

Table of Contents

| | |
|------------------------------|------------------|
| Abstract | i-vi |
| Table of Contents | vii-xiii |
| List of Tables | xiv-xv |
| List of Figures | xvi-xviii |
| List of Abbreviations | |

Chapter 1: Introduction

| | | |
|-----------|--|----|
| 1.1 | Introductory Overview | 1 |
| 1.2 | Fossil Fuels Depletion and Environmental Sustainability | 1 |
| 1.3 | Embracing Renewable Energy: A Necessity for the Future | 2 |
| 1.3.1 | Biomass as a Source of Renewable Energy | 3 |
| 1.3.2 | Biomass Integration for a Resilient Biobased Society | 5 |
| 1.4 | Solving India's Energy Dilemma: A Focus on Renewable Energy Strategies | 5 |
| 1.5 | Biowaste: Generation and Its Management | 7 |
| 1.5.1 | Weed Biowaste | 7 |
| 1.5.2 | Waste Valorization: Strategies for Turning Waste into Valuable Resources | 9 |
| 1.5.2.1 | Various pathways of biomass conversion | 10 |
| 1.5.2.1.1 | Biochemical conversion | 10 |
| 1.5.2.1.2 | Thermochemical conversion | 11 |
| 1.6 | Historical Overview and Evaluation of the Pyrolysis Process | 15 |
| 1.6.1 | Classification of the Pyrolysis Process | 15 |
| 1.6.2 | Pyrolysis Products | 16 |
| 1.6.2.1 | Liquid product | 16 |
| 1.6.2.2 | Gaseous product | 18 |
| 1.6.2.3 | Solid product | 18 |

| | | |
|------|---|----------|
| 1.7 | Methodology for Modelling and Optimization of Pyrolysis Process | 20 |
| 1.8 | Importance of Kinetics and Thermodynamics in Biomass Pyrolysis | 20 21 |
| 1.9 | State of the Art | 22 |
| 1.10 | Benefits of the Research | 22 |
| 1.11 | Research Objectives | 23 |
| 1.12 | Organization of the Thesis | 23 |
| | References | 24 |

Chapter 2: Review of literature

| | | |
|---------|---|----|
| 2.1 | Introduction | 33 |
| 2.2 | Various Waste Biomass and Bio-waste: Their Applicability in Pyrolysis | 34 |
| 2.3 | Effect of Pyrolysis Parameters on Product Yield | 43 |
| 2.3.1 | Feedstocks composition | 43 |
| 2.3.2 | Effect of temperature | 44 |
| 2.3.3 | Effect of heating rate | 45 |
| 2.3.4 | Effect of particle size | 46 |
| 2.3.5 | Effect of inert gas flow rate | 47 |
| 2.4 | Biochemical Components and Pyrolysis Mechanism | 49 |
| 2.5 | Pyrolysis of Lignocellulosic Biomass | 50 |
| 2.5.1 | Pyrolysis of weed biomass | 52 |
| 2.6 | Catalytic Pyrolysis of Biomass | 57 |
| 2.6.1 | Chemical Reactions in Catalytic Pyrolysis | 59 |
| 2.6.2 | Factors Affecting Biomass Catalytic Pyrolysis | 60 |
| 2.6.2.1 | Characteristics of Catalyst | 61 |
| 2.6.2.2 | Biomass to catalyst ratio | 63 |
| 2.6.2.3 | Incorporation of metal to catalyst | 64 |

| | | |
|-------|---|----|
| 2.7 | Exploring the Pyrolysis Kinetics through Thermogravimetric Analysis (TGA) | 65 |
| 2.7.1 | Pyrolysis Kinetics, Reaction Mechanism, and Thermodynamics Studies of Biomass | 67 |
| 2.7.2 | Exploring the Kinetics and thermodynamics in Catalytic Pyrolysis | 71 |
| 2.8 | Methodology for The Optimization of Process Parameters | 73 |
| 2.8.1 | Response surface methodology (RSM) | 73 |
| 2.8.2 | Artificial Neural Network (ANN) | 76 |
| 2.9 | Summary of the Literature Review and Scope of Research | 79 |
| | References | 80 |

Chapter 3: Materials and methods

| | | |
|---------|---|-----|
| 3.1 | Methodology Flow Diagram | 104 |
| 3.2 | Identification and Description of the Feedstock | 105 |
| 3.2.1 | <i>Tithonia Diversifolia</i> : The Feedstock in the Current Investigation | 105 |
| 3.2.1.1 | Distribution of <i>T. diversifolia</i> | 106 |
| 3.3 | Material and Analytical Test Method | 107 |
| 3.3.1 | Sample Preparation | 107 |
| 3.3.2 | Proximate Analysis | 107 |
| 3.3.2.1 | Determination of moisture content | 107 |
| 3.3.2.2 | Determination of ash content | 107 |
| 3.3.2.3 | Determination of volatile matter | 108 |
| 3.3.2.4 | Determination of fixed Carbon | 108 |
| 3.3.3 | Biochemical Analysis of Biomass | 108 |
| 3.3.3.1 | Extractives | 108 |
| 3.3.3.2 | Hemicellulose | 109 |
| 3.3.3.3 | Lignin | 109 |
| 3.3.3.4 | Cellulose | 109 |

