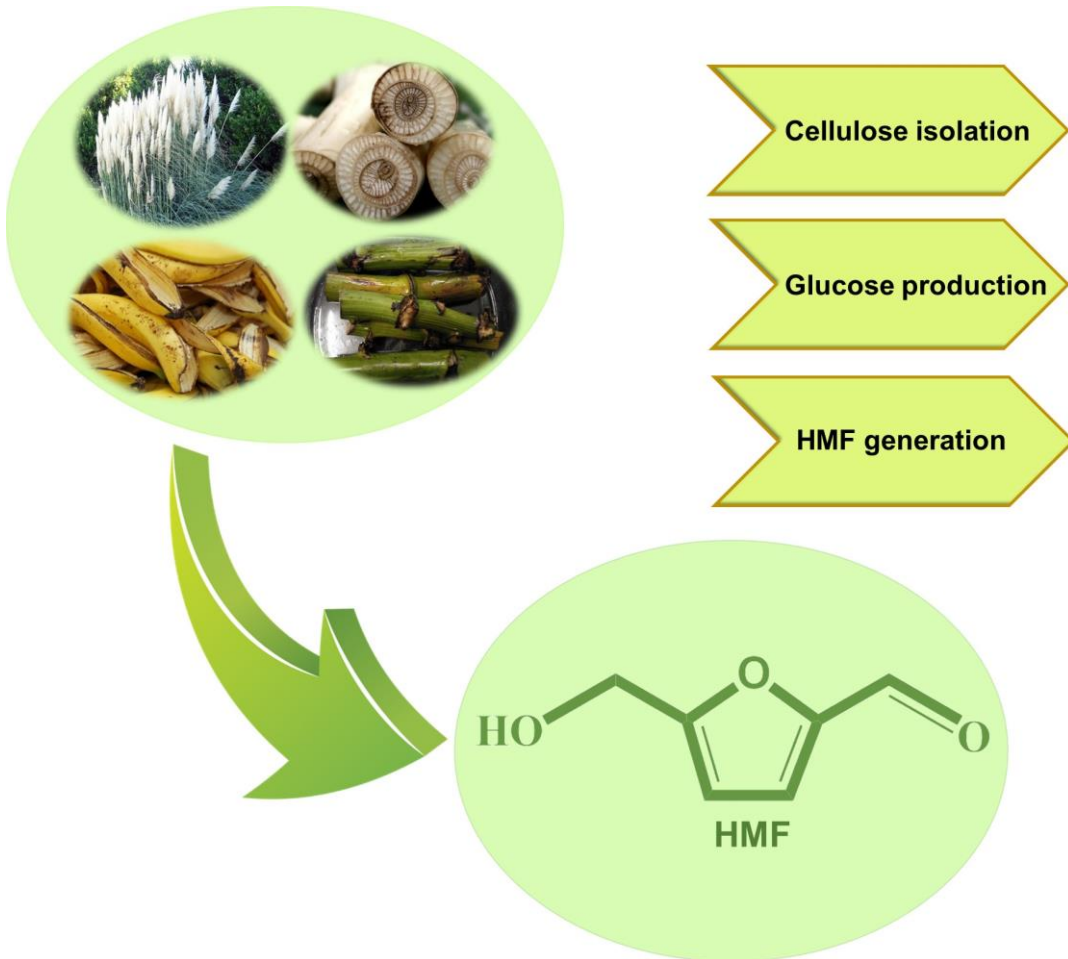


Chapter 1

Introduction



1.1. Introduction

The population of the world is projected to reach 8.5 billion by 2030 and 9.7 billion by 2050. Commensurate with the increasing population, the global energy consumption is expected to rise from 575 British thermal units (BTU), as estimated in 2015, to about 736 quadrillions BTU in 2040, which is a 28% increase over a period of 25 years [1]. The global dependence on non-renewable fossil fuels for meeting the current energy needs, cannot be sustained for long in the face of the depleting fuel reserves. The effects of this excessive dependence are already evident in the escalation of fuel prices, over the past decade and the severe environmental impacts like climate change. With a mere 23.7% utilization of renewable energy sources for energy needs, it is vital that the world switches over to renewable and sustainable energy alternatives, on an urgent basis [2, 3]. Amidst the promising alternative bioenergy sources, biomass represents the most abundant, renewable, and sustainable resources to produce high-value chemicals such as ethanol, fuels, acids, saccharides, phenols, aldehydes, xylitol, and cellulose acetate with low carbon emissions [4, 5]. Biomass involves organic materials including wood, grass, algae, agricultural crops, and their wastes all originating from renewable biomass.

