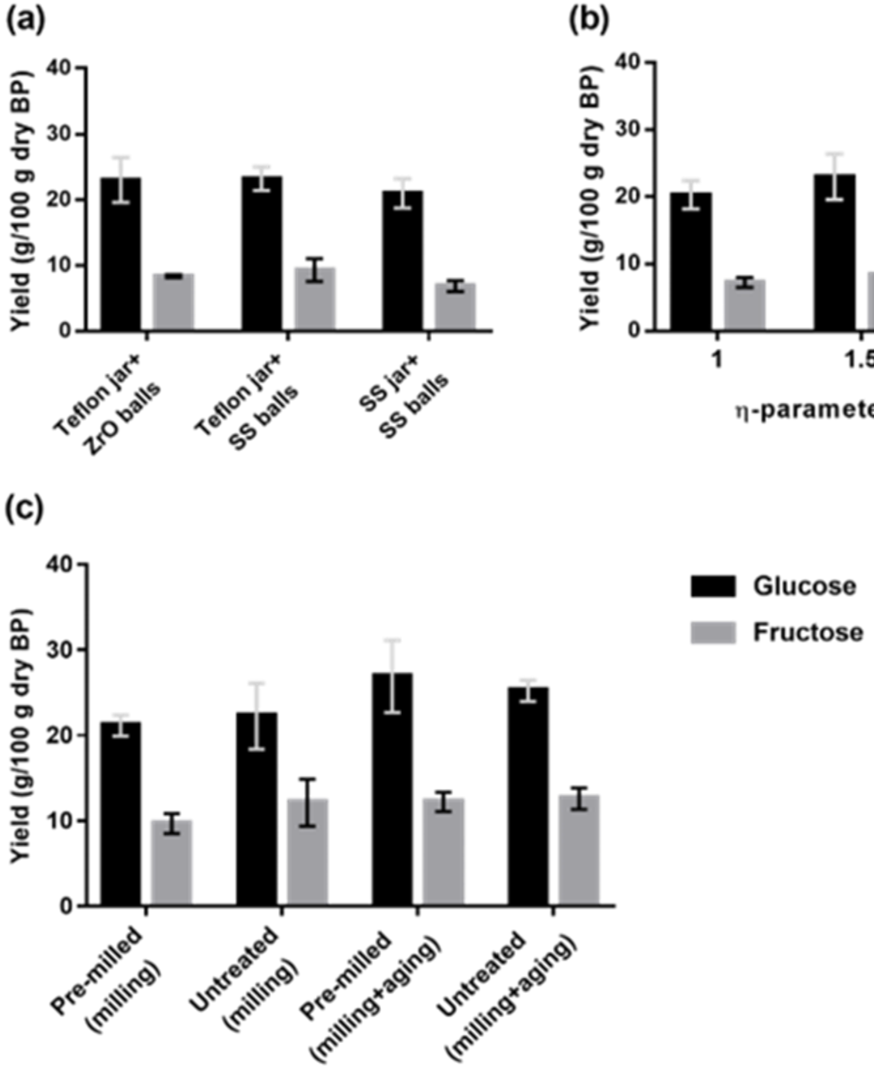

Figure 3.3: Influence of milling jar type (a) (100 mg BP, 45 mg g^{-1} Cellic CTec2 enzyme, η = 1.5 μL mg^{-1}), different η values of water (b) (100 mg BP, 45 mg g^{-1} Cellic CTec2 enzyme, Teflon milling jar), and pre-milling (c) (60 min, 30 Hz, 15 ml stainless steel milling jar) on the mechanoenzymatic hydrolysis of BP. Samples (a and b) were milled for 30 min at 30 Hz and aged for 30 min at 55 °C. Powdered or pre-milled powdered samples (c) (150 mg BP, 45 mg g^{-1} Cellic CTec2 enzyme, η = 1.5 μL mg^{-1}, Teflon milling jar) were milled at 30 Hz for 30 min and aged for 3 days at 55 °C. Sugar concentrations were determined by HPLC. ZrO: Zirconia; SS: Stainless steel.

Next, the impact of different milling times on the enzymatic hydrolysis of BP was investigated. The enzymatic reaction mixture was milled for various durations (5 to 90 min) with or without aging (3 days at 55 °C). The duration of milling was found to have a minor impact on the hydrolysis of BP (Fig. 3.4a). Without aging, the sugar yields reached their maximum with 15-30 min of milling. However, the yields were higher when the mixtures were also aged (again, sugar yields were within error for all milling time-points), suggesting that the enzymes were not denatured during prolonged milling time.

The impact of intermittent milling during the reaction (or RAging) was also investigated. RAging was performed by repeating one-hour cycles of 5 min milling at 30 Hz and 55 min aging at 55 °C. The yield of glucose reached 40.3 g/100 g dry BP after only 3 RAging cycles (total of 3 hours), which is 1.5 folds higher than the maximum glucose yield obtained through a combination of a single milling step followed by 3 days of aging (Fig.3.4a and b). Increasing the number of RAging cycles did not improve the glucose yield any further. Under RAging conditions, the yield of fructose also improved, but the improvements were only marginal in comparison to the glucose yields. The maximum fructose yield of 17.2 g/100 g of BP was achieved after the 7th cycle of RAging, which is about 1.2 folds higher than the maximum yield obtained by a single milling step followed by 3 days of aging (Fig. 3.4a and b). In comparison to in-solution digestion (2.5% dry BP w/v; 24 h) at equal enzyme loadings, RAging gave 1.1 and 1.3 folds higher glucose and fructose yields, respectively, within 6 h (Fig.3.2 and 3.4b).

