INSIGHTS INTO CHEMOCATALYTIC ETHANOL PRODUCTION FROM CELLULOSE

AMBEREEN AZIZ NIAZE

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI, INDIA

JUNE 2025

© Indian Institute of Technology Delhi (IITD), New Delhi, 2025

INSIGHTS INTO CHEMOCATALYTIC ETHANOL PRODUCTION FROM CELLULOSE

by

AMBEREEN AZIZ NIAZE

Department of Chemical Engineering

submitted

in fulfilment of the requirements of the degree of

Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI, INDIA

JUNE 2025

Dedicated to my grandfather Late. Dr. Hameed Niazi and my beloved mother Late. Mrs. Anjum Ara

CERTIFICATE

This is to certify that the thesis titled **“INSIGHTS INTO CHEMOCATALYTIC ETHANOL PRODUCTION FROM CELLULOSE”** being submitted by Mrs. Ambereen Aziz Niaze to the Indian Institute of Technology Delhi for the award of degree of Doctor of Philosophy is a record of bonafide research work carried out by her. Mrs. Ambereen Aziz Niaze has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

Prof. Sreedevi Upadhyayula
Professor & Class of 66 Chair
Department of Chemical Engineering
Indian Institute of Technology Delhi

ACKNOWLEDGEMENTS

I would like to acknowledge several people who have supported me during my PhD thesis. First and foremost, I would like to thank my research advisors **Prof. Sreedevi Upadhyayula**, they have given me incredible guidance and great support throughout the research process. I appreciate all their contributions of time and ideas that made my Ph.D. experience productive and stimulating. They have always made available to clarify my doubts despite their busy schedule and I consider it as a great opportunity to do my doctoral program under their guidance. I am equally thankful to research committee members Prof. Devesh Bhatia, Prof. M. Ali Haider, and Prof. Kuntal Manna for their perspicacious comments, encouragement, and continuous evaluation of my research progress. I am thankful to the staff of the Chemical Engineering Department, IIT Delhi and the vendors for their timely help in procuring the equipment, accessories, and chemicals I needed for my work. I am thankful to the Central Research Facility (CRF) and Nanoscale Research Facility (NRF) at IIT Delhi for providing the instrumentation facilities. I extend my heartiest thank to my senior Dr. Meenakshi Pokhriyal for her immense support and guidance. I also thank my all the lab members, Surya, Chitrangda, Aakash, Alok, Sushant, Debarun, Asha, Swagat, Rupali and Rohit for their constant support and help in my research work. I am fortunate to have Mr. Mairaj Khan as my husband who supported me morally, financially, and in every aspect of my life. Not all this could have been possible without his endless love, support, and encouragement. I am thankful to my father Mr. Abdul Aziz Niaze for his constant support and encouragement. I also thank my family members for their contribution during my Ph.D. I hereby express my hearty and sincere thanks to all who ever supported me either directly or indirectly in the completion of my research work successfully.

Ambereen Aziz Niaze

ABSTRACT

The global bioeconomy places significant importance on the development of economically feasible, scalable, and environmentally sustainable technologies that can effectively convert lignocellulosic biomass into liquid fuels. This objective is crucial in the pursuit of carbon neutrality in the utilisation of lignocellulosic biomass from agro and forest wastes in an agriculture-dependent country. An attempt to transform lignocellulosic biomass into high-value chemicals and fuels, which has become the current research hotspot, is a promising technique for easing the energy crisis due to fossil resources depletion. Besides fermentation and biomass gasification to syngas and its further conversion to ethanol, a direct chemocatalytic conversion of lignocellulosic biomass into ethanol is being investigated as a viable route. The present work is focussed on developing efficient catalysts and also process technology for enhanced ethanol production through chemocatalytic cellulose conversion.

Ethanol production has been improved by developing a machine learning-based model to optimise the process parameters of the industrially produced ethanol in order to selectively increase ethanol yield. However, the optimization of the process variables was performed for the first time using a data synthesis technique in which the normalized dataset which was first synthesized and then passed through an ANN model to get an optimized input variable set for an increase in bioethanol concentration (BEC) in the final product by 1˚GL.

The economic feasibility of ethanol production through the fermentation, gasification (*via* syngas) and chemocatalytic pathway is analysed. The techno-economic analysis is conducted in terms of ethanol selectivity and ethanol production cost. The obtained results show that biomass feedstock and catalyst have major contributions to the production cost. The proposed route which is chemocatalytic route is found to be giving a lower ethanol selling price as compared to the well-researched routes of biomass fermentation to ethanol and biomass gasification followed by syngas conversion to ethanol.