Among biomass-based materials, Hydroxymethylfurfural (HMF) (also known as 5-Hydroxymethylfurfural), a hexose dehydration product, nowadays has gained a lot of interest due to its possibility of transforming into a multitude of high-value-added products and biofuels [6]. The U.S. Department of Energy has listed HMF in the top 10 versatile platform chemicals that could be obtained from lignocellulose [7, 8]. In the last three decades, there has been a rapidly increasing interest in HMF chemistry, which can be described by the increasing number of publications (Fig. 1.1). HMF is a heterocyclic furanic molecule with hydroxide and aldehyde functionalities substituted in 2 and 5 positions. Because of its unique chemical structure, HMF can be used as a starting material for the synthesis of functional replacements for different commodity chemicals (Fig. 1.2). For instance, it can be either oxidized to a dicarboxylic acid such as 2,5-Furan dicarboxylic acid (used in the synthesis of polymer) or reduced to a diol such as 1,6- Hexanediol (used in plastic production) which on subsequent amination gives Caprolactam (monomer of nylon-6). Hydrogenation of HMF yields 2,5-Dimethylfuran (used as transportation fuel) [9], 2,5-Bis(hydroxymethyl)furan (used in making of polyurethane foam) [10], 2,5- Bis(hydroxymethyl)tetrahydrofuran and 2,5- Dimethyltetrahydrofuran (used in making of polyester) [11]. Furthermore, HMF on etherification produces 5- Alkoxy methyl furfural

(a potential diesel additive) which on ethanolysis reaction yields alkyl levulinate (used as solvent, additive and fine chemical) [12].

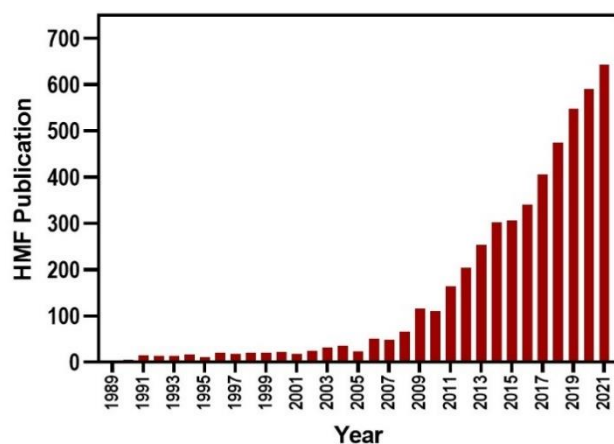


Fig. 1.1. Number of publications on HMF annually from 1989 to 2021 (Source: Web of Science).

HMF is typically produced by dehydrating glucose or fructose in the presence of a catalyst; however, this method is constrained by the inherent limitations of high production costs which are due to low selectivity reactions and expensive raw material costs [13]. Low selectivity is caused by the presence of water in the reaction medium since HMF is rehydrated in water to form several byproducts [14]. To prevent HMF rehydration and increase selectivity, organic solvents have been utilized as an extracting solvent in a biphasic reactor to remove HMF from the aqueous reaction phase [15]. On the other hand, the expensive raw material is the other main reason why HMF is not economically viable yet. To address this issue, there are relatively few studies on the utilization of whole lignocellulosic biomass (LCB) directly to produce HMF. For instance, Binder and Raines reported a 47% yield of HMF from untreated corn stover in a single step at 140°C in an ionic liquid comprising dimethylacetamide and lithium chloride [16]. Mirzae and Karimi reported the use of sulphanilic acid as a bifunctional catalyst in a biphasic solvent system resulting in a 41% yield of HMF at 150°C in 60 min from untreated straw [17]. In another study, Xia et al. used FePO₄ and NaH₂PO₄ as cocatalysts with the addition of 35 wt % NaCl in a biphasic solvent system and reported the production of HMF (~44%) at 160°C from wheat straw [18]. Overall, the research on techniques that use whole biomass for HMF synthesis is limited, and the HMF yields produced are poor. The biggest challenge with lignocellulosic biomass is its recalcitrant structure, making its conversion usually uneconomical and inefficient and leading to the formation of humins and other degradation

products [16, 19]. This calls for the development of new approaches that will allow for even greater improvements in HMF yield from lignocellulosic sources.