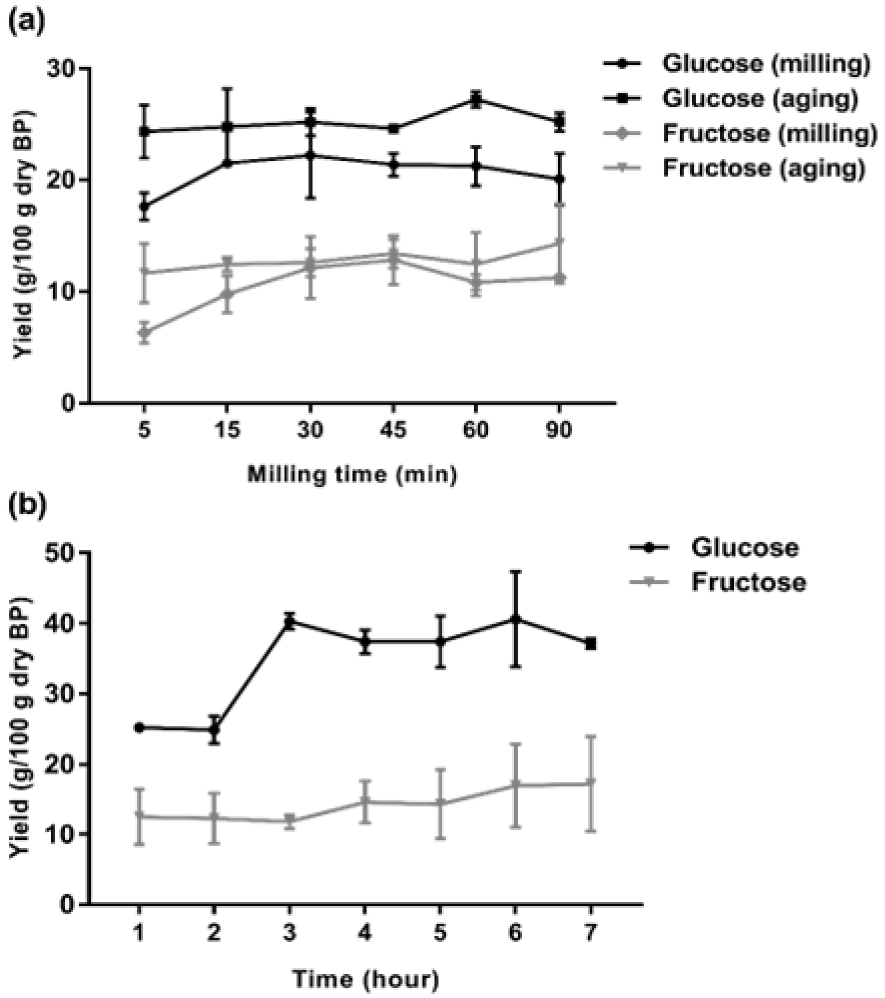

Figure 3.4: (a) Influence of milling times on enzymatic hydrolysis of BP with (milling+aging) or without aging (milling). Samples (300 mg BP, 45 mg g^{-1} Cellic CTec2 enzymes, and water at $\eta = 1.5$ µL mg^{-1}) were milled at 30 Hz in a 15 ml Teflon milling jar and withand with or without aged for 3 days at 55 ºC. (b) Enzymatic hydrolysis of BP using RAging conditions. Samples (300 mg BP, 45 mg g^{-1} Cellic CTec2 enzyme, water at $\eta = 1.5$ µL mg^{-1}) were submitted to 7 cycles of 5 min of milling (30 Hz and 15 ml Teflon milling jar) and 55 min of aging at 55 ºC. Sugar concentrations were determined by HPLC.

3.3. Chemical hydrolysis of BP

The chemical hydrolysis of BP was performed with 0.2 and 0.5 M HCl at 180 ºC. HPLC analysis of the samples hydrolyzed with 0.5 M HCl for 10 minutes showed the presence of glucose only (no fructose), whereas reactions with 0.2 M HCl yielded not only fructose but also 2.2 fold more glucose after 10 min (Fig. 3.5). The 0.2 M HCl solution was used to hydrolyze BP for three additional time points of 5, 15, and 30 min. No improvement in glucose yield was observed, while the highest fructose yield was achieved in 5 min (14.5 g/100 g of BP, which was reduced to 8.1 g/100 g of BP after 10 min). Fructose was not detectable in samples hydrolyzed for 15 and 30 min, presumably due to its conversion into different degradation products (Chen, 2015). In comparison to enzymatic hydrolysis under RAging conditions, the chemical hydrolysis of BP yielded 1.2 and 1.9 folds lower glucose and fructose yields, respectively.

