
**SINGLE AND CO-FEED PYROLYSIS OF ERYTHRINA INDICA AND
AZADIRACHTA INDICA: ANALYSIS OF PRODUCTS, KINETICS
AND THERMODYNAMICS**

A Thesis

*submitted in partial fulfilment of the
requirements for the degree*

of

DOCTOR OF PHILOSOPHY

by

Gaffer Ahmed

(Roll No.: 186107005)



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
ASSAM-781039, INDIA**

August 2024





Department of Chemical Engineering
Indian Institute of Technology Guwahati
Guwahati-781039
Assam, India

STATEMENT

I hereby declare that the content embodied in this thesis entitled “**Single and Co-Feed Pyrolysis of *Erythrina Indica* and *Azadirachta Indica*: Analysis of Products, Kinetics and Thermodynamics**” is the result of investigations and experiments carried out by me at Sustainable and Renewable Energy Laboratory (C1-146), Transit Complex and Non-Newtonian Flow Laboratory (210L), Department of Chemical Engineering of Indian Institute of Technology Guwahati, under the supervision of **Prof. Nanda Kishore**. In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

Guwahati

August, 2024

Gaffer Ahmed

186107005





Department of Chemical Engineering
Indian Institute of Technology Guwahati
Guwahati-781039
Assam, India

CERTIFICATE

This is to certify that the work contained in this thesis entitled “**Single and Co-Feed Pyrolysis of *Erythrina Indica* and *Azadirachta Indica*: Analysis of Products, Kinetics and Thermodynamics**” has been carried out by **Mr. Gaffer Ahmed (Roll. No 186107005)** under my supervision and I affirm that this work has not been previously submitted to meet requirements for a degree at this or any other higher education institution.

Guwahati
August, 2024

Prof. Nanda Kishore
Department of Chemical Engineering
Indian Institute of Technology Guwahati
Guwahati-781039
Assam, India



Abstract

Growing concerns over fossil fuel utilization and their impending scarcity have spurred a transition towards renewable energy sources. Among these, biomass has gained remarkable traction due to its widespread availability and adaptability. Pyrolysis, amid various biomass conversion routes, boasts advantages like moderate operating conditions, facile handling and efficient product distribution. Nonetheless, the commercialization of pyrolysis faces hurdles because of large fraction of non-fuel phase containing pyrolytic bio-oil; and thus, a key challenge involves extracting the fuel phase from raw bio-oil. While numerous studies focus on biomass pyrolysis, comprehensive examinations of fuel phase extraction and subsequent characterization remain limited. Therefore, this thesis work deals with the pyrolytic conversion of single and co-feeds of *Erythrina indica* (EI) and *Azadirachta indica* (AI) biomass followed by extraction of the fuel phases using dichloromethane and n-hexane. The average yield of bio-oil, biochar and non-condensable gases from EI biomass pyrolysis were found to be 26.873 wt.%, 42.870 wt.% and 30.257 wt.%, respectively, whereas for pyrolysis of AI biomass the corresponding values were found to be 27.286 wt.%, 41.053 wt.% and 31.662 wt.%, respectively. The fuel phase extraction from the raw bio-oil was carried out using dichloromethane and n-hexane at four vol.% (10, 20, 30 and 40%) of solvent relative to the volume of pyrolytic raw bio-oil and compared to those without using solvents. Among the two solvents, n-hexane emerged as the superior solvent for isolating fuel phases, exhibiting improved physiochemical properties in terms of density, viscosity and calorific value compared to those extracted without using any solvent and extracted using dichloromethane. Fuel phases extracted using 30 vol.% and 40 vol.% n-hexane depicted properties similar to conventional gasoline in terms of energy content (calorific value), density and pH. The pyrolysis products were also analysed by various analytical techniques including Fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance spectroscopy (^1H NMR), gas chromatography and mass spectroscopy (GC-MS), thermogravimetric analysis (TGA), powder X-ray diffraction (XRD) analysis, field emission scanning electron microscope (FESEM), energy dispersive X-ray (EDX) spectroscopy and gas chromatograph (GC). The average calorific values of biochar obtained from pyrolysis of EI and AI biomass were 28.030 MJ/kg and 28.500 MJ/kg, respectively. Similarly, the average calorific values of non-condensable gases produced from EI and AI biomass pyrolysis were 14.486 MJ/Nm³ and 14.882 MJ/Nm³,

respectively. EI and AI biochar exhibited physiochemical properties, flowability and combustion indices comparable to conventional coal. In the non-condensable gases obtained from EI and AI biomass pyrolysis, approximately 50-65% (by volume) of the gases were constituted by combustible gases including H₂, CO and CH₄. The non-condensable gases from EI biomass pyrolysis exhibited volumetric compositions of 16.822% H₂, 24.664% CO, 23.183% CH₄ and 35.329% CO₂, while those obtained from pyrolysis of AI biomass had volumetric compositions of 15.874% H₂, 26.656% CO, 23.849% CH₄ and 33.620% CO₂.