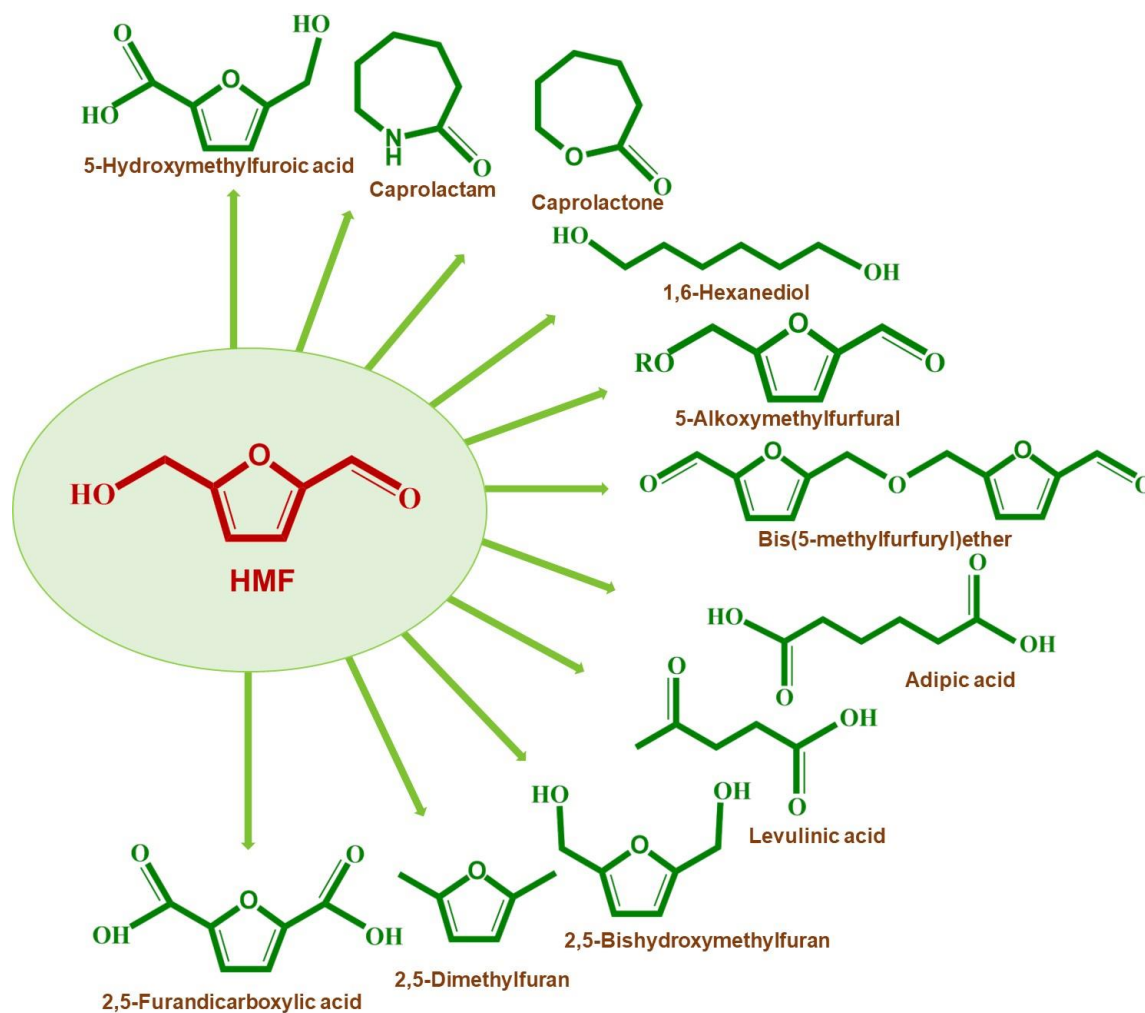


Fig. 1.2. HMF as a platform chemical for the synthesis of various value-added chemicals.

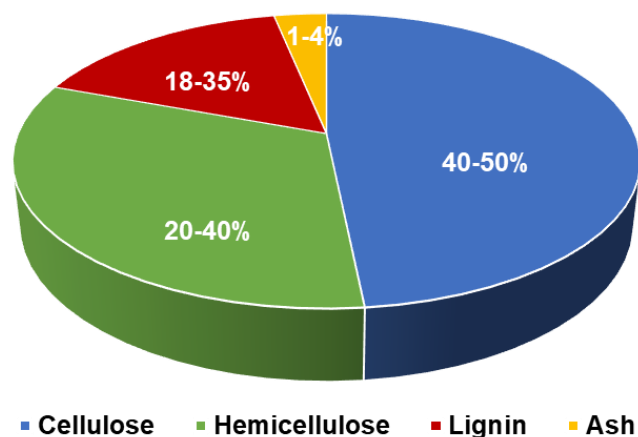


Fig. 1.3. Percentage composition of lignocellulosic sources.