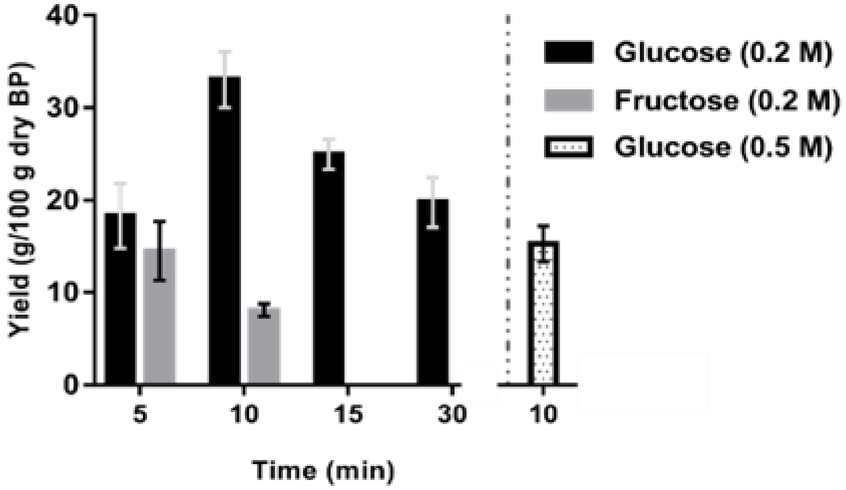

Figure 3.5: Chemical hydrolysis of BP using HCl. Reaction conditions: 25 mg dry BP incubated with 0.2 or 0.5 M HCl (2 ml) at 180 °C. Sugar concentrations were determined by HPLC

3.4. Conversion of mechanoenzymatically hydrolyzed BP to HMF

HMF is mainly synthesized from the dehydration of fructose in the presence of Brønsted acids. However, to produce HMF from glucose, an additional step is required in which glucose is isomerized to fructose using a Lewis acid. Metal salts with Lewis acidity, such as $AlCl_3$, are widely used for efficient conversion of sugars into HMF (Zhao et al., 2021). One advantage of metal salts is that they can act as bifunctional catalysts for the isomerization and dehydration reactions required for the conversion of glucose to HMF. During HMF production by metal salts, glucose isomerization is catalyzed by a Lewis acid, while partial hydrolysis of metal ions in the aqueous medium provides indirect Brønsted acidity for the dehydration reaction (Yu et al., 2016). In this study, $AlCl_3 \times H_2O$ was used as a Lewis acid for the conversion of hydrolyzed BP to HMF. The reactions were conducted at 140 °C for 1 h using a DMSO-to-water ratio of 9:1. Pagán-Torres et al. (2012) had reported that when metal salts are supplemented with mineral acids, they exhibit a better selectivity towards HMF production from glucose (Pagán-Torres et al., 2012). Therefore, additional reactions were also conducted at pH 2.5 (with addition of HCl). As shown in Figure 3.6, in the absence of a Lewis acid catalyst, the acidic conditions produced approximately 35 mol% of HMF. The use of $AlCl_3 \times H_2O$ without HCl produced 43 mol% of HMF. However, the addition of the mineral acid to $AlCl_3 \times H_2O$ catalyzed reactions resulted in a 1.7 folds increase in the HMF yield (71.9 mol%), which, to our knowledge, is higher than any previously reported HMF yield from cellulosic food waste (Table 3.1).

Table 3.1: Comparison of HMF production from fruit and vegetable waste between previous work and this study

Substrates	Catalysts	Solvents	Reaction conditions	HMF yields	Reference
Mixed food waste	Zirconium phosphate (ZrP)	Water	160 °C, 6 h	4.3 wt%	(Parshetti et al., 2015)
Raw mixed vegetables	$SnCl_4$ $Zr(o)Cl_2$	DMSO/water	160 °C, 20 min	4.9 wt% 2 wt%	(Yu et al., 2017b)
	$FeCl_3$ $CrCl_3$ $AlCl_3$	DMSO/water	160 °C, 40 min	1.5 wt% 1.9 wt% 2.8 wt%	
Unskinned kiwifruit	$SnCl_4$ $Zr(o)Cl_2$ $FeCl_3$ $CrCl_3$ $AlCl_3$	DMSO/water	160 °C, 20 min	13.7 wt% 8 wt% 7.3 wt% 6.6 wt% 4.9 wt%	
Watermelon flesh	$SnCl_4$ $Zr(o)Cl_2$ $FeCl_3$ $CrCl_3$ $AlCl_3$	DMSO/water	160 °C, 20 min	13.2 wt% 4.2 wt% 4.2 wt% 3.8 wt% 3.1 wt%	
Corn Taro	$SnCl_4$	acetone/H_2O	$scCO_2$-treatment; 140 °C, 10 min	19 wt% 20 wt%	(Yu et al., 2019)
Lettuce Bean sprout	$SnCl_4$	acetone/H_2O	$scCO_2$-treatment; 140 °C, 20 min	2.3 wt% 2.2 wt%	
Watermelon peel	HCl	Water	135 °C, 6 min	3.8 wt%	(Shao et al., 2019)
Orange waste Apple wastes	D001-cc resin	[Bmim]Cl	Ultrasound-[Bmim]Cl pretreatment; 160 °C, 40 min	42.2 mol% 44.7 mol%	(Ji et al., 2020)
Apple waste	Sn Amberlyst-15 resin	Methyl isobutyl ketone (MIBK)	Filtration with 54 µm filter; 120 °C, 2 h	18 wt%	(Tempelman et al., 2021)
Mango pulp and skin	H_2SO_4	Water	150 °C, 20 min	21.2 mol%	(Muñiz-Valencia et al., 2020)
Banana peel	$AlCl_3{}_{\times}H_2O$; pH 2.5 (HCl)	DMSO/water	Mechanoenzymatic hydrolysis; 140 °C, 1 h	71.9 mol%	This study