The co-feed pyrolysis of EI and AI biomass resulted in bio-oil yields ranging from 29.512 wt.% to 32.399 wt.%, while biochar and non-condensable gas yields varied between 38.249 wt.% to 42.480 wt.% and 26.901 wt.% to 30.730 wt.%, respectively. The fuel phase separated by 10 vol.% of n-hexane solvent, particularly at the co-feed ratio of 1:1, exhibited improved physicochemical and fuel properties, with a maximum calorific value of 36.798 MJ/kg which is the best achievement of this work. The corresponding volumetric composition of non-condensable gases included 7.452% H₂, 34.257% CO, 21.322% CH₄ and 36.969% CO₂, with a calorific value of 13.761 MJ/Nm³. The biochar obtained at the EI:AI-1:1 co-feed ratio also displayed the maximum calorific value of 29.233 MJ/kg. The co-feed pyrolysis of EI and AI biomass proved successful in improving both the yield and quality of pyrolysis oil and biochar, with optimal outcomes observed at the EI:AI-1:1 co-feed ratio especially in terms of calorific value. In order to establish techno-economic feasibility, an economic analysis for establishing a 10-ton batch-type pyrolysis plant for single-feed pyrolysis of EI and AI biomass, as well as their co-feed pyrolysis at 1:1 ratio was also conducted. The analysis revealed viable projects with positive net present values and returns exceeding the initial investment by the end of the project. For the single-feed pyrolysis of EI biomass, the payback period was found to be 3.90 years, whereas for pyrolysis of AI biomass, the payback period was found to be 6.46 years. For the co-feed ratio of 1:1, the payback period was determined to be 4.05 years.

The kinetics and thermodynamics of a given process are very vital in the design of the reactors. Thus, the kinetics and thermodynamics of single-feed and co-feed non-isothermal pyrolysis of EI and AI biomass were investigated at heating rates of 10, 20, 30 and 40°C/min. Five different iso-conversional methods, viz. the differential Friedman method (DFM), Kissinger-Akharria-Sunose (KAS), Ozawa-Flynn-Wall (OFW), Starink (STK) and distributed activation energy model (DAEM) were adopted for kinetics investigation. Average values of activation energy for EI and AI biomass pyrolysis ranged from 176.861 kJ/mol to 184.787 kJ/mol and 187.613 kJ/mol to 196.635 kJ/mol, respectively. The corresponding average values

of enthalpy change, Gibbs free energy change and entropy change for EI biomass varied from 171.781 kJ/mol to 179.890 kJ/mol, 168.191 kJ/mol to 170.083 kJ/mol and 0.003 kJ/mol·K to 0.019 kJ/mol·K, respectively. Meanwhile, for AI biomass, the corresponding values varied from 182.425 kJ/mol to 191.638 kJ/mol, 167.288 kJ/mol to 173.742 kJ/mol and 0.014 kJ/mol·K to 0.039 kJ/mol·K, respectively. Strong correlations ($R^2 > 0.98$) in kinetic plots indicated excellent agreement of the iso-conversional methods for both biomasses. Complex reaction mechanisms, as revealed by Criado's master plots and integral approach, were observed for both EI and AI biomass pyrolysis. Synergistic effect of co-feed pyrolysis was observed in the average activation energy required at various co-feed ratios. The co-feed ratio of EI:AI-1:1 displayed average values of activation energy and enthalpy change in the range of 169.643 kJ/mol to 179.808 kJ/mol and 164.421 kJ/mol to 174.819 kJ/mol, respectively. Finally, based on the properties (density, pH and calorific value) of pyrolytic products, economic analysis and potential applications, one may consider co-feed pyrolysis of EI and AI at a 1:1 ratio as a better choice.