Based on the economic feasibility of the most promising route, the catalysts TiO_2 nanowires (NWs) and WO_3 NWs were synthesized by plasma-assisted method, and then Pt/Ru was impregnated onto these NWs. The direct conversion of cellulose to ethanol and propanol using tungsten-based co-catalysts was enhanced even at low temperatures. The NWs supported catalysts when combined with various tungsten-based co-catalysts improved the catalytic performance. X-ray photoelectrons spectroscopy (XPS) and Raman analysis show the oxygen vacancy (Ov) enrichment on the surface of Pt/TiO_2 in presence of tungsten co-catalysts which

improved their catalytic activity. Moreover, the role of metallic platinum (Pt^o) was also investigated and found to have a linear relationship with the activity as follows: H_2WO_4 > $(NH_4)_6H_2W_{12}O_{40}.xH_2O$ > $H_3PW_{12}O_{40}$. Based on the experimental results, the reaction pathway is proposed which elaborates the activation and cleavage of specific C-C and C-O bonds.

The hydrolysis of cellulose to ethanol is still uneconomical with a low yield of this desired product; hence, it is important to develop a promising multifunctional catalyst that can convert cellulose to selectively high yields of ethanol. Herein, Ru/WO_3 NWs catalyst is synthesized which will give a highly active catalytic surface with both the metal and support participating in the reaction to improve ethanol yields from 28.94% to 44.56%. WO_3 not only helps the C-C cleavage of glucose but also suppresses the isomerization of glucose so that no propanol is produced, and the selective yield of ethanol improves. The combined electronic properties of Ru^o and W^{6+} participate in enhancing the catalytic activity and increasing the cellulose conversion to ethanol.

Based on the product distribution for the best catalytic system using the combination of Ru/WO_3 and WO_3 NWs, a reaction network is elucidated, and a phenomenological kinetic model is developed. The kinetic parameters are estimated in the temperature range of 493 K to 523 K. The model is validated well with the experimental data. The analytical solution of the overall reaction is evaluated by introducing the kinetic parameters of all four consecutive reactions; hydrolysis of cellulose, the RAC reaction of glucose, the hydrogenation of GA to produce EG, and the hydrogenolysis of EG to EtOH. C-C cleavage of glucose is important and crucial to enhance ethanol yield and hence is determined as the rate limiting step.

सार

वैश्विक जैव अर्थव्यवस्था प्रौद्योगिकियों के विकास पर आर्थिक रूप से व्यवहार्य, मापनीय और पर्यावरण की दृष्टि से महत्वपूर्ण महत्व रखती है जो लिग्नोसेल्यूलोसिक बायोमास को प्रभावी रूप से तरल ईंधन में परिवर्तित कर सकती हैं। कृषि-निर्भर देश में कृषि और वन अपशिष्टों से लिग्नोसेल्यूलोसिक बायोमास के उपयोग में कार्बन तटस्थता की खोज में यह उद्देश्य महत्वपूर्ण है।जीवाश्म संसाधनों की कमी के कारण ऊर्जा संकट को कम करने के लिए लिग्नोसेल्यूलोसिक बायोमास को उच्च-मूल्य वाले रसायनों और ईंधन में बदलने का प्रयास एक आशाजनक तकनीक है,, जो वर्तमान शोध का अतिक्षेत्र बन गया है। किण्वन और बायोमास गैसीकरण से सिनगैस और इसके आगे इथेनॉल में रूपांतरण के अलावा, लिग्नोसेल्यूलोसिक बायोमास का इथेनॉल में प्रत्यक्ष केमोकैटेलिटिक रूपांतरण एक सक्षम मार्ग के रूप में जांचा जा रहा है। वर्तमान कार्य केमोकैटेलिटिक सेल्यूलोज के माध्यम से कार्यक्षम उत्प्रेरक विकसित करने और संवर्धित इथेनॉल उत्पादन पर केंद्रित है।

मशीन लर्निंग आधारित मॉडल विकसित करके इथेनॉल उत्पादन छमता में विर्द्धि हुई है जोकि उत्पादित एथेनॉल के प्रक्रिया मापदंडों को अनुकूलित करके एथेनॉल उत्पादन को बढ़ता है। हालाँकि, प्रक्रिया चर का अनुकूलन पहली बार डेटा संश्लेषण तकनीक का उपयोग करके किया गया था, जिसमें सामान्यीकृत डेटासेट को पहले संश्लेषित किया गया था और फिर अंतिम उत्पाद में बायोएथेनॉल सांद्रता (बीईसी) में 1°GL की वृद्धि के लिए एक अनुकूलित इनपुट चर सेट प्राप्त करने के लिए एक एएनएन मॉडल के माध्यम से पारित किया गया था।