Finally, as a control experiment, the direct conversion of BP powder to HMF using the optimum chemical conditions mentioned above was attempted. An HMF yield of 22.7 mol% was obtained after 1 h of incubation with $AlCl_3$-HCl, which is about 3 times less than the yield obtained from mechanoenzymatically hydrolyzed BP (Fig. 3.6). Yu et al. (2017b) reported 4.9, 3.1, and 2.8 wt% of HMF produced from unskinned kiwifruit, watermelon flesh and mixed vegetables, respectively, under microwave heating at 140 °C for 20 min using a $AlCl_3$ and DMSO/water solvent system. They reported that the conversion of cellulosic wastes to HMF was limited by the marginal hydrolysis of crystalline cellulose (Yu et al., 2017b). Ji et al. later utilized ultrasound-[Bmim]Cl pretreatment to improve the conversion of sugary fruit wastes to HMF (Ji et al., 2020). They achieved 42 and 45 mol% HMF yields from orange and apple wastes, respectively, using the optimal ultrasound-[Bmim]Cl pretreatment over a D001-cc cation exchange resin (Ji et al., 2020). Overall, findings from this study indicate that the inclusion of mechanoenzymatic hydrolysis significantly increased the release of sugars from BP without requiring pretreatment or harsh chemical conditions and resulting in a higher HMF yield.

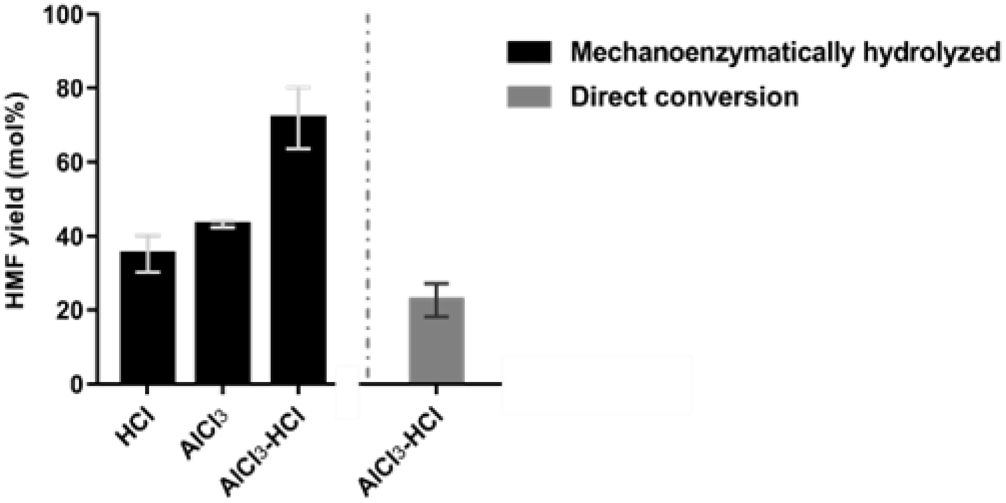

Figure 3.6: HMF yield from mechanoenzymatically hydrolyzed BP or directly from BP powder (direct conversion). Reaction conditions: 20 mol% $AlCl_3{\times}H_2O$ (55.5 mM) in DMSO/H_2O (9:1) at 140 °C and 600 rpm for 1 hour. pH adjusted to 2.5 with HCl ($AlCl_3$-HCl).

4. Conclusion

Enzymes offer several advantages over chemical catalysts, including their superior selectivity, gentle reaction conditions, and minimal toxicity. The application of mechanoenzymology for lignocellulose biomass hydrolysis has attracted interest recently, owing to the solvent-free reaction conditions that significantly reduce waste generation. In this work, it was demonstrated that BP can be efficiently hydrolyzed to glucose and fructose under mechanoenzymatic conditions without bulk solvent. Specifically, with the RAging process, it is possible to achieve up to 40 wt% glucose yield within 3 hours of hydrolysis without chemical pre-treatment. The crude sugars obtained after hydrolysis can be efficiently converted to HMF using the $AlCl_3{\times}H_2O$ -DMSO/H_2O system under milder conditions than the standard process. Adding a Brønsted acid to the Lewis acid catalyst significantly increased the yield of HMF. Compared to the direct conversion of BP to HMF by $AlCl_3{\times}H_2O$, the inclusion of first mechanoenzymatic hydrolytic step increased the HMF yield by about 3 folds. In summary, this study showcased mechanoenzymology as a highly efficient and more sustainable alternative for producing HMF from biomass, particularly cellulosic food waste, which is currently challenging to achieve using existing production methods.

Chapter 4

Comprehensive Scholarly Discussion

The growing need for food on a global scale has led to a rise in the amount of waste produced, which poses a serious threat to our economy and the environment. Approximately one-third of all food, including vegetable, meat, dairy, and bread products, is lost or wasted annually in the food supply chain (Ishangulyyev et al., 2019). Based on the composition, food waste can be divided into several types such as fruit and vegetable waste, dairy waste, meat waste, and cereals and grains processing waste. Current food waste management strategies rely primarily on landfilling or dumping, with certain wastes processed into animal feed, fertilizer, or utilized in anaerobic digestion (Trivedi et al., 2020). A more sustainable option of recycling food waste is to utilize it as a raw material for fuel and chemical production.