Table of Contents

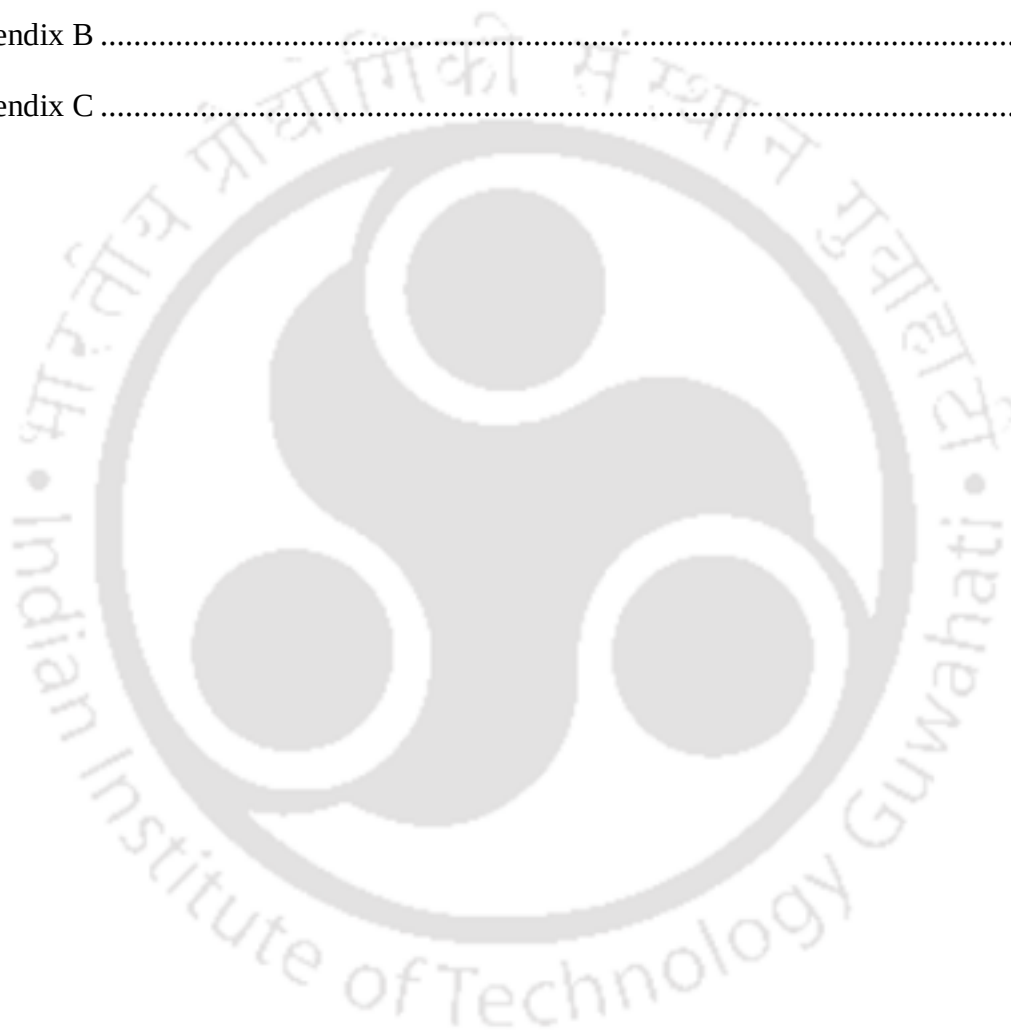
Abstract	i
Table of Contents	iv
List of Figures	ix
List of Tables	xvi
List of Abbreviations.....	xviii
Acknowledgements	xx
Chapter 1: Introduction	1
1.1 Background	1
1.2 Lignocellulosic Biomass -A renewable energy source	3
1.3 Biomass to energy conversion pathways	5
1.3.1 Physiochemical conversion.....	5
1.3.2 Biochemical conversion.....	6
1.3.2.1 Fermentation	6
1.3.2.2 Anaerobic digestion	6
1.3.3 Thermochemical conversion.....	7
1.3.3.1 Combustion.....	7
1.3.3.2 Pyrolysis	7
1.3.3.3 Hydrothermal carbonization	8
1.3.3.4 Gasification.....	8
1.3.3.5 Hydrothermal liquefaction	9
1.4 Pyrolysis: A prominent and efficient technology.....	9
1.5 Kinetics and thermodynamics of biomass pyrolysis	11
1.5.1 Experimental methods	12
1.5.2 Calculation methods	13
1.6 Organization of the thesis	13
Chapter 2: Literature Review	17
2.1 Challenges with bio-oil obtained from pyrolysis	17

2.1.1 Single-feed pyrolysis	18
2.1.2 Co-feed pyrolysis	20
2.2 Techniques for upgrading bio-oil	21
2.2.1 Fuel phase extraction	24
2.3 Kinetics and thermodynamics of biomass pyrolysis	25
2.3.1 Single-feed pyrolysis kinetics and thermodynamics	26
2.3.2 Co-feed pyrolysis kinetics and thermodynamics	27
2.4 Summary of this chapter	28
Chapter 3: Motivation and Objectives	31
3.1 Research gaps and motivation	31
3.2 Objectives	32
Chapter 4: Materials and Methods	33
4.1 Feedstock collection and characterization	33
4.1.1 Physiochemical characterization	34
4.1.2 Density and porosity analysis	36
4.1.3 Flowability indices	37
4.1.4 Combustion indices	39
4.1.5 Thermogravimetric and differential thermogravimetric analysis	40
4.1.6 X-ray diffraction analysis	41
4.1.7 Field emission scanning electron microscopy	42
4.2 Solvents	43
4.3 Experimental procedure of pyrolysis	43
4.4 Distribution of pyrolysis products	44
4.5 Solvent extraction of fuel phase of bio-oil	45
4.6 Pyrolysis product characterization	45
4.6.1 Characterization of bio-oil	45
4.6.1.1 Physiochemical properties and calorific value	45
4.6.1.2 Fourier transform infrared spectroscopy	45
4.6.1.3 Proton nuclear magnetic resonance spectroscopy	46
4.6.1.4 Gas chromatography and mass spectroscopy	47

4.6.2	Characterization of biochar	48
4.6.2.1	Energy-dispersive X-ray spectroscopy	48
4.6.3	Characterization of non-condensable gases	49
4.6.3.1	Gas chromatography	49
4.7	Economic analysis	50
4.7.1	Break-even analysis	53
4.7.2	Net present value	53
4.7.3	Internal rate of return	54
Chapter 5: Kinetics and Thermodynamics Study of Pyrolysis Process.....		55
5.1	Thermogravimetric and differential thermogravimetric analysis	55
5.2	Evaluation of kinetic triplets	55
5.2.1	Calculation of apparent activation energy (E_a) and pre-exponential factor (k_0)	57
5.2.1.1	Differential Friedman method	57
5.2.1.2	Kissinger-Akharria-Sunose method	57
5.2.1.3	Ozawa-Flynn-Wall method	58
5.2.1.4	Starink method	58
5.2.1.5	Distributed activation energy model	59
5.2.2	Reaction mechanism	59
5.2.2.1	Criado's master plot	60
5.2.2.2	Master plots based on the integral form of kinetic data	61
5.3	Thermodynamic Properties	61
Chapter 6: Results and Discussions		63
6.1	Feedstock characterization	63
6.2	Solvent characterization	65
6.3	Single-feed pyrolysis of <i>Erythrina indica</i> and <i>Azadirachta indica</i> biomass	66
6.3.1	Yield analysis of products	66
6.3.2	Fuel phase extraction of bio-oil	67
6.3.3	Pyrolysis product characterization	68
6.3.3.1	Characterization of bio-oil	68
6.3.3.2	Characterization of biochar	87
6.3.3.3	Characterization of non-condensable gases	95