| | | |
|-----------|---|-----|
| 3.3.4 | Pyrolysis Experiment | 110 |
| 3.3.4.1 | Effect of operating conditions on product | 111 |
| 3.3.5 | Statistical Modelling | 112 |
| 3.3.5.1 | Response surface methodology | 112 |
| 3.3.5.2 | ANN modelling | 115 |
| 3.3.5.2.1 | Topology | 115 |
| 3.3.5.3 | Prediction capability of the RSM and ANN models | 117 |
| 3.3.5.4 | Application of catalysts in biomass pyrolysis | 118 |
| 3.3.5.4.1 | Preparation of catalysts | 118 |
| 3.3.5.4.2 | Catalytic pyrolysis | 118 |
| 3.3.6 | Instrumental Characterization | 119 |
| 3.3.6.1 | Elemental characterization | 119 |
| 3.3.6.2 | Higher heating value (HHV) | 119 |
| 3.3.6.3 | FTIR analysis | 119 |
| 3.3.6.4 | ¹ H-NMR | 120 |
| 3.3.6.5 | GC-MS | 120 |
| 3.3.6.6 | Determination of pH | 120 |
| 3.3.6.7 | Electrical conductivity | 120 |
| 3.3.6.8 | SEM | 121 |
| 3.3.6.9 | XRD analysis | 121 |
| 3.3.6.10 | Surface area analysis of catalysts | 121 |
| 3.3.7 | Thermogravimetric analysis (TGA) | 121 |
| 3.4 | Kinetic Study | 122 |
| 3.4.1 | Determination of Kinetic Parameters | 122 |
| 3.4.1.1 | Friedman method | 123 |
| 3.4.1.2 | Kissinger-Akahira-Sunose method | 123 |
| 3.4.1.3 | Flynn-Wall-Ozawa method (FWO) | 123 |
| 3.4.1.4 | Miura-Maki distributed activation energy method | 124 |
| 3.4.2 | Derivation of Degradation Mechanisms | 124 |
| 3.4.3 | Determination of Arrhenius Constant | 124 |

| | |
|---|-----|
| 3.4.4 Sestak-Berggren Combined Kinetic Model | 126 |
| 3.4.5 Determination of Thermodynamic Parameters | 126 |
| References | 127 |

Chapter 4: Results and Discussion

Chapter 4(A)

| | |
|---|-----|
| 4A.1 Introduction | 130 |
| 4A.2 Physicochemical Characterization of Biomass | 130 |
| 4A.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Biomass | 132 |
| 4A.4 Effects of Operating Parameters on Products Yield | 133 |
| 4A.4.1 Temperature | 133 |
| 4A.4.2 Heating rate | 134 |
| 4A.4.3 Particle Size | 134 |
| 4A.4.4 Inert Gas Flow Rate | 136 |
| 4A.5 Product Characterization | 136 |
| 4A.5.1 Physicochemical Characterization of Bio-Oil | 136 |
| 4A.5.2 FTIR Analysis of Bio-Oil | 138 |
| 4A.5.3 ¹ H NMR Analysis | 139 |
| 4A.5.4 GCMS | 140 |
| 4A.6 Characterization of Biochar | 142 |
| 4A.6.1 Physicochemical Characterization | 142 |
| 4A.6.2 FTIR Analysis | 144 |
| 4A.6.3 SEM | 146 |
| 4A.7 Summary | 148 |
| References | 149 |

Chapter 4(B)

| | |
|--|-----|
| 4B.1. Introduction | 154 |
| 4B.2 Experimental Design and Statistical Analysis by RSM | 155 |

| | |
|--|-----|
| 4B.2.1 Response Plots | 158 |
| 4B.2.1.1 Optimization and Validation of Model | 159 |
| 4B.2.2 Prediction of Bio-Oil Yield by ANN | 159 |
| 4B.3 Comparative Evaluation of RSM and ANN Models | 161 |
| 4B.4 Relative Importance of Parameters on Bio-Oil Yield | 163 |
| 4B.5 Optimization and Modelling of Bio-oil Yield: A comparison of Classical Approach vs RSM and ANN | 164 |
| 4B.6 Summary | 165 |
| References | 166 |

Chapter 4(C)

| | |
|---|-----|
| 4c.1 Introduction | 168 |
| 4C.2 Thermogravimetric Analysis | 169 |
| 4C.3 Determination of the Thermal Decomposition Model | 171 |
| 4C.4 Evaluation of Kinetic Parameters | 172 |
| 4C.5 Evaluations of Thermodynamic Parameters | 176 |
| 4C.6 Combined Kinetic Model | 178 |
| 4C.7 Kinetic Compensation Effect | 180 |
| 4C.8 Summary | 182 |
| References | 183 |

Chapter 4(D)

| | |
|---|-----|
| 4D.1 Introduction | 187 |
| 4D.2 Characterization of Catalysts | 188 |
| 4D.2.1 XRD | 188 |
| 4D.2.2 SEM and EDX Analysis | 189 |
| 4D.2.3 Surface Analysis | 191 |
| 4D.3 Fixed-Bed Pyrolytic Conversion and Products Distribution | 193 |
| 4D.3.1 Bio-oil Characterization | 194 |

| | |
|--|-----|
| 4D.4 TG and DTG Analysis | 200 |
| 4D.5 Evaluations of Kinetic and Thermodynamic Parameters | 202 |
| 4D.5.1 Kinetic Parameters | 202 |
| 4d.5.2 Master Plot Method | 207 |
| 4d.5.3 Thermodynamic Parameters | 210 |
| 4D.6 Summary | 212 |
| References | 213 |

Chapter 5: Summary and conclusions

| | |
|---------------------------|-----|
| 5.1 Summary | 217 |
| 5.2 Conclusion | 217 |
| 5.3 Potential Limitations | 220 |
| 5.4 Future Scope | 221 |

List of Publications

Conferences, seminars attended and poster presented

Appendices