HMF, as a platform chemical, can undergo a wide range of chemical processes, including oxidation, reduction, etherification, esterification, amination, acetalization, decarboxylation, and halogenation to generate a vast array of compounds with significant applications such as chemicals, plastics, fibers, and polymers (Hu et al., 2021). A valuable chemical derivative of the oxidation of HMF is FDCA, which serves as a building block for a wide range of products. As FDCA manufacturing is dependent on HMF, an economical HMF production is crucial. However, current HMF manufacturing is expensive because it is primarily made from syrup extracted from sugary crops (Menegazzo et al., 2018). Consequently, attempts are now being made to find more cost-effective raw materials for HMF synthesis. As food waste is a low-cost, widely available biomass with a high carbohydrate content, it can serve as an alternative source of raw material for HMF synthesis. However, converting food waste into HMF is still challenging, and therefore it is crucial to develop an efficient manufacturing system that ensures a high output of HMF at a low cost.

In this thesis, banana peel (BP) was transformed into HMF using a combination of enzymatic and chemical catalytic methods (Fig. 4.1).

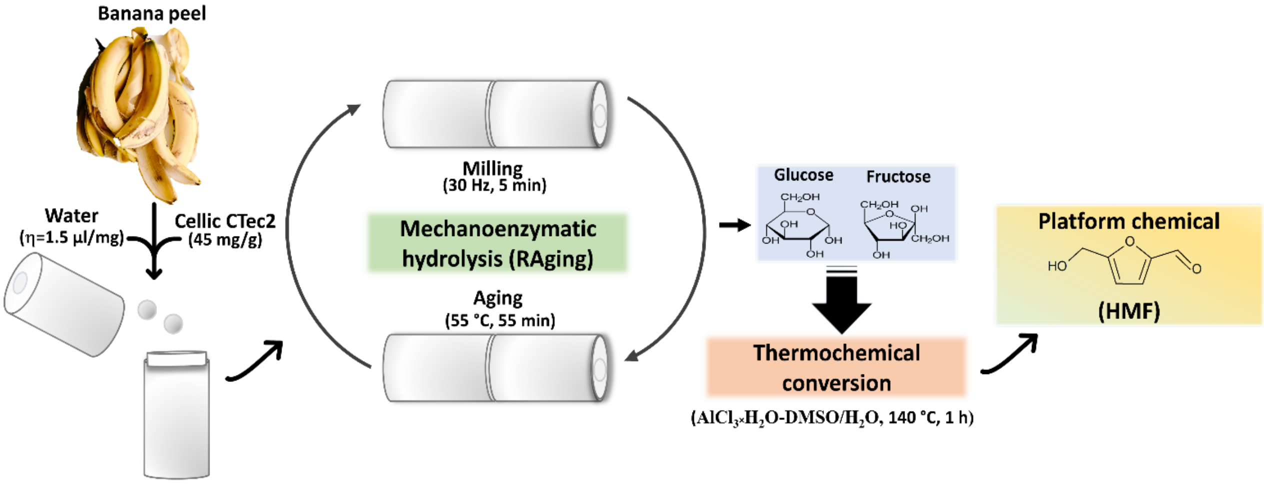

Figure 4.1: Conversion of BP into HMF by using an integrated mechanoenzymatic/catalytic approach

The lignocellulose content of BP was determined by analyzing its composition with a fiber analyzer and thermogravimetric analysis (TGA). Analyses of the composition detected the presence of polysaccharides including cellulose, hemicellulose, pectin, and aromatic polymer lignin. According to fiber analysis, BP contains 10.5 and 10.1 wt% cellulose and hemicellulose, respectively. As per different literature, the cellulose and hemicellulose contents of BP can range from 12.2 to 59.1% and 9.2 to 39.7%, respectively (Emaga et al., 2008; Harini et al., 2018; Oberoi et al., 2011; Odedina et al., 2017; Pereira et al., 2021). Variation in the amount of different polysaccharides in BP can be influenced by a variety of factors, including genetic differences between banana cultivars, variable climate conditions, and variation in the chemical characterization techniques (Pereira et al., 2021). In general, cellulose makes up the majority of lignocellulose. It is a fibrous organic substance that is insoluble in water and made of Danhydroglucose ($C_6H_{11}O_5$) linked by β-(14) glycosidic linkages. The disaccharide cellobiose acts as a repeating unit as each subsequent glucose residue rotates 180 ° relative to the previous one (Marriott et al., 2016). Hydroxyl groups present in glucose enable the development of intramolecular (same chain) and intermolecular (different chain) hydrogen bonds, resulting in the formation of an elementary fibril consisting of aggregates of 36 cellulose chains (Vidal et al., 2011). The elementary fibrils are further packed into larger microfibrils that are organized into crystalline and amorphous regions. In the crystalline region, intra- and inter-hydrogen bonds and van der Waals interactions pack cellulose chains so tightly together that even water cannot penetrate this region. As a result, the enzyme or chemical catalyst during cellulose hydrolysis is unable to properly reach the crystalline region, resulting in a low hydrolysis rate (Hamid et al., 2015; Rytioja et al., 2014). In contrast, in the amorphous regions, cellulose chains are less organized and greater space is available between chains for hydrogen bonding with other molecules, such as water (Visakh and Thomas, 2010). Cellulose can exist in a variety of polymorphs, including I, II, II, and IV. Cellulose I is the native polymorph of cellulose and can exist in two crystalline forms; Iα and Iβ. Cellulose Iβ is found in plants with antiparallel-oriented cellulose chains, whereas cellulose Iα has parallel-oriented cellulose chains and is most commonly found in bacteria (Zhang and Lynd, 2004).