किण्वन, गैसीकरण (सिनगैस के माध्यम से) और केमोकैटेलिटिक मार्ग के माध्यम से इथेनॉल उत्पादन की आर्थिक व्यवहार्यता का विश्लेषण किया गया है। इथेनॉल चयनात्मकता और इथेनॉल उत्पादन लागत के संदर्भ में तकनीकी-आर्थिक विश्लेषण किया गया है। प्राप्त परिणामों से पता चलता है कि बायोमास फीडस्टॉक और उत्प्रेरक का इथेनॉल उत्पादन लागत में प्रमुख योगदान है। प्रस्तावित मार्ग जो कि केमोकैटेलिटिक मार्ग है, बायोमास किण्वन से इथेनॉल और बायोमास गैसीकरण के बाद सिनगैस से इथेनॉल में रूपांतरण के अच्छी तरह से शोध किए गए मार्गों की तुलना में कम इथेनॉल बिक्री मूल्य देता है।

सबसे आशाजनक मार्ग की आर्थिक व्यवहार्यता के आधार पर, उत्प्रेरक TiO_2 नैनोवायर (NWs) और WO_3NWs को प्लाज्मा-सहायता विधि द्वारा संश्लेषित किया गया, और फिर इन NWs पर Pt/Ru क्लस्टर को लगाया गया। कम तापमान पर भी टंगस्टन-आधारित सह-उत्प्रेरक का उपयोग करके सेल्यूलोज का

इथेनॉल और प्रोपेनॉल के सीधे में विर्द्धि हुई थी। विभिन्न टंगस्टन-आधारित सह-उत्प्रेरक के साथ संयुक्त होने पर NWs समर्थित उत्प्रेरक ने उत्प्रेरक प्रदर्शन में सुधार किया। एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी (XPS) और रमन विश्लेषण टंगस्टन सह-उत्प्रेरक की उपस्थिति में Pt/TiO2 की सतह पर ऑक्सीजन रिक्ति (Ov) संवर्धन दिखाते हैं जिसने उनकी उत्प्रेरक गतिविधि में सुधार किया। इसके अलावा, धात्विक प्लैटिनम (Pto) की भूमिका की भी जांच की गई और पाया गया कि इसका गतिविधि के साथ एक रैखिक संबंध निम्नलिखित नुसार है : $H_2WO_4 > (NH_4)_6H_2W_{12}O_{40}.xH_2O > H_3PW_{12}O_{40}$। प्रायोगिक परिणामों के आधार पर, प्रतिक्रिया मार्ग प्रस्तावित किया गया है जो विशिष्ट C-C और C-O बंधों के सक्रियण और दरार को विस्तृत करता है।

इस वांछित उत्पाद की कम उपज के साथ सेल्यूलोज का इथेनॉल में हाइड्रोलिसिस अभी भी अलाभकारी है; इसलिए, एक आशाजनक बहुक्रियाशील उत्प्रेरक विकसित करना महत्वपूर्ण है जो सेल्यूलोज को इथेनॉल की चुनिंदा उच्च उपज में परिवर्तित कर सके। यहां, Ru/WO3 NWs उत्प्रेरक को संश्लेषित किया गया है जो इथेनॉल की उपज को 28.94% से 44.56% तक सुधारने के लिए प्रतिक्रिया में भाग लेने वाले धातु और समर्थन, दोनों के साथ एक अत्यधिक सक्रिय उत्प्रेरक सतह देगा। WO3 न केवल ग्लूकोज के C-C विभाजन में मदद करता है बल्कि ग्लूकोज के आइसोमेराइजेशन को भी दबाता है ताकि कोई प्रोपेनॉल न बने और इथेनॉल की चयनात्मक उपज में सुधार हो। Ru^o और W^{6+} के संयुक्त इलेक्ट्रॉनिक गुण उत्प्रेरक गतिविधि को बढ़ाने और सेल्यूलोज को इथेनॉल में बदलने में वृद्धि करते हैं।

Ru/WO_3 और WO_3 NWs के संयोजन का उपयोग करके सर्वोत्तम उत्प्रेरक प्रणाली के लिए उत्पाद वितरण के आधार पर, एक प्रतिक्रिया नेटवर्क स्पष्ट किया गया है और एक परिघटना संबंधी गतिज मॉडल विकसित किया गया है। गतिज मापदंडों का अनुमान 493 K से 523 K के तापमान रेंज में लगाया जाता है। प्रयोगात्मक डेटा के साथ मॉडल की अच्छी तरह से पुष्टि की गई है। समग्र प्रतिक्रिया के विश्लेषणात्मक समाधान का मूल्यांकन सभी चार क्रमिक प्रतिक्रियाओं के गतिज मापदंडों को शामिल करके किया जाता है; सेल्यूलोज का हाइड्रोलिसिस, ग्लूकोज की RAC प्रतिक्रिया, EG का उत्पादन करने के लिए GA का हाइड्रोजनीकरण और EG से EtOH का हाइड्रोजनोलिसिस। इथेनॉल की उपज बढ़ाने के लिए ग्लूकोज का C-C विभाजन महत्वपूर्ण और निर्णायक है, इसलिए इसे दर सीमित करने वाले चरण के रूप में निर्धारित किया जाता है।

