An Integrated Approach for Generation of Hydroxymethylfurfural Platform Chemical from Renewable Lignocellulosic Sources

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Chapter 7

Conclusion and future perspective

7.1. Summary and conclusions

The current thesis has focused on the effective synthesis of the extremely significant platform chemical hydroxymethylfurfural (HMF) from renewable lignocellulosic biomass. Lignocellulosic biomass is a readily available, inexpensive, and renewable source of biopolymers that may be processed through biochemical or thermochemical methods to produce liquid fuels and chemicals as an alternative to fuels derived from non-renewable fossil resources. In this context, biorefinery that exploits lignocellulosic biomass as a source of sustainable carbon feedstock and renewable energy is a viable way to minimize our excessive dependence on finite fossil fuels while also addressing climate change and other environmental issues. However, because lignocellulosic biomass is recalcitrant and over-functionalized, producing desired products from biomass necessitates a sequence of intricate breakdowns and catalytic conversions. In the biorefinery strategy, hydroxymethylfurfural (HMF) stands out as a gateway between biomass raw materials and substitute fuels, chemicals, and materials that potentially replace petroleum-derived goods.

Cell wall constituents such as cellulose, hemicellulose, and lignin are linked together in lignocellulosic biomass by a complex intra/intermolecular hydrogen bond network. Because of the complexity of carbohydrates and lignin, cellulose is naturally unavailable and has a high degree of polymerization. Together, these factors render lignocellulosic biomass recalcitrant in nature and inaccessible to cellulases, preventing them from interacting with cellulose. Thus, pretreatment is a prerequisite step prior to transforming lignocellulosic biomass into HMF for the liberation of the cellulose portion in a reasonable yield with minimal losses from the tightly woven lignocellulosic structure. This thesis outlines an integrated method for converting lignocellulosic biomass to HMF that includes a pretreatment, enzymatic hydrolysis, and catalytic approach. The key conclusions obtained from our research work are outlined under the headings below:

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

The isolation of cellulose from *Saccharum spontaneum* and banana agrowastes was carried out through the integrated treatment of alkali (NaOH), chlorine-free bleaching (H_2O_2), and acid hydrolysis (H_2SO_4). The detailed characteristics of various physicochemical properties of the lignocellulosic feedstocks, their samples at different

stages of treatment, and the final product confirm that the isolation procedure was effective. Chemical composition analysis and FTIR results showed the cellulosic structure of cellulose and also indicated the removal of considerable amount of lignin and hemicellulose during the chemical treatments. The crystalline structure of the isolated cellulose had been validated by XRD analysis and TGA had demonstrated its purity in terms of thermal stability. The morphological study revealed cellulose fibers with a rod-like morphology, and further uniformity in the structure of cellulose was obtained after acid hydrolysis. The parameters of the acid hydrolysis process were optimized using the Taguchi design of experiment to determine the influences of acid concentration, reaction time, temperature, and pulp-to-solution ratio on the isolated cellulose yield, crystallinity index, degree of polymerization, and thermal stability. The findings of the characterization revealed that re-optimizing the acid hydrolysis parameters facilitated the production of high-yield celluloses with a low degree of polymerization of 100–155, hence improving the enzymatic efficiency. The extracted cellulose had an excellent cellulose content of ~83% from *Saccharum spontaneum* at an optimal condition of 5% H_2SO_4 concentration, 2 h hydrolysis time, 50°C temperature, and 1:15 pulp to solution ratio. Likewise, ~81% of cellulose has been isolated from banana peduncle, under the optimum processing conditions of 5% H_2SO_4 concentration, 5 h hydrolysis time, 80°C temperature, and 1:20 pulp to solution ratio. Hydrolysis with lower acid concentrations (5% H_2SO_4 concentration), along with a chlorine-free bleaching procedure, made the extraction environment friendly, resulting in hazardous chemical savings. As a result, this approach is applicable to other lignocellulosic sources as well.

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

Followed by the isolation, the *Saccharum spontaneum* and banana peduncle-derived celluloses are subjected to enzymatic hydrolysis for the production of glucose. The hydrolysis process was optimized to maximize glucose yield values using response surface methodology (RSM), artificial neural network (ANN), and adaptive neuro-fuzzy inference system (ANFIS) approaches in modeling the experimental parameters, and their prediction efficacies were evaluated. All three models predicted the optimal conditions of enzyme loading of 30 FPU/g, substrate concentration of 50 mg/mL, surfactant concentration of 5 mg/mL, and incubation period of 96 h. The most influencing parameter observed was

incubation time in both the cases of *Saccharum spontaneum* and banana peduncle. The optimal condition led to a glucose turnover of 97.21% and 97.87% for *Saccharum spontaneum* and banana peduncle, respectively. The RSM outputs were well matched by the ANN validated yields of 95.93% and 93.51%, and the ANFIS validated yields of 96.1% and 97.42% for *Saccharum spontaneum* and banana peduncle, respectively. According to the seven statistical error indices, the ANN and ANFIS models for glucose yield prediction performed better than the RSM model; however, ANFIS performed marginally better than ANN. This is the first sequential investigation of an efficient and eco-friendly technique for producing glucose from lignocellulosic extracted celluloses through improved enzymatic hydrolysis.