Hemicellulose is another major polysaccharide that makes up the BP. In plant, hemicellulose is found covalently attached to cellulose and usually has branched and amorphous structures. Hemicellulose can be composed of several monomeric sugars such as β-D-xylose, α-L-arabinose, β-D-mannose, β-D-glucose or α-D-galactose (Gírio et al., 2010). There are four major forms of hemicellulose present in plants: xyloglucan, xylan, mannan, and β-glucan. The amount of each form of hemicellulose might differ depending on the type of plant (Rytioja et al., 2014). Xylan is the most abundant hemicellulose in plants. The primary structure of xylan consists of β-(1→4)-linked D-xylose residues. Additionally, xylan has different branched monomers that include arabinose, galactose, glucose, acetic acid, and uronic acid units. Among the branching monomers, arabinose residue is most frequently found attached to xylan and serves an essential function in the binding of hemicellulose to cellulose and lignin (Pereira et al., 2021). Pereira et al. (2021) performed the deconstruction of BP to determine the carbohydrate composition by sequentially treating it with acid, alkaline, and enzymes. They reported 17.3 wt% hemicellulose in raw BP, which was primarily comprised of xylose and arabinose. In addition, they recovered 0.5% xylooligosaccharides following successive acid and alkaline treatments (Pereira et al., 2021).

Pectin is another significant polysaccharide found in BP. Pectin is a soluble heteropolysaccharide that performs crucial roles in the development of plant cell walls. Although the precise chemical composition of pectin is unknown, it is predominantly formed of galacturonic acid connected in chain by α-(1-4)-glycosidic linkages, with different proportions of carboxyl groups esterified with methyl groups. As side chains, a minor amount of neutral sugars can be present (Lara-Espinoza et al., 2018; Pawar et al., 2008; Voragen et al., 2009). TGA analysis of BP in this study revealed a pectin content of 15.1 wt%. The amount of pectin found in BP can varies between 10 to 22 wt%, possibly due to the genetic differences in banana cultivars (Pereira et al., 2021). Emaga et al. (2008) analyzed the dietary fiber components and chemical characteristics of pectin in two genotypes of Musa peels (plantain and banana). After sequential extraction of pectin from the fruit peels with water, ammonium oxalate, and dilute HCl, they observed a higher pectin content in banana peels (21.7 wt %) than in plantain peels (14.6 wt %) (Emaga et al., 2008).

BP contains substantial quantities of the aromatic polymer lignin. Lignin is a crucial structural component of the plant cell wall that aids in plant defense from external microbial attacks (Marriott et al., 2016). It is capable of covalently crosslink with sugars contained in the hemicellulose side chain, such as arabinose found in xylans. Besides, lignin embeds cellulose together with hemicellulose and serves as a barrier for cellulose during the enzymatic hydrolysis. Lignin in general is made up of three monolignol alcohols: p-coumaryl, coniferyl, and sinapyl, which are linked together by alkyl-aryl, alkyl-alkyl, and aryl-aryl ether linkages. In comparison to dicotyledonous plants, monocotyledonous plants, such as bananas, often have a lower lignin content (D'hont et al., 2012; Jørgensen et al., 2007). TGA analysis reveals that the BP used in this study contains 6.6 wt% lignin. However, the lignin percentage reported in the literature varies, ranging from 2.9 to 31.6 wt%. Interestingly, Pereira et al. (2021) reported a higher lignin content (31.6 wt%) than cellulose or hemicellulose in BP (Pereira et al., 2021). Emaga et al. (2008) observed a significant variation in the lignin content of two Musa genotypes, plantain and banana. Compared to banana peels, the plantain peel had a significantly higher lignin content. They also reported that during ripening, the lignin percentage dropped in banana peels but increased in plantain peels (Emaga et al., 2008).