6.4	Co-feed pyrolysis of <i>Erythrina indica</i> and <i>Azadirachta indica</i> biomass	96
6.4.1	Yield analysis of products.....	96
6.4.2	Pyrolysis product characterization	98
6.4.2.1	Characterization of bio-oil.....	98
6.4.2.2	Characterization of biochar	106
6.4.2.3	Characterization of non-condensable gases.....	121
6.5	Potential applications of the pyrolysis products.....	121
6.6	Economic analysis	122
6.6.1	Break-even analysis.....	126
6.6.2	Net present value	126
6.6.3	Internal rate of return.....	126
6.7	Kinetics and thermodynamics of single-feed pyrolysis of <i>Erythrina indica</i> and <i>Azadirachta indica</i> biomass	128
6.7.1	Thermogravimetric and differential thermogravimetric analysis	128
6.7.2	Evaluation of the kinetic triplets	129
6.7.2.1	Calculation of activation energy	130
6.7.2.2	Calculation of pre-exponential factor	131
6.7.2.3	Reaction mechanism	135
6.7.2.3.1	Criado's master plots method.....	135
6.7.2.3.2	Master plot based on integral form of kinetic data.....	137
6.7.3	Thermodynamic properties	140
6.8	Kinetics and thermodynamics of co-feed pyrolysis of <i>Erythrina indica</i> and <i>Azadirachta indica</i> biomass	150
6.8.1	Thermogravimetric and differential thermogravimetric analysis	150
6.8.2	Evaluation of the kinetic triplets	153
6.8.2.1	Calculation of activation energy	153
6.8.2.2	Calculation of pre-exponential factor	154
6.8.2.3	Reaction mechanism.....	164
6.8.2.3.1	Criado's master plots method	164
6.8.2.3.2	Master plots based on integral form of kinetic data..	169
6.8.3	Thermodynamic properties	174
6.9	Summary of this chapter	200

6.10 Limitations and challenges encountered during this research work.....	201
Chapter 7: Conclusions	203
Chapter 8: Future Scope of this Work	207
Research Output	209
Bibliography	211
Appendices	233
Appendix A	233
Appendix B	237
Appendix C	248



List of Figures

Figure 1.2.1 Representative structure of lignocellulosic biomass [28].	3
Figure 1.3.1 Biomass conversion pathways to value-added products [34].	5
Figure 1.5.1 Methods for studying solid-state kinetics of biomass pyrolysis.	12
Figure 2.1.1 Limitations and causes of negative characteristics of bio-oil obtained through pyrolysis [88].	18
Figure 2.2.1 Operating conditions, reaction, advantages and disadvantages of existing bio-oil upgrading techniques [97].	23
Figure 4.1.1 (a) <i>Erythrina indica</i> biomass and (b) <i>Azadirachta indica</i> biomass.	33
Figure 4.1.2 Schematic diagram of CHNS elemental analyser [125].	35
Figure 4.1.3 Schematic diagram of bomb calorimeter [127].	36
Figure 4.1.4 Schematic diagram for calculating angle of repose.	38
Figure 4.1.5 Schematic diagram of thermogravimetric analyser [134].	41
Figure 4.1.6 Schematic diagram of powder X-ray diffraction system [135].	42
Figure 4.1.7 Schematic diagram of field emission scanning electron microscope [137].	43
Figure 4.3.1 Schematic representation of the tubular reactor system used for pyrolysis reactions.	44
Figure 4.6.1 Schematic diagram of Fourier transform infrared spectrometer [141].	46
Figure 4.6.2 Schematic diagram of proton nuclear magnetic resonance spectrometer.	47
Figure 4.6.3 Schematic diagram of gas chromatography-mass spectrometer [142].	48
Figure 4.6.4 Working principle of energy-dispersive X-ray analysis [143].	49
Figure 4.6.5 Schematic diagram for gas chromatograph [147].	50
Figure 4.7.1 Schematic diagram of the scaled-up pyrolysis unit [151].	51
Figure 6.1.1 Thermogravimetric and differential thermogravimetric curves of (a) EI and (b) AI biomass.	65
Figure 6.2.1 Chemical structure of (a) dichloromethane and (b) n-hexane.	66

