ABSTRACT

The World Energy Annual Report ranked India as the fourth largest energy consumer after China, USA and the European Union with an estimated requirement of 754 million tons of oil equivalent (mtoe), which is 5.6 percent of the global primary energy consumption [1]. The report projected India's energy requirements to exceed 2 billion tons of oil equivalent by 2050, considering the trimeric increase in GDP ($19k/capita), population (1.72 billion) and urbanization (50% increase) [2]. The Draft National Energy Policy, released by the NITI Aayog, Govt. of India, on 27 June 2017, states that the nation's energy imports being predominantly fossil based, shall be critically impacted by the goal of accessibility and is likely to conflict the sustainability goals with increasing fuel prices [3]. As such, India encounters the trilemma of attaining an increased access to energy, alongside greater energy security through sustainable means. In this context, biomass represents the most abundant, renewable and sustainable resource for the production of alternative fuel sources like bio-fuels and high-value chemicals with low carbon emissions [4]. Biomass involves organic materials including wood, grass, algae, agricultural crops and their wastes all originating from renewable biomass [5]. Among the bio-derived value-added products, 5-Hydroxymethylfurfural (HMF) is an attention-drawing building block which can serve as an excellent precursor in the synthesis of a multitude of marketable products such as polymers, pharmaceuticals, and bio fuels, enabling the establishment of sustainable chemical industry [6]. In fact, the U.S. Department of Energy has listed HMF in the top 10 versatile platform chemicals that could be obtained from lignocellulose. HMF is a heterocyclic furanic molecule with hydroxide and aldehyde functionalities substituted in 2 and 5 positions [7, 8]. Because of its unique chemical structure, HMF can be used as a starting material for the synthesis of functional replacements to different commodity chemicals. For instance, it can be either oxidized to a dicarboxylic acid such as 2,5-Furan dicarboxylic acid (use in the synthesis of polymer) or reduced to a diol such as 1,6-Hexanediol (use in plastic production) which on subsequent amination gives caprolactum (monomer of nylon-6). Hydrogenation of HMF yields 2,5-Dimethylfuran (use as transportation fuel) [9], 2,5-Bis(hydroxymethyl) furan (used for production of polyurethane foam) [10], 2,5- Bis (hydroxymethyl) tetrahydrofuran and 2,5- Dimethyltetrahydrofuran (used for production of polyester) [11]. Furthermore, HMF on etherification produces 5- Alkoxymethylfurfural (a potential diesel additive)

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

Extensive research has been carried out on HMF synthesis from edible monosaccharides like fructose and glucose. But this raises the imminent concern about its adverse effect on world food supply and sustainability [13]. Therefore, recent research interests extended to the use of lignocellulosic biomass as an inexpensive renewable feedstock due to its potential illustrated by high cellulosic content of 40-50% on a dry mass basis [14]. A recent study has achieved a maximum HMF yield of 30% of the wheat straw used representing the necessity and importance of technology development [15]. In another study, maximum HMF yield of 35% was achieved from dry fruit shells [16]. 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 leads to the formation of humins and other degradation products [17]. This calls for the development of new approaches that will allow for even greater improvements in HMF yield from lignocellulosic sources.

In lignocellulosic biomass, crystallized cellulose and hemicellulose polymer matrix are encrusted by the high polymerized phenolic lignin that leads to the difficulties in the conversion processes. Therefore, the 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 [18]. For this, several pretreatment techniques have been accomplished up to now for the efficient breakdown of hemicellulose and lignin and to increase the accessibility of cellulose. However, this pretreatment phase is the most expensive step which constitutes at least 20% of the total energy cost yielded from lignocellulosic biomass [19]. Therefore, improvement of the available pretreatment processes is necessary for a cost-efficient and economical conversion. On the other hand, the conversion of cellulose to HMF involves three consecutive reactions [20]:

(i) Hydrolysis of cellulose to glucose,

(ii) Isomerization of glucose to fructose and

(iii) Dehydration of fructose to HMF.

The hydrolysis of cellulose into glucose can be accomplished via chemical or enzymatic hydrolysis. The isomerization is typically promoted by Lewis acids (i.e., electron pair acceptors) while the dehydration reactions are catalyzed by Bronsted acids (i.e., protons) [21]. However, both types of acids may also incur undesirable side reactions such as polymerization between sugars and intermediates [22], as well as rehydration of HMF leading to the formation of levulinic acid and formic acid as byproducts [21]. The key to high yield HMF is to promote the favorable reactions and suppresses the undesired side reactions that could be achieved by tuning the selectivity of catalytic systems.

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 multiple-step method that requires significantly lower quantity of reagents making 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) tools for modelling the experimental parameters of the hydrolysis process to achieve an efficient condition for maximum glucose yield. To convert the biomass-derived glucose into HMF, heterogeneous solid acid catalysts have been synthesized with bifunctional characteristic. Since the solvent appears to have a substantial impact on the reaction's outcome, the solvent systems utilised have been thoroughly investigated. Furthermore, the optimization of the catalytic reaction parameters was carried out based on response surface methodology (RSM) and artificial neural network (ANN) with the objective of achieving sustainability.