In this study, BP was hydrolyzed with microbial enzymes, which is considered a sustainable and environmentally friendly approach for biofuel and chemical production. Enzymes are often chosen over chemical catalysts since the latter method requires the use of aggressive chemicals (strong acid or base), harsh conditions (higher temperature and pressure), and side reactions due to lower selectivity (Hammerer et al., 2020). In contrast, enzymatic hydrolysis requires milder reaction conditions and offers a higher level of selectivity, which prevents the side reactions. Traditional enzyme-based lignocellulose hydrolysis involves chemical pretreatment of the substrate and the use of a large volume of solvent during hydrolysis. In addition, hydrolysis efficiency can also be negatively impacted by factors such as low substrate conversion rates and the suppression of the enzyme activity caused by high substrate concentrations (Hammerer et al., 2018). Therefore, in this study, BP was hydrolyzed utilizing a unique process called mechanoenzymatic hydrolysis, which is performed in the absence of bulk solvent. The method uses hydrolysis and ball milling simultaneously for degrading plant biomass. The ball milling aids in breaking the crystalline structure of cellulose during hydrolysis, thereby eliminating the need for a separate chemical pretreatment of the substrate. In addition, it enables hydrolysis of lignocellulose at higher substrate loadings, resulting in greater sugar yields following hydrolysis for subsequent conversion into desirable end products (Hammerer et al., 2020, 2018). For mechanoenzymatic hydrolysis of BP, the commercial enzyme mixture Cellic CTec2 was used. Cellic CTec2 is a cocktail mixture of different enzymes that can breakdown lignocellulose efficiently (Cannella et al., 2012). Cellulose is hydrolyzed by cellulase enzymes: endoglucanase (EG), cellobiohydrolases (CBH 1 and CBH 2), and β-glucosidases (BGL). The need for multiple enzymes for cellulose hydrolysis is particularly due to its recalcitrant crystalline structure (Hamid et al., 2015). During cellulose hydrolysis, EG mainly degrades the less ordered amorphous region whereas CBHs mainly act on the crystalline part of the cellulose. CBH1 acts on the reducing end of cellulose, whereas CBH2 functions on the non-reducing end. The action of EG and CBHs generates cellobiose and glucooligosaccharides, which are later converted to glucose by BGL. During the hydrolysis of cellulose by cellulases, synergistic actions have been observed amongst enzymes. For example, action of EG makes new ends for CBHs to bind, while BGL breaks down cellobiose that acts as an inhibitor for CBHS at high concentrations. Typically, cellulase enzymes contain two domains: a cellulose binding domain (CBM) and a catalytic domain (CD). During cellulose hydrolysis, CBM aids in substrate recognition and binding (Hamid et al., 2015; Mansfield et al., 1999; Rytioja et al., 2014). In contrast to cellulose, hemicellulose hydrolysis necessitates the action of several debranching enzymes in conjunction with backbone degrading hemicellulases. For instance, the backbone of xylan can be broken down by endoxylanases (XLN) and beta-xylosidases (BXL). XLN cleaves β-(14)-linked xylose chains to liberate xylooligomers and xylobiose, which are then cleaved by BXL to release xylose. Debranching enzymes such as arabinoxylan arabinofuranohydrolases (AXH), α-galactosidases (AGL), β-galactosidases (LAC) can remove arabinose, α- D-galactose and β- D-galactose residues from xylan, respectively (Rytioja et al., 2014; Van Den Brink and De Vries, 2011). On the contrary, lignin is composed of phenolic compounds and has a more complicated structure than cellulose and hemicellulose. Lignin degrading enzymes fall into two categories: lignin-modifying enzymes (LME) and lignin-degrading auxiliary enzymes (LDA). LME is comprised of lignin peroxidases (LiP), manganese peroxidases (MnP), versatile peroxidases (VP), and laccases (Lac), while LDA contains glyoxal oxidase (GLOX), aryl alcohol oxidases (AAO), pyranose 2-oxidase (POX), cellobiose dehydrogenase (CDH) and glucose oxidase. LDA promotes lignin depolymerization by generating hydrogen peroxide for LME (Furukawa et al., 2015; Janusz et al., 2017).

In this study, BP was initially hydrolyzed with varying concentrations of Cellic CTec2 enzymes in order to determine the optimal enzyme loading for hydrolysis. The sugar concentration initially rose when the Cellic CTec2 enzyme loading was increased, and the maximum hydrolysis yield was achieved with an enzyme loading of 45 mg per gram of BP. Increasing the enzyme loadings further had no influence on sugar yields, most likely due to the overcrowding of enzymes on the substrate's surface. Effective enzyme mobility on the cellulose surface is important for improving the hydrolysis of cellulosic substrates. When the substrate concentration becomes limited, increasing the enzyme loading beyond a certain point causes the overcrowding of cellulases on the substrate surface, resulting in interference between enzyme movement, and thus reducing the hydrolysis efficiency (Igarashi et al., 2011).

Ball milling is a vital aspect of mechanoenzymatic hydrolysis, and the milling material can influence the conversion of lignocellulosic biomass under mechanochemical circumstances. According to Hammerer et al. (2018), Teflon milling has a slightly greater conversion rate than stainless steel milling because the samples adhere less to the jar walls (Hammerer et al., 2018). In this study, during the mechanoenzymatic hydrolysis of BP, a minor increase in sugar yields was also found with Teflon milling jars as compared to stainless steel jars. For mechanoenzymatic hydrolysis, it is essential to determine the ideal reaction volume (η). Lignocellulosic biomass often requires a higher η value than pure cellulosic substrate (Hammerer et al., 2020). For BP, a η value of 1.5 μl mg^{-1} produced the maximum conversion rate.

For certain lignocellulosic biomass, premilling the substrate prior to the hydrolysis helps in achieving a higher conversion rate. Hammerer et al. (2020) reported that the premilling of corn stover, wheat straw, and sugarcane bagasse considerably enhanced the subsequent mechanoenzymatic transformation. Premilling helps to break down the recalcitrant structure of lignocellulose, allowing enzymes to quickly bind and begin hydrolysis (Hammerer et al., 2020). In this study, however, the pre-milling of BP did not improve sugar yields after subsequent mechanoenzymatic transformation, likely due to the low cellulose content of BP (10.1% wt) as compared to other plant biomass such as corn stover, wheat straw, and sugarcane bagasse (33.5, 34.4, 40.1 wt%, respectively) (Hammerer et al., 2020).