TABLE OF CONTENTS

CERTIFICATE i

ACKNOWLEDGEMENTS ii

ABSTRACT iii

सार v

TABLE OF CONTENT vii

LIST OF FIGURES xii

LIST OF SCHEMATICS xvi

LIST OF TABLES xvii

LIST OF APPENDICES xix

NOMENCLATURE xx

1. INTRODUCTION

1.1 Background 2
1.2 Classification of biofuels 4
1.3 Potential of ethanol production from biomass waste 5
1.4 Sustainable technology for ethanol production 8
1.4.1 Fermentation route 9
1.4.2 Thermochemical process for converting biomass to ethanol 9
1.4.2.1 Gasification route 10
1.4.2.2 Chemocatalytic route 12
1.5 Thermochemical property prediction of possible route for cellulose conversion to ethanol and other side products 13
1.6 Motivation and research goal 15
1.7 Research objective 16
1.8 Thesis organization 17

2. LITERATURE REVIEW

2.1 Introduction 20
2.2 Simulation tools and ANN Models 21
2.3 Comparison of Techno-economics analysis on various techniques 21

2.4 Possible reaction mechanism for chemocatalytic conversion of cellulose to ethanol 22
2.5 Role of hot water in cellulose degradation 24
2.6 Technical efficiency of the chemocatalytic route 28
2.6.1 Two-step cellulose to ethanol conversion 28
2.6.2 One-step cellulose to ethanol conversion 29
2.7 Literature Lacunae 35

3. DATA-DRIVEN ARTIFICIAL NEURAL NETWORK MODELING FOR HIGH SELECTIVE YIELDS OF BIOETHANOL

3.1 Introduction 38
3.2 Software and data bank used to simulate the model 39
3.3 Selection of input variables 40
3.4 Data processing 43
3.5 Data normalization 44
3.6 Training and testing of the ANN model 44
3.7 Model development 45
3.8 Optimization of the process input variables 50
3.9 Conclusion 52

4. TECHNO-ECONOMIC ANALYSIS OF ETHANOL PRODUCTION ROUTES

4.1 Introduction 55
4.2 Process design and simulation of fermentation route 56
4.2.1 Pretreatment of raw biomass 57
4.2.2 Acidic Pretreatment and Conditioning 58
4.2.3 Enzymatic Hydrolysis and Fermentation 58
4.2.4 Cellulase Production 58
4.2.5 Product Separation 59
4.2.6 Mass and Energy Balances 59
4.2.7 Economics 60
4.3 Process design and simulation of gasification/syngas route 65
4.3.1 Biomass Gasification 66
4.3.2 Syngas Clean-up 66
4.3.3 Catalytic Conversion of Syngas to Ethanol 67
4.3.4 Ethanol Separation 68
4.3.5 Mass and Energy Balances 68
4.3.6 Economics 69

4.4 Process design and simulation of chemocatalytic route 70
4.4.1 Ethanol Synthesis by Chemocatalytic route 70
4.4.2 Ethanol Separation 71
4.4.3 Heat and Power 71
4.4.4 Mass and Energy Balances 72
4.4.5 Economics 73
4.5 Techno-economic comparison of the process routes 73
4.6 Process sensitivity of the economically viable chemocatalytic route 75
4.7 Conclusion 75

5. DEVELOPMENT OF CHEMOCATALYTIC CELLULOSE CONVERSION TO ETHANOL

5.1.1 Introduction 78
5.1.2 Materials 81
5.1.3 Catalysts preparation 81
5.1.3.1 Synthesis of TiO_2 81
5.1.3.2 Synthesis of Pt/TiO_2 81
5.1.4 Catalysts characterization 82
5.1.5 Catalytic activity 82
5.1.6 Results and discussion 84
5.1.6.1 Phases and lattice structure identification of the material 84
5.1.6.2 N_2 surface area characterization of the pristine catalysts 85
5.1.6.3 Oxidation state analysis by XPS technique 86
5.1.6.4 Analysing oxygen defects using RAMAN spectroscopic techniques 87
5.1.6.5 Morphological features of the developed material 88
5.1.6.6 Effect of temperature and time on the performance of the catalytic conversion of C_2 and C_3 alcohols 89
5.1.6.7 Catalytic activity performance for the tandem reaction 94
5.1.6.8 Effect of various tungsten-based co-catalysts 96
5.1.6.9 Spent catalysts characterization 98
5.1.6.10 Stability test of the catalysts 107
5.1.7 Understanding the activation and cleavage of specific C-C and C-O bonds for the formation of C_2 and C_3 alcohols 108
5.1.8 Conclusion 111
5.2.1 Introduction 113