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

Here, we reported the synthesis of a bifunctional catalyst (Fe$_3$O$_4$@SPAN) by integrating Fe$_3$O$_4$ nanoparticles into a polyaniline matrix and supporting sulfonic acid groups (-SO$_3$H) on the polyaniline chain for the conversion of glucose to HMF. The catalysts were fully characterized by FTIR, XRD, Raman spectroscopy, TGA, NH$_3$-TPD measurements, ICP-AES, VSM, XPS, SEM, EDX, HRTEM, and N$_2$ adsorption-desorption isothermal analysis. Initially, the study of conversion reactions and their optimization was carried out using commercial glucose. DMSO/Water (4:1) was found to be the most effective solvent system after the reaction was initially examined in a variety of monophasic and biphasic solvents. The effects of reaction parameters on the conversion of glucose and yield of HMF were evaluated by the two multivariate experimental designs Response Surface Methodology (RSM) and Artificial Neural Network (ANN). Based on the results, a possible reaction mechanism over the catalyst was also proposed where we have shown that Fe$_3$O$_4$ acts as a Lewis acid, causing glucose to isomerize into fructose *via* ring opening, whereas the H-bonded -SO$_3$H groups are in charge of fructose dehydration to HMF. The highest HMF yield of ~75% is obtained from glucose after being optimized through CCD-based RSM and MLP-based ANN models with complete inhibition of HMF rehydration to byproducts. The optimum reaction conditions were found to be 40 mg catalyst loading, 80 mMol substrate, 150°C, and 4 h reaction time. After optimization, we further conducted the reaction using *Saccharum spontaneum*-derived glucose and banana peduncle-derived glucose which resulted in 73.88% and 74.11% yield of HMF,

respectively with no byproducts. Furthermore, the magnetic Fe_3O_4 nanoparticle in the polymer matrix allows for easy catalyst recovery through magnetic separation. In addition, the catalyst showed recyclability for at least five runs without significant activity loss. Based on the results, a possible reaction mechanism over the catalyst was also proposed. The proposed mechanism was further established by DFT study where we explored the catalytic dehydration of glucose to HMF using x-Fe_3O_4@SPAN-y/z-based catalyst *via* the potential energy diagram and thermo-chemical parameters.

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

Here, we focused on the synthesis of HMF from glucose by designing an acid-bifunctional mesoporous silicate catalyst. A well-ordered cubic three-dimensional sulfonated Nb-KIT-6 catalyst with different Si/Nb atomic ratios was successfully synthesized using a hydrothermal synthesis procedure. The catalyst with an atomic ratio of 20 Si/Nb was observed to be highly efficient in glucose conversion and HMF generation. The catalysts were fully characterized by FTIR, XRD, SAXS, UV-Vis, NH_3-TPD, TGA, BET, XPS, SEM, EDX, and TEM. The *Ia3d* symmetry of the synthesized catalyst has been confirmed by SAXS and TEM analysis. The activity of the catalyst was examined in different monophasic and biphasic solvents where the biphasic MIBK/H_2O(NaCl) system was found to be the most suitable. After being optimized using CCD-based RSM and MLP-based ANN models, the catalyst demonstrated remarkable activity with > 90% glucose conversion and 80% HMF yield with a high HMF selectivity of 85%. Under the optimal reaction conditions, 78.88% and 79.40% of HMF yields have been obtained from *Saccharum spontaneum*-derived glucose and banana peduncle-derived glucose, respectively. Furthermore, the catalyst shows recyclability for at least five runs with comparable yields of the targeted HMF.

7.2. Future prospects of the current work

The current research aims to use renewable lignocellulosic biomass to produce an important platform chemical, hydroxymethylfurfural (HMF), which can lead to contributions toward the sustainable production of chemicals. Hence, the thesis deals with an integrated approach comprising cellulose extraction from feedstocks, enzymatic hydrolysis for glucose production, and synthesis of solid acid catalysts for the dehydration

of glucose to HMF. The most significant findings of the research work have been discussed and, we would like to discuss their future prospects in this section.

(i) The current approach can also be extended to perform with other lignocellulosic or carbohydrate-rich renewable feedstocks. In the present age of rampant urbanization and industrialization, food-based wastes have tremendous potential to be used as a bioresource using renewable biorefinery mode. Food waste generally refers to the organic waste generated by the food industries during production and processing, wholesale and retail preparation, after-meal leftovers, and expired foods. Although, the food waste valorization technique has widely been adopted in western countries, in countries like India where food security surpasses energy needs, the utilization of household or industrial food wastes can gradually help our society to achieve a circular economy based on zero waste.

(ii) Recent research has focused on integrated biorefinery, which involves applying several conversion techniques in series. For instance, the discarded fractions (hemicellulose and lignin) of lignocellulosic biomass during the extraction of cellulose can be converted to other value-added products. The hemicellulosic portion generates simple sugars, which may then be fermented to produce biofuels, while the polyphenolic lignin can be transformed into value-added compounds as well as building blocks for commercially important chemicals. In this way, biomass valorization creates a circular bio-economy by allowing for more effective recovery of each reuse source to produce a variety of products such as biofuels, platform chemicals, and improved biomaterials.

(iii) Understanding the processes underlying the conversion of glucose to HMF using different catalysts and solvents is also critical. Efforts should be made to comprehend the molecular level interactions between the feedstock, catalyst, and solvents, and finally to define their specific function for the dehydration of glucose to HMF with high activity and selectivity, which will aid in the design of novel heterogeneous catalysts and solvent systems.

(iv) When considering industrial-scale applications, isolating HMF from the reaction system is also a significant challenge. However, this element has not been addressed in the current research work. More efforts should be made to develop and implement effective techniques for isolating HMF from various reaction systems, which will be advantageous for commercial production and further exploitation of HMF from glucose.

(v) The current study was on a lab-scale that used relatively low feedstock loadings, which might make it difficult to scale up and commercialize the conversion technique. This problem has to be addressed in future studies on biomass valorization by heterogeneous catalysts in order to scale up the process for industrial applications from both a sustainable and economical perspective. To summarise, HMF is a potential platform chemical for the future bio-based economy, but it must be synthesized economically and with a low environmental imprint in order to be commercialized successfully.