OPTIMIZATION OF BIO-CHEMICAL CONVERSION OF RICE STRAW TO 5-(HYDROXYMETHYL)FURFURAL

Poornima Nishadhi Wanninayake

198080N

Master of Philosophy

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DECLARATION

I declare that this is my own work and this Thesis does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or Institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text. I retain the right to use this content in whole or part in future works (such as articles or books).

Signature: Date: 2024-02-08

The supervisors should certify the Thesis with the following declaration.

The above candidate has carried out research for the Master of Philosophy Thesis under our supervision. We confirm that the declaration made above by the student is true and correct.

Name of Supervisor: Prof. S. H. P. Gunawardena

Signature of the Supervisor: Date: 02-08-2024

Name of Supervisor: Dr. S. A. D. T. Subasinghe

Signature of the Supervisor: Date: **08-02-2024**

Name of Supervisor: Dr. H. H. M. P. Rathnayake

Signature of the Supervisor: Date: 08-02-2024

DEDICATION

This thesis is dedicated,

To my husband Thilina, for his understanding, love, and support which helped me a lot to overcome the barriers I have faced.

To my father and mother, the shadow of my success and for their unconditional love.

To all my teachers from University of Moratuwa, University of Peradeniya, and Eppawala Central College, for making me who I am today.

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ABSTRACT

Agricultural waste-based biorefinery merges waste and production sectors to develop a circular economy. One such biorefinery product, 5-(hydroxymethyl) furfural (5-HMF) has gained increasing interest as a versatile platform chemical to produce chemicals and fuels, and rice straw will be an ideal feedstock to produce 5-HMF. Limited studies on the direct conversion of rice straw to 5-HMF reveal the requirement of extensive research. This MPhil research study focuses to identify the most feasible conversion process to convert rice straw into 5-HMF, and optimize the required process parameters in laboratory-scale to be used in unit processes in scaled-up implementation. As the first objective, this thesis has proposed a roadmap, elucidating the existing methods for rice straw pretreatment to convert cellulose and cellulose conversion to 5-HMF processes. Then cellulose conversion to 5-HMF was evaluated, considering catalyst used, solvent system, process temperature, and process time. Eventually, an evaluation method, based on a generalized objective function with penalty scores, was developed and used its minimum value to find the optimal process configuration at the lowest cost for large-scale 5-HMF production. However, considering the feasibility of large-scale application of these processes in Sri Lankan context, combinatory acid/ alkaline pretreatment method and mineral acid-catalyzed cellulose to 5-HMF conversion process were selected for the optimization. The final objective was experimentally optimization of the process parameters of each, using an advanced optimization technique, response surface methodology. Central composite design-based experiments were used to develop statistical models for each process. Quantitative analyses were performed, using regression techniques, analysis of variance, and residual analysis, whereas qualitative analyses were carried out via Fourier Transform Infrared Spectroscopy. The pretreatment process was carried out to maximize the outcome of rice straw biorefinery. It included two steps: (1) dilute sulphuric acid treatment at reduced temperatures to optimize hemicellulose removal, and (11) dilute sodium hydroxide treatment at reduced temperatures to optimize lignin removal. The maximum hemicellulose removal ($15.78\,\%$) was observed at optimal conditions of $0.26\,\mathrm{mol\,dm^{-3}}$ acid concentration, $98.1\,°\mathrm{C}$ reaction temperature, and 30.48 min reaction time. The maximum removal of lignin ($20.98\,\%$) was obtained at $2.55\,\mathrm{mol\,dm^{-3}}$ sodium hydroxide concentration, $80.5\,°\mathrm{C}$ reaction temperature, 106.48 min reaction time. An optimized acid- catalyzed hydrothermal process for the in-situ production of 5-HMF from rice straw extracted cellulose was obtained, using a biphasic reaction system. The maximum yield of 5-HMF was $23.51\,\%$ at optimal conditions of $0.046\,\mathrm{mol\,dm^{-3}}$ dilute hydrochloric acid concentration, $180\,°\mathrm{C}$ process temperature, and 107 min process time. Finally, validation experiments were performed, and the observed optimum results showed close agreement with the predicted, confirming rice straw biorefinery process optimization.

Keywords: Rice straw, Biorefinery, 5-(hydroxymethyl) furfural, Pretreatment, Cellulose, Catalytic conversion, Optimization, Response surface methodology

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LIST OF ABBREVIATIONS

Abbreviated Terms

CCD	Central composite design
CMF	Cellulose microfibrill
DAP	Dilute acid pretreatment
DES	Deep eutectic solvent
DOE	Design of experiments
DSAP	Dilute sulphuric acid pretreatment
HTC	Hydrothermal carbonization
LCC	Lignin-carbohydrate complex
OFAT	One factor at one time
RSM	Response surface methodology

Chemical Substances

BMIMCl	1-butyl-3-methylimidazolium chloride
DMF	2,5–dimethylfuran
DMSO	Dimethyl sulfoxide
EL	ethyl levulinate
EMF	5-ethoxymethylfuran
EmimAc	1-ethyl-3-methylimidazolium acetate
FDCA	2,5–dicarboxylic acid
GVL	γ-Valero lactone
H2SO4	Sulphuric acid
HCl	Hydrochloric acid
HMF	5-hydroxymethylfurfural
ILs	Ionic liquids
MIBK	Methyl isobutyl ketone
NaOH	Sodium hydroxide
THF	Tetrahydrofuran

Other Symbols

α_i	Relative weightage to represent the significance of i^{th} parameter to the overall process
θ_k	Process temperature of the k^{th} process
C_k	Catalysts used of the k^{th} process
E	Energy required to reach and maintain the operating temperature
$E_{1,k}$	Energy needed to heat the reaction system comprised of cellulose, solvents, and catalyst
$E_{2,k}$	Energy required to maintain the temperature for process time t_k

P_k	Process considered
RS_k	Reaction system of the k^{th} process
t_k	Process time of the k^{th} process
y_k	Yield of the k^{th} process