5.2.2 Materials 114
5.2.3 Catalysts synthesis 115
5.2.3.1 Synthesis of Tungsten oxide nanowires 115
5.2.3.2 Synthesis of Ru-loaded tungsten oxide nanowires 115
5.2.4 Catalysts characterization 115
5.2.5 Catalytic activity testing for cellulose conversion to ethanol in a stirred batch reactor 116
5.2.6 Results and discussion 117
5.2.6.1 Morphology feature of the developed nanomaterials 117
5.2.6.2 Phases and lattice structure identification of the material 118
5.2.6.3 Elemental mapping and chemical compositions of the catalysts using EDX and ICP-MS 119
5.2.6.4 Electronic properties of catalysts by XPS and RAMAN analysis techniques 120
5.2.6.5 Catalysts activity performance for efficient conversion of cellulose to ethanol in integrated system and its effects on reaction parameters 122
5.2.6.6 Investigating the catalytic activity of WO_3 as a co-catalyst 124
5.2.6.7 Stability testing of the catalysts 127
5.2.6.8 Proposed reaction pathway based on the product distribution 128
5.2.7 Conclusion 131

6. PHENOMENOLOGICAL KINETIC MODEL DEVELOPMENT AND PARAMETER ESTIMATION FOR INTEGRATED SYNTHESIS OF CELLULOSE TO ETHANOL

6.1 Introduction 134
6.2 Mass transfer effects in the stirred batch reactor 135
6.3 Simplified reaction network for ethanol selective synthesis 136
6.4 Phenomenological kinetic model development 138
6.5 Finding the order of reaction 140
6.6 Iterative nonlinear optimization method to find the model parameters 143
6.7 Model Validation 146
6.8 Conclusion 147

7. CONCLUSION AND FUTURE RECOMMENDATION

7.1 Summary and overall conclusion 150
7.2 Future recommendations 152

REFERENCES 153

APPENDICES 169

PUBLICATIONS 186

CURRICULUM VITAE 187

LIST OF FIGURES

Figure 1.1 Visions and goals on Biofuels 4
Figure 1.2 Classification of biofuels based on feedstock availability and Commercialisation 5
Figure 1.3 Various routes for ethanol production 8
Figure 1.4 Various fermentation technologies to produce ethanol 9
Figure 1.5 Thermochemical methods for ethanol production 11
Figure 1.6 Comparative limitations and advancement of various ethanol production routes 13
Figure 1.7 Kernel density plot of with and without W-based catalysts 16
Figure 2.1 Development of catalytic system over time for cellulose to ethanol Conversion 30
Figure 2.2 The impact of acid on the process of converting cellulose to ethanol using Ni@C-700. 33
Figure 3.1 Simplified process flow diagram of the fermenter's unit with input and output variables. 41
Figure 3.2 Correlation matrix for input and output variables 43
Figure 3.3 Artificial neural network (ANN) model for increasing bioethanol concentration in final product 44
Figure 3.4 Mean Square Error (MSE) vs Epochs plot for Artificial Neural Network Model for Sugar mill 45
Figure 3.5 The architecture of the ANN model 48
Figure 3.6 Linearity of the response obtained using ANN model for (a) testing and (b) training dataset 49
Figure 3.7 Percent error for the response of the ANN model for (a) testing (b) training dataset 50
Figure 4.1 Different process routes for ethanol production 56
Figure 4.2 Process flow diagram for the fermentation route 57
Figure 4.3 Cost component 60
Figure 4.4 Process flow diagram for gasification via syngas route 66
Figure 4.5 Process flow diagram for chemocatalytic route 71
Figure 4.6 Effect of (a) biomass cost (b) catalyst cost (c) ethanol yield, and (d) higher alcohols cost on MESP 75

Figure 5.1.1 (a) Photograph of the experimental setup of HEL high pressure slurry batch reactor (b) Schematic diagram of the reactor setup 83

Figure 5.1.2 XRD pattern of catalyst TiO_2 and Pt/TiO_2 85

Figure 5.1.3 N_2 adsorption-desorption isotherm of Pt/TiO_2 and pore size distribution in the inset 85

Figure 5.1.4 High resolution XPS spectra (a) Pt 4*f* (b) Ti 2*p* (c) O 1*s* of pristine Pt/TiO_2 87

Figure 5.1.5 Raman spectra for pristine TiO_2 and Pt/TiO_2 in the range of 100 – 800 cm^{-1} 88

Figure 5.1.6 (a) TEM (b) HRTEM image and Lattice fringes of Pt and TiO_2 in inset (c) SAED pattern of representing (hkl) values, (d) particle size distribution of FESEM image at (e) 4 µm (f) 500nm (g) EDS spectra of pristine Pt/TiO_2 89

Figure 5.1.7 FTMS + pESI spectra of catalytic conversion of cellulose (a) R1 (493 K, 5h) (b) R2 (493 K, 10h) (c) R3 (523 K, 5h) (d) R4 (523 K, 10h) 90

Figure 5.1.8 Colour of the samples after reaction R1, R2, R3 and R4 using Pt/TiO_2 + H_2WO_4 91