HMF can be produced by hydrolysing lignocellulose into cellulose and glucose which can further be dehydrated to produce HMF. However, various factors, particularly its recalcitrant structure, limit the economic sustainability of lignocellulosic biomass processing.

Lignocelluloses are mainly composed of cellulose (40-50%), hemicelluloses (25-40%), and lignin (18-35%) along with a small quantity of ash (Fig. 1.3) where the components are rigidly associated through non-covalent bonds and covalent cross-linkages [20]. Cellulose can be converted into glucose *via* chemical or enzymatic hydrolysis and subsequently utilized in the production of ethanol, platform chemicals like hydroxymethylfurfural (HMF) and levulinic acid (LA), and liquid fuels [21, 22, 23]. Hemicellulose, on the other hand, is more reactive than cellulose, simpler to extract from lignocellulosic biomass, and is usually employed in the synthesis of furfural, and furfural derivatives [24, 25]. Lignin, although has the potential to be converted into fuels as well as high-value chemicals, its complexity and non-uniform composition make it more challenging to work with than the other fractions [26]. Crystallized cellulose and hemicellulose polymer matrix are encrusted by the high polymerized phenolic lignin which leads to difficulties in the conversion processes. Thus, to increase the digestibility of cellulose, the efficient breakdown of hemicellulose and lignin is the targeted step of pretreatment in converting lignocellulosic materials into fuels and chemicals [27]. During the pretreatment process, the recalcitrant structure of lignocellulose is disturbed, resulting in rupture of lignin sheath, hemicellulose degradation, and a decrease in cellulose crystallinity and polymerization degree (Fig. 1.4). Several pretreatment techniques have been accomplished up to now, which can be broadly classified into physical, chemical,

physico-chemical and biological processes. However, this pretreatment phase is the most expensive step which constitutes at least 20% of the total energy cost yielded from lignocellulosic biomass [28]. Therefore, improvement of the available pretreatment processes is necessary for a cost-efficient and economical conversion.

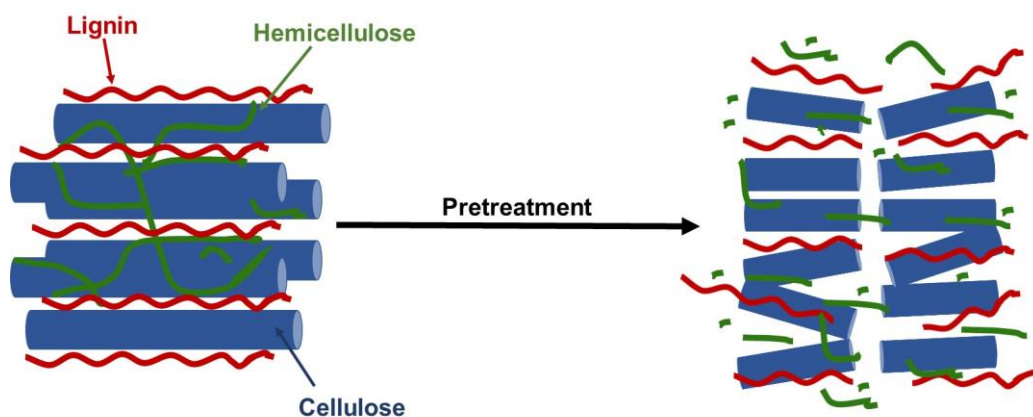


Fig. 1.4. Effect of pretreatment on lignocellulosic biomass.

A pre-requisite for transforming LCB into HMF is the liberation of the cellulose portion in a reasonable yield with minimal losses from the tightly woven lignocellulosic structure. The conversion of cellulose to HMF involves three consecutive reactions: (i) Hydrolysis of cellulose to glucose, (ii) Isomerization of glucose to fructose, and (iii) Dehydration of fructose to HMF [29]. The hydrolysis of cellulose into glucose can be accomplished *via* chemical or enzymatic hydrolysis, whereas the isomerization is typically promoted by Lewis acids (i.e., electron pair acceptors). The hydrolysis and dehydration reactions, on the other hand, are catalyzed by Bronsted acids (i.e., protons) [30]. However, both types of acids may also incur undesirable side reactions such as polymerization between sugars and intermediates [31], as well as rehydration of HMF leading to the formation of levulinic acid and formic acid as byproducts [30]. The key to high-yield HMF is to promote favorable reactions and suppresses the undesired side reactions that could be achieved by tuning the selectivity of the catalytic systems.