Figure 6.3.1 Fourier transform infrared spectra of fuel and non-fuel phases of bio-oil obtained from single-feed pyrolysis of EI biomass.....	75
Figure 6.3.2 Fourier transform infrared spectra of fuel and non-fuel phases of bio-oil obtained from single-feed pyrolysis of AI biomass.	76
Figure 6.3.3 Fourier transform infrared spectra of (i) dichloromethane (ii) n-hexane.....	78
Figure 6.3.4 Proton nuclear magnetic resonance spectra of fuel phase of bio-oil obtained from single-feed pyrolysis of EI biomass.	80
Figure 6.3.5 Proton nuclear magnetic resonance spectra of fuel phase of bio-oil obtained from single-feed pyrolysis of AI biomass.....	81
Figure 6.3.6 Thermogravimetric and differential thermogravimetric curves of (a) EI biochar and (b) AI biochar obtained from single-feed pyrolysis of EI and AI biomass.	89
Figure 6.3.7 Powder X-ray diffractogram of (a) EI biomass and biochar and (b) AI biomass and biochar obtained from single-feed pyrolysis of EI and AI biomass.	90
Figure 6.3.8 Field emission scanning electron microscopy images of (a) (i) EI biomass (ii) AI biomass and (b) (i) EI biochar (ii) AI biochar obtained from single-feed pyrolysis of EI and AI biomass.	91
Figure 6.3.9 Energy dispersive X-ray spectroscopic analysis of biochar obtained from single-feed pyrolysis of EI biomass.	93
Figure 6.3.10 Energy dispersive X-ray spectroscopic analysis of biochar obtained from single-feed pyrolysis of AI biomass.	94
Figure 6.4.1 Pyrolysis product distribution (in wt.%) of co-feed pyrolysis of EI and AI biomass.	97
Figure 6.4.2 Fuel and non-fuel phase distribution (in vol.%) of bio-oil produced through co-feed pyrolysis of EI and AI biomass.	98
Figure 6.4.3 Fourier transform infrared spectra of fuel phases obtained from co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (i) EI:AI-1:4, (ii) EI:AI-1:3, (iii) EI:AI-1:2, (iv) EI:AI-1:1 (v) EI:AI-2:1, (vi) EI:AI-3:1 and (vii) EI:AI-4:1.	100
Figure 6.4.4 ¹ H NMR spectra of fuel phases obtained from co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (i) EI:AI-1:4, (ii) EI:AI-1:3, (iii) EI:AI-1:2, (iv) EI:AI-1:1 (v) EI:AI-2:1, (vi) EI:AI-3:1 and (vii) EI:AI-4:1.	102

Figure 6.4.5 GC-MS spectra of fuel phases obtained from co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (i) EI:AI-1:4, (ii) EI:AI-1:3, (iii) EI:AI-1:2, (iv) EI:AI-1:1 (v) EI:AI-2:1, (vi) EI:AI-3:1 and (vii) EI:AI-4:1.	103
Figure 6.4.6 (a) Thermogravimetric and (b) differential thermogravimetric curves of biochar produced through co-feed pyrolysis of EI and AI biomass.	110
Figure 6.4.7 Powder X-ray diffractogram of biochar obtained from co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (i) EI:AI-1:4, (ii) EI:AI-1:3, (iii) EI:AI-1:2, (iv) EI:AI-1:1 (v) EI:AI-2:1, (vi) EI:AI-3:1 and (vii) EI:AI-4:1.	111
Figure 6.4.8 FESEM images of (i) EI and AI biomass and biochar produced through co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (ii) EI:AI-1:4, (iii) EI:AI-1:3, (iv) EI:AI-1:2, (v) EI:AI-1:1 (vi) EI:AI-2:1, (vii) EI:AI-3:1 and (viii) EI:AI-4:1.....	113
Figure 6.4.9 Energy dispersive X-ray spectroscopic analysis of biochar obtained from co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (a) EI:AI-1:4, (b) EI:AI-1:3, (c) EI:AI-1:2, (d) EI:AI-1:1 (e) EI:AI-2:1, (f) EI:AI-3:1 and (g) EI:AI-4:1.....	120
Figure 6.7.1 TGA curves for (a) EI and (b) AI biomass at four heating rates of 10, 20, 30 and 40°C/min.....	129
Figure 6.7.2 DTG curves for (a) EI and (b) AI biomass at four heating rates of 10, 20, 30 and 40°C/min.....	129
Figure 6.7.3 (a-e) Iso-conversional plots of EI biomass pyrolysis: (a) DFM, (b) KAS, (c) OFW, (d) STK, (e) DAEM and (f) apparent activation energy vs. conversion.	133
Figure 6.7.4 (a-e) Iso-conversional plots of AI biomass pyrolysis: (a) DFM, (b) KAS, (c) OFW, (d) STK, (e) DAEM and (f) apparent activation energy vs. conversion.	134
Figure 6.7.5 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI biomass using DFM results.	136
Figure 6.7.6 (a-d) Criado's master plots for reaction mechanism of pyrolysis of AI biomass using DFM results.	137
Figure 6.7.7 (a-d): Master plot based on integral method for reaction mechanism of pyrolysis of EI biomass using DFM results.....	138
Figure 6.7.8 (a-d): Master plots based on integral method for reaction mechanism of pyrolysis of AI biomass using DFM results.	139

Figure 6.7.9 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots for EI biomass pyrolysis.	141
Figure 6.7.10 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots for AI biomass pyrolysis.	142
Figure 6.7.11 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) plots for EI biomass pyrolysis.	144
Figure 6.7.12 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) plots for AI biomass pyrolysis.	145
Figure 6.7.13 (a-e) Change in entropy (ΔS) vs. conversion (α) plots for EI biomass pyrolysis.	147
Figure 6.7.14 (a-e) Change in entropy (ΔS) vs. conversion (α) plots for AI biomass pyrolysis.	148
Figure 6.8.1 Thermogravimetric analysis curves of EI and AI biomass at co-feed ratios of (a) 1:4, (b) 1:3, (c) 1:2, (d) 1:1, (e) 2:1, (f) 3:1 and (g) 4:1.	151
Figure 6.8.2 Differential thermogravimetric analysis curves of EI and AI biomass at co-feed ratios of (a) 1:4, (b) 1:3, (c) 1:2, (d) 1:1, (e) 2:1, (f) 3:1 and (g) 4:1.	152
Figure 6.8.3 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:4: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.	155
Figure 6.8.4 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:3: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.	156
Figure 6.8.5 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:2: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.	157
Figure 6.8.6 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:1: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.	158
Figure 6.8.7 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 2:1: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.	159
Figure 6.8.8 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 3:1: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.	160