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:

i) Isolation of cellulose from lignocellulosic feedstocks (*Saccharum spontaneum* and Banana agrowastes) using an integrated pretreatment technique: Process optimization and structural characterization.

ii) Optimization of enzymatic hydrolysis of cellulose extracted from *Saccharum spontaneum* and banana peduncle using RSM, ANN, and ANFIS statistical tools.

iii) Synthesis of magnetically recoverable polyaniline-based bifunctional solid-acid catalyst for the catalytic transformation of biomass-derived glucose into 5-Hydroxymethylfurfural.

iv) Design of acid bifunctionality (Lewis and Brønsted) on mesoporous silicate, KIT-6 for the conversion of biomass-derived glucose into 5-Hydroxymethylfurfural.

The current thesis is divided into seven chapters, four of which summarise the research findings. The conclusion and future prospective of the study are addressed separately in the end of the thesis in chapter seven.

Chapter 1 provides a brief overview of the research subject as well as the limitations that have been recognized in the broad area of research involving production of 5-Hydroxymethylfurfural from lignocellulosic sources.

Chapter 2 describes a concise background of the study and research questions addressed so far. This chapter can be broadly classified into two parts. In the first part, we undertook a literature survey of the recent developments in the pretreatment techniques employed on lignocellulosic biomass. current strategies employed for HMF production with more attention on solid catalysis. In the second part, we conducted a literature review of current HMF production strategies, with a focus on solvent effect and solid acid catalysis.

Chapter 3 involves the isolation of cellulose from *Saccharum spontaneum* and banana agrowastes (peel, pseudostem, and peduncle) and analysis of its physicochemical and morphological characteristics. The isolation was carried out using an integrated treatment coupling alkali, steam explosion and ammonia/chlorine-free bleaching. The cellulose yield, compositional, microstructural, and morphological analysis initially obtained from *S. spontaneum* and three post-harvest banana agrowastes (peel, pseudostem, and peduncle) were surveyed. Banana peduncle yielding the highest recovery of cellulose among the three agrowastes was proceeded for further optimization. To achieve high-quality cellulose with the maximum yield, the isolation parameters for *S. spontaneum* and banana peduncle agrowaste, the most efficient precursors, were reconfigured for acid hydrolysis using an orthogonal L9 array of Taguchi design. The cellulose source at its different stages of processing was submitted to various analytical techniques for morphological and physiochemical investigations. Effects of solution-to-pulp ratio, acid

concentration, temperature, and reaction time on physicochemical parameters were assessed.

Chapter 4 embodies the production of glucose from *Saccharum spontaneum* and banana peduncle derived celluloses. Cellulose was converted into glucose via enzymatic hydrolysis process using readily available commercial enzyme Cellulase (from *Aspergillus niger*) in a simple, effective, and ecologically sound way. To obtain an efficient condition for maximal glucose yield, the experimental parameters of the hydrolysis process were modelled using three statistical tools: response surface methodology (RSM), artificial neural network (ANN), and adaptive neuro-fuzzy inference system (ANFIS). This was investigated using enzyme loading, substrate concentration, surfactant concentration, and incubation time as the influencing parameters.

Chapter 5 describes the synthesis of a heterogenous bifunctional catalyst for the conversion of *Saccharum spontaneum* derived glucose and banana peduncle derived glucose to 5-hydroxymethylfurfural. A magnetically recoverable bifunctional catalyst (Fe_3O_4@SPAN) was successfully synthesized by incorporating Fe_3O_4 nanoparticles into polyaniline matrix while supporting sulfonic acid groups ($-SO_3H$) on the backbone of the polyaniline chain. The catalytic performance of the catalyst was investigated in different catalytic systems. The structure, morphology, and physiochemical properties of the catalysts are characterized by means of FT-IR, p-XRD, Raman spectroscopy, TGA, NH_3-TPD measurements, ICP-AES, VSM, XPS, SEM, EDX, HRTEM and N_2 adsorption-desorption isothermal analysis. The reaction parameters affecting on the yield of 5-hydroxymethylfurfural such as reaction temperature, reaction time, catalyst loading, and substrate concentration were optimized using multivariate experimental designs viz., Response Surface Methodology (RSM) and Artificial Neural Network (ANN), as well as the reusability of the catalyst was investigated. A probable reaction mechanism over the catalyst was also hypothesised based on the findings which was established through Density Functional Theory (DFT) study.

Chapter 6 describes the synthesis of niobium doped mesoporous silica framework (KIT-6) using hydrothermal self-assembly method which was then functionalized by propyl-sulfonic acid groups. The as-synthesized catalyst was investigated for its performance in producing 5-hydroxymethylfurfural from *Saccharum spontaneum* derived glucose and banana peduncle derived glucose. The structure, morphology, and physiochemical properties of the catalysts are characterized by means of FT-IR, p-XRD, SAXS, TGA, Diffuse reflectance UV-Vis, NH_3-TPD measurements, N_2 adsorption-desorption isothermal analysis, XPS, SEM, EDX and HRTEM analysis. The catalytic performance of the catalyst was also investigated in different solvent systems. The reaction parameters affecting on the yield of HMF such as temperature, reaction time, catalyst loading, and substrate concentration were optimized using multivariate experimental designs viz., Response Surface Methodology (RSM) and Artificial Neural Network (ANN), as well as the reusability of the catalyst was investigated. A probable reaction mechanism over the catalyst was also hypothesised based on the findings.

Chapter 7 summarizes the findings of the study and discusses about the potential futures in light of the existing findings.