Figure 5.1.9 Product analysis using ^{1}H NMR spectroscopy for reaction (a) R1 (493 K, 5h) (b) R2 (493 K, 10h) (c) R3 (523 K, 5h) (d) R4 (523 K, 10h) 92

Figure 5.1.10 Effect of reaction condition for catalytic conversion of cellulose to C_2 and C_3 alcohols using Pt/TiO_2 + H_2WO_4. Reaction run number; R1 (493 K, 5h); R2 (493 K, 10h); R3 (523 K, 5h); R4 (523 K, 10h) 93

Figure 5.1.11 Schematic representation of tandem catalytic system and integrated catalytic system 95

Figure 5.1.12 FTMS + pESI spectra of catalytic performance of cellulose to C_2 and C_3 alcohols for various co-catalyst (a) $H_3PW_{12}O_{40}$ (b) $(NH_4)_6H_2W_{12}O_{40}.xH_2O$ 98

Figure 5.1.13 XRD spectra of Catalyst Pt/TiO_2, Co-Catalyst H_2WO_4, support TiO_2 and spent of reaction R1, R2, R3, and R4 indicated in the Figure as spent 1, spent 2, spent 3, and spent 4 under reaction conditions, respectively 99

Figure 5.1.14 XRD spectra of pristine catalyst Pt/TiO_2, spent Pt/TiO_2, and co-catalysts H_2WO_4, $(NH_4)_6H_2W_{12}O_{40}.xH_2O$, $H_3PW_{12}O_{40}$, and spent when used in combination with Pt/TiO_2 under the same reaction condition 100

Figure 5.1.15 N_2 adsorption-desorption isotherm of spent Pt/TiO_2 when used in combination with (a) H_2WO_4 (b) $(NH_4)_6H_2W_{12}O_{40}.xH_2O$ (c) $H_3PW_{12}O_{40}$ and corresponding pore size distribution in the inset of the figure 101

Figure 5.1.16 XPS spectra of O 1*s* (a-c), Pt 4*f* (d-e), Ti2*p* (g-i) and W 4*f* (j-l) of spent Pt/TiO2 using various co-catalysts H_2WO_4, $(NH_4)_6H_2W_{12}O_{40}.xH_2O$ and $H_3PW_{12}O_{40}$ 103

Figure 5.1.17 Metallic Pt – activity relationship 104

Figure 5.1.18 Raman spectra in the range of 100 – 800 cm^{-1} of spent Pt/TiO_2 using various co-catalysts H_2WO_4, $(NH_4)_6H_{2}{}_{12}O_{40}.xH_2O$ and $HPW_{12}O_{40}$ 105

Figure 5.1.19 FESEM image of spent Pt/TiO_2 using different co-catalysts H_2WO_4 (a) 4 µm (b) 500nm, $H_3PW_{12}O_{40}$ (c) 4 µm (d) 500nm, $(NH_4)_6H_2W_{12}O_{40}.xH_2O$ (e) 4 µm (f) 500nm when used in combination with Pt/TiO_2 106

Figure 5.1.20 Energy dispersive spectroscopy (EDS) spectra and its corresponding elemental composition of pristine (a) Pt/TiO_2, spent of reaction using different co-catalysts (b) H_2WO_4 (c) $H_3PW_{12}O_{40}$ (d) $(NH_4)_6H_2W_{12}O_{40}.xH_2O$ in combination with Pt/TiO_2 107

Figure 5.1.21 Reusability of the spent catalysts 108

Figure 5.1.22 Reaction performance with various (a) catalysts (b) reactants 109

Figure 5.2.1 TEM image of (a) WO_3 (b) Ru/WO_3, FESEM images of WO_3 at (c) 1µm (d) 100nm, Ru/WO_3 at (e) 1µm (f) 100nm 117

Figure 5.2.2 XRD of pristine catalysts 118

Figure 5.2.3 HRTEM of (a) WO_3 (b) Ru/WO_3 at 20nm (c) WO_3 (d) Ru/WO_3 at 5nm 119

Figure 5.2.4 Elemental mapping of (a) WO3 with elements (c) W (d) O and (b) Ru/WO3 with elements (e) W, (f) O (g) Ru 120

Figure 5.2.5 XPS spectra O 1*s* of (a) WO_3 (b) Ru/WO_3, W 4*f* of (c) WO_3 (d) Ru/WO_3, Ru 3*p* of (e) Ru/WO_3 (f) Raman spectra of Ru/WO_3 and WO_3 122

Figure 5.2.6 Catalytic activity of different catalysts either alone or in combination 125

Figure 5.2.7 XRD pattern of cellulose before and after reaction 125

Figure 5.2.8 Comparison of XRD pattern of pristine and spent catalyst 127

Figure 5.2.9 Recycling experiments for the catalytic conversion of cellulose to ethanol using Ru/WO_3 128

Figure 5.2.10 Sample collected after the reaction with different substrate under same reaction condition 130