Figure 6.8.9 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 4:1: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.....	161
Figure 6.8.10 (a-g) Apparent activation energy vs. conversion of co-feed pyrolysis of EI:AI at (a) 1:4, (b) 1:3, (c) 1:2, (d) 1:1, (e) 2:1, (f) 3:1 and (g) 4:1; and (h) average activation energy using different iso-conversional models at various co-feed ratios.....	162
Figure 6.8.11 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:4.....	165
Figure 6.8.12 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:3.....	166
Figure 6.8.13 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:2.....	166
Figure 6.8.14 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:1.....	167
Figure 6.8.15 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 2:1.....	168
Figure 6.8.16 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 3:1.....	168
Figure 6.8.17 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 4:1.....	169
Figure 6.8.18 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:4.	170
Figure 6.8.19 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:3.	171
Figure 6.8.20 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:2.	171
Figure 6.8.21 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:1.	172
Figure 6.8.22 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 2:1.	173

Figure 6.8.23 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 3:1.	173
Figure 6.8.24 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 4:1.	174
Figure 6.8.25 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 1:4.	176
Figure 6.8.26 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 1:3.	177
Figure 6.8.27 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 1:2.	178
Figure 6.8.28 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 1:1.	179
Figure 6.8.29 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 2:1.	180
Figure 6.8.30 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 3:1.	181
Figure 6.8.31 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 4:1.	182
Figure 6.8.32 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:4.	184
Figure 6.8.33 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:3.	185
Figure 6.8.34 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:2.	186
Figure 6.8.35 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:1.	187
Figure 6.8.36 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 2:1.	188

Figure 6.8.37 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 3:1.	189
Figure 6.8.38 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 4:1.	190
Figure 6.8.39 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:4.	191
Figure 6.8.40 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:3.	192
Figure 6.8.41 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:2.	193
Figure 6.8.42 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:1.	194
Figure 6.8.43 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 2:1.	195
Figure 6.8.44 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 3:1.	196
Figure 6.8.45 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 4:1.	197

List of Tables

Table 4.7.1 Bases for pyrolysis unit to study economic feasibility.....	51
Table 4.7.2 Sources for calculating the fixed and variable costs to operate the pyrolysis plant.	52
Table 5.2.1 Expressions of different reaction models for solid state reactions.	60
Table 6.1.1 Physiochemical properties, different types of densities, porosity, flowability and combustion indices of EI and AI biomass.	64
Table 6.2.1: Physiochemical properties of dichloromethane and n-hexane.	65
Table 6.3.1 Pyrolysis product distribution (wt.%) of single-feed pyrolysis of EI and AI biomass.	67
Table 6.3.2 Fuel and non-fuel phase distribution (vol.%) of bio-oil obtained from single-feed pyrolysis of EI and AI after separation using DCM and n-hexane and without using any solvent.	68
Table 6.3.3 Density, pH, dynamic viscosity, kinematic viscosity and calorific value of fuel and non-fuel phases of bio-oil obtained from single-feed pyrolysis of EI and AI biomass.	71
Table 6.3.4 Functional groups present in the fuel and non-fuel phases of bio-oil obtained from single-feed pyrolysis of EI and AI biomass.	77
Table 6.3.5 Probable compounds identified through gas chromatography-mass spectroscopy analysis of fuel phases of bio-oil obtained from single-feed pyrolysis of EI biomass using DCM, n-hexane and without any solvent.	83
Table 6.3.6 Probable compounds identified through gas chromatography-mass spectroscopy analysis of fuel phases of bio-oil obtained from single-feed pyrolysis of AI biomass using DCM, n-hexane and without any solvent.	85
Table 6.3.7 Physiochemical properties, different types of densities, porosity, flowability and combustion indices of biochar produced through single-feed pyrolysis of EI and AI biomass.	88
Table 6.3.8 FWHM and crystallite size of EI and AI biomass and biochar produced through single-feed pyrolysis of EI and AI biomass.	91

Table 6.4.1 Density, pH and calorific value of fuel and non-fuel phases of bio-oil obtained from co-feed pyrolysis of EI and AI biomass.....	99
Table 6.4.2 Functional groups present in the fuel phases of bio-oil obtained from co-feed pyrolysis of EI and AI biomass.....	101
Table 6.4.3 Probable chemical compounds identified through GC-MS analysis of fuel phases of bio-oil obtained from co-feed pyrolysis of EI and AI biomass.	104
Table 6.4.4 Physiochemical properties, different types of densities, porosity, flowability and combustion indices of biochar produced through co-feed pyrolysis of EI and AI biomass. .	108
Table 6.4.5 FWHM and crystallite size of biochar produced through co-feed pyrolysis of EI and AI biomass.	112
Table 6.6.1 Initial cost of setting up the pyrolysis plant.....	122
Table 6.6.2 Cost analysis of biomass pyrolysis unit having capacity of 10 tons per day.	123
Table 6.6.3 Yield of pyrolysis products per annum.	123
Table 6.6.4 Revenue generated from the pyrolysis plant per annum.	125
Table 6.7.1 Average activation energy (kJ/mol), pre-exponential factor (min^{-1}) and R^2 for EI and AI biomass pyrolysis.	135
Table 6.7.2 Average values of enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI and AI biomass pyrolysis.	149
Table 6.8.1 Average values of activation energy (kJ/mol), pre-exponential factor (min^{-1}) and R^2 for EI and AI biomass pyrolysis at various co-feed ratios.	163
Table 6.8.2 Average values of enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI and AI biomass pyrolysis at various co-feed ratios. .	198