Acid hydrolysis of cellulose is a conventional way of converting cellulose to glucose that can be performed with either dilute or concentrated acid. The major benefit of cellulose hydrolysis using dilute acid is that the acid does not need to be recovered [32], but it has numerous drawbacks, including the necessity for high temperatures (minimum 180°C) and pressure (about 10 atm), which still results in poor glucose yields [33]. For

example, following pre-treatment with 0.7% H₂SO₄ at 190°C for 3 min, cellulose hydrolyzed with 0.4% acid at 215°C for 3 min yielded just 50% glucose [34]. Cellulose hydrolysis with concentrated acid, on the other hand, occurs at a moderate temperature and pressure and provides greater glucose yields [34], but it takes a longer time (2–6 h) and is challenging to economically separate the glucose while recovering the acid. To this end, enzymatic hydrolysis is preferred since it is gentle, extremely selective, and prevents the formation of inhibitors for downstream enzymatic conversions [35].

1.2.Problem Statement

Current research on the production of HMF from lignocellulosic sources, to resolve the major gaps in the study listed as follows:

- (i) Major studies focus on the production of HMF from simple starting materials such as glucose or, fructose and the use of lignocellulosic biomass or biomass-derived carbohydrates for HMF synthesis is very limiting.
- (ii) Though there are several reported studies on the isolation of cellulose from different lignocellulosic sources, a simple and sustainable way with high product yield is limited.
- (iii) No study has been pursued on the extraction of cellulose and subsequent production of glucose from lignocellulosic biomass prior to catalytic dehydration reactions.
- (iv) Production of HMF with high selectivity is still challenging.
- (v) Very few studies have carried out the optimization study of reaction parameters which plays a major role in catalytic dehydration reactions.

In light of the above considerations, the current research aims to establish an integrated strategy for converting lignocellulosic biomass to HMF that includes cellulose extraction, glucose generation, and HMF production from biomass-derived glucose through catalytic conversion. For this, extraction of cellulose from selected non-edible lignocellulosic precursors was carried out using a multiple-step method that requires a significantly lower quantity of reagents and generates very low effluents from material washes, which makes the process more economical and environment-friendly. This was followed by the enzymatic hydrolysis of the isolated celluloses using commercial cellulase enzyme (from *Aspergillus niger*) for the production of glucose and optimized through response surface methodology (RSM), artificial neural network (ANN), and adaptive

neuro-fuzzy inference system (ANFIS) techniques for modeling the experimental parameters of the hydrolysis process to achieve an efficient condition for maximum glucose yield. To convert biomass-derived glucose into HMF, heterogeneous solid acid catalysts have been synthesized that possess both Lewis and Brønsted acidity. Since the solvent appears to have a substantial impact on the reaction's outcome, the solvent systems utilized have been thoroughly investigated. Furthermore, the optimization of the catalytic reaction parameters was carried out based on RSM and ANN.

1.3. Objectives

The overall objective of the thesis is to conceptualize and optimize an eco-friendly and cost-effective integrated approach for converting biomass-derived carbohydrates into HMF. Considering the significance of HMF and highlighting the main obstacles in utilizing lignocellulosic biomass as feedstock, we have tried to address the major gaps in the conversion process by undertaking the following objectives:

1. Isolation of cellulose from lignocellulosic feedstocks (*Saccharum spontaneum* and Banana agrowastes) using an integrated pretreatment technique: Process optimization and structural characterization.
2. Optimization of enzymatic hydrolysis of cellulose extracted from *Saccharum spontaneum* and banana peduncle using RSM, ANN, and ANFIS statistical tools.
3. Synthesis of magnetically recoverable polyaniline-based bifunctional solid-acid catalyst for the catalytic transformation of biomass-derived glucose into hydroxymethylfurfural.
4. Design of acid bifunctionality (Lewis and Brønsted) on mesoporous silicate, KIT-6 for the conversion of biomass-derived glucose into hydroxymethylfurfural.

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