Figure 6.1 Effect of mass transfer based on (a) rpm and (b) catalyst loading 136

Figure 6.2 Possible overall reaction network for cellulose conversion to ethanol and propanol 137
Figure 6.3 Simplified reaction network of the conversion of cellulose to ethanol 137
Figure 6.4 Reaction performed with glycolaldehyde as a reactant 139
Figure 6.5 Simplified reaction network for finding the kinetic parameters 140
Figure 6.6 Concentration-time plot for (a) zero order (b) first order (c) second order of reaction R_1 141
Figure 6.7 Concentration-time plot for (a) zero order (b) first order (c) second order of reaction R_2 141
Figure 6.8 Concentration-time plot for (a) zero order (b) first order (c) second order of reaction R_6 141
Figure 6.9 Concentration-time plot for (a) zero order (b) first order (c) second order of reaction R_8 141
Figure 6.10 Proposed methodology for estimation of kinetic parameters 144
Figure 6.11 Effect of reaction time and temperature on (a) cellulose conversion (b) ethanol yield 144
Figure 6.12 Arrhenius plot and activation energies (Ea) for various reactions (a) R_1; (b) R_2; (c) R_6; and (d) R_8 146
Figure 6.13 Experimental and calculated (model) results for the overall reaction of cellulose to ethanol at different temperatures (a) 493K (b) 503K (c) 513K and (d) 523K 147

LIST OF SCHEMES

Scheme 1.1 Direct conversion of cellulose to ethanol by chemocatalytic route 12

Scheme 1.2 Possible pathways for all reactions involved in cellulose conversion to ethanol 14

Scheme 2.1 Possible reaction mechanism to solely produce ethanol 23

Scheme 2.2 Hydrolysis of cellulose to glucose 25

Scheme 2.3 Reaction pathway of cellulose fragmentation in HCW for the temperature profile 453 -533 K. 27

Scheme 2.4. Chemocatalytic conversion process for ethanol production 29

Scheme 2.5. Hydrogenation and hydrogenolysis of glucose 31

Scheme 2.6. One-step conversion of cellulose to ethanol using Mo/Pt/WOx catalyst 31

Scheme 2.7. One-step conversion of cellulose to ethanol using Ru-WOx/HZSM-5 Catalyst 32

Scheme 2.8 (a) Reaction pathway for C-C cleavage of glucose to form $C_2 + C_4$ compounds (b) Borate-assisted reaction pathway for retro aldol condensation reaction of C_6 carbon compound (Glucose/Mannose) to form glycolaldehyde (GA) and erythrose (ERO) and aldol condensation reaction of 2 GA to form ERO 35

Scheme 4.1. Possible reaction mechanism for chemocatalytic conversion 72

Scheme 5.1.1 Proposed reaction pathway for C_2 and C_3 alcohols and keto-enol tautomerization reaction mechanism (given in box) 80

Scheme 5.1.2 Bond functionality is based on the activation and cleavage of bonds for the formation of C_2 and C_3 alcohols 111

Scheme 5.2.1. Schematic representation of cellulose conversion to ethanol 113

Scheme 5.2.2 Glucose-WO_3 complex formation 131

Scheme 5.2.3 Proposed reaction mechanism for catalytic conversion of cellulose over Ru/WO_3 catalyst and WO_3 co-catalyst 131

LIST OF TABLES

Table 1.1 Various industries worldwide production of ethanol 7

Table 1.2 Thermochemical property prediction for various pathway producing Ethanol 14

Table 3.1 Pearson Correlation Analysis of input variables for Sugar mill, India 41

Table 3.2 A traditional approach to interpreting a correlation coefficient 42

Table 3.3 Number of input nodes selected 48

Table 3.4 The architecture of ANN from Keras 49

Table 3.5 Optimized scenario for increasing bioethanol concentrations (BEC) by 1˚GL 52

Table 4.1 Hydrolysis and fermentation reactions 59

Table 4.2 Material and energy balance for fermentation route 60

Table 4.3 Scaling exponent of various equipment in chemo-catalytic, gasification and fermentation route 61

Table 4.4 Installation factor of various equipment in chemo-catalytic, gasification and fermentation route 61

Table 4.5 Direct cost components 62

Table 4.6 Indirect cost components correlation 63

Table 4.7 Fixed operating cost components correlation 63

Table 4.8 Economics for fermentation process 64

Table 4.9 Produced gases composition after gasifier 66

Table 4.10 Gasification and catalytic reactions 67

Table 4.11 Ultimate analysis of woody residue on dry basis 68

Table 4.12 Material and energy balance for gasification/syngas route 68

Table 4.13 Economics for gasification and syngas route 69

Table 4.14 Chemical composition of dried woody residue (% dry basis) 72

Table 4.15 Material and energy balance calculations for chemocatalytic route 72

Table 4.16 Economics for chemocatalytic route 73

Table 4.17 Techno-economic comparison of the process routes 74

Table 5.1.1 Reaction conditions for the conversion of cellulose to C_2 and C_3 alcohols 84