List of Abbreviations

EI	<i>Erythrina indica</i>
AI	<i>Azadirachta indica</i>
TGA	<i>Thermogravimetric analysis</i>
ΔH	<i>Enthalpy change</i>
ΔG	<i>Gibbs free energy change</i>
ΔS	<i>Entropy change</i>
DFM	<i>Differential friedman method</i>
KAS	<i>Kissinger Akharia Sunose</i>
OFW	<i>Ozawa Flynn Wall</i>
STK	<i>Starink</i>
DAEM	<i>Distributed activation energy model</i>
DCM	<i>Dichloromethane</i>
MC	<i>Moisture content</i>
AC	<i>Ash content</i>
VM	<i>Volatile matter content</i>
FC	<i>Fixed carbon</i>
CV	<i>Calorific value</i>
TCD	<i>Thermal conductivity detector</i>
CHNS	<i>Carbon Hydrogen Nitrogen Sulphur</i>
H/C	<i>Hydrogen to carbon ratio</i>
O/C	<i>Oxygen to carbon</i>
ρ_b	<i>Bulk density</i>
ρ_{tb}	<i>Tapped density</i>
ρ_p	<i>Particle density</i>
ε_0	<i>Porosity</i>
θ	<i>Angle of repose</i>
HR	<i>Hausner ratio</i>
CCI	<i>Carr compressibility index</i>
FR	<i>Fuel ratio</i>
CI	<i>Combustibility index</i>
VI	<i>Volatile ignitability</i>
XRD	<i>X-ray diffractogram</i>
FESEM	<i>Field emission scanning electron microscopy</i>
FTIR	<i>Fourier transform infrared</i>
^1H NMR	<i>Proton nuclear magnetic resonance</i>
GC-MS	<i>Gas chromatography and mass spectroscopy</i>

EDX	<i>Energy dispersive X-ray</i>
E_{α}	<i>Apparent activation energy</i>
k_o	<i>Pre-exponential factor</i>
Z_{α}	<i>Reaction mechanism</i>
α	<i>Conversion</i>
β	<i>Heating rate</i>
T_{α}	<i>Temperature at certain conversion</i>
$f(\alpha)$	<i>Differential form of rate law</i>
$g(\alpha)$	<i>Integral form of rate law</i>
$p(x)$	<i>Exponential integral</i>
T_m	<i>Peak decomposition temperature</i>



Acknowledgements

At the culmination of this academic endeavour, I am filled with gratitude for the multitude of individuals who have played pivotal roles in the realization of this thesis. This journey has been one of growth, challenges and triumphs, and I extend my heartfelt thanks to those whose unwavering support and contributions have made it possible.

*First and foremost, I express my deepest appreciation to **my family**—specifically, **my parents and sister**—whose enduring love, encouragement and sacrifices have been the bedrock of my academic pursuits. Their unwavering belief in my abilities has been a guiding light and I am profoundly grateful for their constant support.*

*I am indebted to **Prof. Nanda Kishore**, my esteemed supervisor, for his invaluable guidance, unwavering support and scholarly insights that have played a pivotal role in shaping the course of my doctoral research. His commitment to excellence and patient guidance has been a source of inspiration, and I am truly fortunate to have the opportunity to work under his supervision.*

*I extend my sincere thanks to the members of the doctoral committee, **Prof. Ramagopal V.S. Uppaluri**, **Prof. Prabu Vairakannu**, Department of Chemical Engineering and **Prof. Selvaraju Narayanasamy**, Department of Biosciences and Bioengineering for their time, expertise and constructive feedback through the course of my doctoral research. Their rigorous evaluation and insightful suggestions have significantly elevated the quality of this work.*

*To the replacement committee, **Prof. Prasanna Venkatesh Rajaraman** and **Prof. Subrata Kumar Majumder**, Department of Chemical Engineering, I deeply appreciate your willingness to step in and contribute your expertise during critical junctures. Your commitment to upholding the academic rigor of the evaluation process has not gone unnoticed.*

*I would like to extend my sincere gratitude to **Dr. Thallada Bhaskar** (Chief Scientist), Thermo-catalytic Processes Area, CSIR-IIP, Dehradun and **Prof. Lasse Rosendahl**, Department of Energy, Aalborg University, Denmark, my thesis examiners, for their invaluable suggestions and constructive criticism. Their expert feedback has been instrumental in refining and improving the quality of this thesis, making it a valuable contribution to the field of waste management and biofuel production.*

I also thank **Prof. Prasanna Venkatesh Rajaraman**, Department of Chemical Engineering and **Prof. Debasish Das**, Department of Biosciences and Bioengineering for their involvement in my PhD viva examination, providing valuable insights and encouragement during the final stages of my doctoral journey.

Special thanks to **Prof. Kannan Pakshirajan** for providing access to the GC facility available in his lab.