To determine the effect of milling time on hydrolysis, BP was milled for up to 90 minutes under mechanoenzymatic conditions. The milling duration had little effect on sugar yields, most likely due to the low lignocellulose content BP, which could be hydrolyzed within the first few minutes of milling. Finally, BP was hydrolyzed using RAging conditions in which the substrate was milled for a brief period of time (5 min) and then subjected to static incubation for a longer period of time (55 min). This 1-hour cycle can be repeated multiple times until enough hydrolysis is achieved. The major advantage of this method is that it can achieve a greater degree of hydrolysis in a shorter amount of time than conventional enzymatic hydrolysis. In this work, glucose yield of up to 40 wt% was reached in just 3 h of employing RAaging cycles, which was higher than the glucose yields obtained using standard enzymatic and chemical hydrolysis. Pereira et al. (2021) also carried out enzymatic hydrolysis of BP using Cellic CTec2 enzymes. Prior to hydrolysis, BP was pretreated with acid and alkaline to remove pectin and lignin, respectively. Hydrolysis of pretreated BP at 5% wt solid loading and 6% wt enzyme loading yielded 8.2 wt% glucose after 30h (Pereira et al., 2021). This result suggested that, under RAging circumstances, mechanoenzymatic hydrolysis considerably increased the sugar output without the need for substrate pretreatment. Finally, employing $AlCl_3 \times H_2O$ as a catalyst, the crude sugars produced via mechanoenzymatic hydrolysis were transformed into HMF. The maximum HMF yield (71.9 mol %) was achieved when $AlCl_3 \times H_2O$ was added with HCl.

Future perspectives

According to TGA analysis, BP contains a substantial amount of pectin (15.9 wt%), but the hydrolysis of BP was performed without the addition of pectinase enzymes. According to Oberoi et al. (2011), a combination of cellulase and pectinase is required for effective BP hydrolysis, and pectinase can greatly increase the hydrolysis of the insoluble polysaccharide fractions of BP (Oberoi et al., 2011). Therefore, future research should be conducted to assess the effect of pectin degrading enzymes on the hydrolysis of BP under mechanoenzymatic conditions by complementing pectinase with cellulolytic enzymes.

Recently, synergistic proteins like expansin and loosenin have been found in bacteria, fungi, and plants that can modify the structure of lignocellulose. Although these proteins lack catalytic activity, it is projected that they will modify the structure of crystalline cellulose by disrupting intramolecular and intermolecular hydrogen bonds. As a result, when these proteins are combined with lignocellulose degrading enzymes, the enzymes have an easier access to the cellulose chain, resulting in a higher hydrolysis rate at lower enzyme loadings (Georgelis et al., 2015; Sampedro and Cosgrove, 2005). This can significantly lower the cost of the enzyme for hydrolysis. Therefore, future research may combine non-catalytic proteins with lignocellulose degrading enzymes to investigate their effects on the mechanoenzyme hydrolysis of BP.

Food waste is a complex mixture of several elements, including lipids, fiber, carbohydrates, and proteins. However, existing literature on the valorization of food waste to HMF focuses mostly on the exploitation of the carbohydrate fraction while the rest of the valuable resources are often discarded throughout the production process. To ensure the sustainable management of food waste, it is required to design a more integrated production process that maximizes the product/feedstock ratio. For instance, lipid present in the BP can be extracted to utilize for biodiesel production. Besides, BP are rich in bioactive compounds and nutrients such as phenolics, flavonoids, anthocyanins and amino acids (Mohd Zaini et al., 2022). These compounds have important applications in medicinal and pharmaceutical preparations as well as in functional food formulation (Mohd Zaini et al., 2022). The bioactive compounds from food wastes can be extracted using various extraction approaches such as solvent extraction, supercritical fluid extraction, subcritical water extraction, enzymes assisted extraction, extracting using ultrasounds and microwaves (Kumar et al., 2017). Overall, the adaptation of such integrated biorefinery approaches could alleviate the waste disposal and environmental problems, while increasing the economic viability of the process by providing additional sources of value-added products.

Chapter 5

Final Conclusion and Summary

The first objective of this thesis was to review the literature and identify the major challenges associated with food waste valorization to HMF, and to recommends possible research directions to improve their conversion. The second objective was to efficiently convert BP into a HMF by using an integrated mechanoenzymatic/catalytic approach. Detailed conclusions related to both objectives are listed as follows:

1. The conversion of food waste to HMF has recently gained a lot of scientific interest because of its potential application in the production of alternative fuels and chemicals. Despite numerous attempts to produce HMF from food waste, the yield is still not economically viable, especially on a large scale. The major challenges include poor cellulose conversion, insufficient selectivity of catalysts, high manufacturing costs, and the creation of byproducts. Food conversion to HMF can be improved by pretreating waste with a suitable pretreatment method selected based on waste composition. Among the various pretreatment options, a combined pretreatment method is more advantageous in terms of saving time and reducing inhibitors formation. For the conversion of sugars to HMF, heterogeneous catalysts, particularly bifunctional catalysts accompanied by a biphasic solvent system, are a promising choice since they have been shown to improve selectivity toward desirable reactions and limit side reactions while enhancing HMF recovery.

2. As part of this thesis, BP was hydrolyzed under mechanochemical conditions in the absence of a bulk solvent, and the resultant sugars were transformed into HMF using $AlCl_3 \times H_2O$ as a catalyst. Under optimum reaction conditions, the solvent-free mechanoenzymatic method yielded approximately 40 wt% glucose and 11.8 wt% fructose after 3 h of hydrolysis, which was higher than the sugar yields obtained from standard enzymatic and chemical hydrolysis. The crude

sugars recovered after hydrolysis were converted to HMF utilizing the $AlCl_3 \times H_2O$-DMSO/H_2O system with a 71.9 mol% yield, which is higher than any previously reported HMF yield from cellulosic food waste.

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