Table 5.1.2 Table of d-spacing calculation from SAED pattern 89

Table 5.1.3 Catalytic performance for the conversion of cellulose to C_2 and C_3 alcohols under different reaction conditions 93

Table 5.1.4 Catalytic activity and comparison of tandem and integrated catalytic system 96

Table 5.1.5 Cellulose conversion and product selectivity for different co-catalyst 97

Table 5.1.6 Physicochemical properties of the pristine and spent catalysts 101

Table 5.2.1 Elemental composition of pristine catalysts by EDX and ICP-MS analysis 120

Table 5.2.2 Effect of various parameter on product yield 124

Table 5.2.3 ICP-MS analysis of Ru species in Ru/WO_3 of spent catalyst 128

Table 5.2.4 Product Distribution over Ru/WO_3 under optimized reaction conditions 129

Table 6.1 R^2 of different order of reactions R_1, R_2, R_6, and R_8 142

Table 6.2 Rate constant value k_i at different temperatures 145

LIST OF APPENDICES

APPENDIX A

APPENDIX B

APPENDIX C

NOMENCLATURE

AAD	Absolute average deviation
ANN	Artificial neuron network
BEC	Bioethanol concentration
BEC$GL_{Industrial}$	Industrial bioethanol concentration
BET	Branauer-Emmet-Teller
BJH	Barret-Joyner-Halenda
BE	Binding energy
CAGR	Compound annual growth rate
CBP	Consolidated bioprocessing
Cell	Cellulose
CVD	Chemical vapor deposition
DP	Degree of polymerization
dp	Pore diameter
DFB	Dual fluidized bed
DEPG	Dimethyl ether of polyethylene glycol
DMSO	Deuterated dimethyl sulfoxide
EBP	Ethanol blending programme
EG	Ethylene glycol
ERO	Erythrose
EtOH	Ethanol
ESI	Electrospray ionization
EDS	Energy dispersive spectroscopy
FNN	Feed forward neural network

FESEM	Field emission electron microscopy
FTMS	Fourier transform mass spectroscopy
FID	Flame ionization detector
FTO	Fluorinated tin oxide
FCI	Fixed capital investment
fcc	Face centered cubic
FM	Concentration of cells in fermenters
GHG	Green-house gases
GL	Gay Lussac
GA	Glycolaldehyde
GC	Gas chromatography
Glu	Glucose
HCW	Hot compressed water
HRTEM	High resonance transmission electron microscopy
HP	High pressure
ISBL	Inside battery limit
IEA	International energy agency
IW	pH of inlet wash
IIT	Indian Institute of Technology
ICP-MS	Inductively coupled mass spectroscopy
Kw	Dissociation constant
LCB	Lignocellulosic biomass
LP	Low pressure
LCA	Life cycle assessment

MSW	Municipal solid waste
MESP	Minimum ethanol selling price
Mo	Molybdate
MSE	Mean squared error
MFC	Mass flow controller
MCC	Microcrystalline cellulose
NREL	National renewable energy laboratory
Ni	Nickel
NMR	Nuclear magnetic resonance
NWs	Nanowires
OF	Objective function
PSO	Particle swarm optimization
Pt	Platinum
PrOH	Propanol
PFM	Concentration of cells in pre fermenters
PXRD	Powder X-ray diffraction
ReLU	Rectified linear unit
RID	Refractive index detector
RAC	Retro aldol condensation
Ru	Ruthenium
Rh	Rhodium
r	Pearson correlation coefficient
SHF	Separate hydrolysis and fermentation
SSF	Simultaneous saccharification and fermentation

SSCF	Simultaneous saccharification and co-fermentation
SSFF	Simultaneous saccharification filtration and fermentation
SAA	Single atom alloy
SG	Specific gravity of wash
SMSI	Strong metal support interaction
SEM	Scanning electron microscopy
SAED	Selected area electron diffraction
SGFMW	Specific gravity of fermented wash
TSSFMWD	TSS of fermented wash before decanter
TSCWAD	TSS of Clarified wash after decanter
TRSMRP	TRS of molasses received for process
TRSTCSD	Random TRS of tanker coming from sugar division
TNWs	TiO_2 nanowires
TMS	Trimethyl silane
Ti	Titanium
TCI	Total capital investment
TOC	Total operating cost
TCD	Thermal conductivity detector
TDC	Total direct cost
TIDC	Total indirect cost
TEM	Transmission electron microscopy
TRL	Total readiness level
W	Tungsten
WFMpH	Water fermentation pH

WFH	Water fermentation hardness
WCI	Working capital investment
WBC	Tungsten-based catalysts
WO_3NWs	Tungsten oxide nanowires
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YV	Concentration of cells in yeast vessels