My heartfelt thanks also go to my **friends, lab-mates** (especially **Sneha, Praveen and Ashish**) and other **well-wishers** for their camaraderie, support and shared moments of both triumph and challenge. Your friendship has been a source of inspiration, making the academic journey not only intellectually enriching but also enjoyable.

I extend my appreciation to the **staffs** of the **Guwahati Biotech Park** and **Central Instrument Facility, Centre for Environment** and **Department of Chemical Engineering** at **Indian Institute of Technology Guwahati** for their administrative support and the conducive research environment they have cultivated.

In conclusion, this thesis stands as a collective effort, and each person mentioned has played an integral role in its fruition. I am profoundly thankful for the support, encouragement and positive impact that each of you has had on my academic and personal growth.

Gaffer Ahmed



Chapter 1: Introduction

1.1 BACKGROUND

Energy is one of the most significant basic needs in our day-to-day life. Over the past two decades, the global energy landscape has witnessed remarkable transformations. These changes are marked by a growing demand for energy resources driven by population growth and industrialization to fuel the ever-expanding human activities [1]. This surge in energy requirements has largely been satisfied by fossil fuels, such as coal, oil and natural gas [2–4]. The preference for these fuels is due to their high rate of production, low production cost, easy handling, high calorific value and most importantly they are easily accessible and can be used directly in the existing fuel combustion technologies. Approximately 80% of the total global energy requirement in 2020 has been satisfied by fossil fuels [5]. These conventional sources have been the backbone of energy production and have propelled economic growth and development on a massive scale.

In an era defined by burgeoning energy demands and environmental concerns, the global community finds itself at a crossroads, grappling with the imminent consequences on environment of over-reliance on fossil fuels. The relentless extraction and consumption of these finite resources have given rise to a prevailing energy crisis characterized by hike in its prices, skyrocketing greenhouse gas emissions and the looming spectre of climate change [6–8]. The usage of fossil fuels also has a number of detrimental repercussions on the ecosystem, including acid rain, ozone loss, global warming, smog creation, etc. [6,9]. Conferring to reports made by Intergovernmental Planet on Climate Change (IPCC), fossil fuel emissions were found to be the prime culprit for global warming. Nearly 90% of the worldwide CO₂ emissions for the year 2018 is attributed to fossil fuels and industry [10]. Thus, the need of the hour is to shift towards a renewable and sustainable source which can replace the conventional fossil fuels.

A shift towards renewable energy will not only minimize the detrimental repercussions caused by fossil fuels but will also help in sustainable economic growth of the nation by creating job opportunities for the youths. Thus, to reduce emissions across all sectors by 50% by 2030, the IPCC plans to use less fossil fuels, promote electrification, improve energy efficiency and switch to alternative renewable sources [10]. Consequently, worldwide governments, businesses and individuals are increasingly adopting renewables to fulfill their

energy requirements [11]. Over the past few years, extensive research has also been conducted globally with the aim of developing technologies that not only produce clean energy from eco-friendly and sustainable sources but also ensure their sustainability in the near future [12,13]. As per the reports made by the International Energy Agency (IEA) and British Petroleum (BP) statistics, the demand for renewables increased by 3% in 2020 while a decline of 8.8% in oil, 4% in coal and 1.9% in natural gas was observed [14]. The transition to renewable energy is also motivated by other factors like rising fossil fuel costs, energy security and independence [15]. By the end of 2022, the objective for generating renewable power in India alone was 175 GW, which comprises of 100 GW coming from solar in addition to 60 GW from wind, 10 GW from biomass and 5 GW from small hydropower. As of 2021, India has successfully installed 40.08 GW of wind power along with 49.34 GW of solar power, 10.61 GW of biopower and 4.83 GW of small hydropower [16].

Renewable energy comes from a variety of sources, including solar, biomass, wind, tidal, hydro and geothermal [11]. However, biomass has prevailed in these contests during the past few years due to its accessibility and recent thorough investigation [17,18]. The utilization of biomass waste as an energy source is marked by several compelling advantages. It is one of those renewable resource that is abundantly available [19], can be sustainably produced, reduces carbon dioxide emissions when employed in place of fossil fuels and addresses waste management concerns by utilizing organic materials that might otherwise be discarded. Further, its versatility allows it to be converted into fuels of all phases-liquid, solid and gaseous through various biomass conversion pathways [20,21]. It can also be directly converted to heat energy through combustion. However, there are certain limitations of using it directly, such as low calorific value, bulk in size, presence of moisture and low combustion efficiency. In addition to these, there are high losses owing to moisture from hydrogen combustion, losses due to convection and radiation and exhaust of dry flue gas, and also it cannot be used directly to run engines in its raw state. Hence, it is very much necessary to convert the biomass into high-end usable products such as biofuels (bio-oil, biochar, charcoal, ethanol, hydrogen, etc.) and by-products (industrially relevant chemicals).

Biomass waste comes from a variety of sources including virgin wood, energy crops, agricultural residues, arboricultural residues, food waste, industrial waste and co-products and many more. India being an agrarian country and more than 20% of the area covered with forest it is obvious that a huge amount of biomass waste will be generated. It is estimated that India has the potential to generate approximately 460 million tonnes of agricultural waste every year

[22]. Utilization of these biomass waste to high-end valuable products can serve as a good source of green energy. Thus, the importance and advantage of biomass energy cannot be overstated, as they hold the capacity to significantly address the growing global energy crisis while also promoting sustainable development.

1.2 LIGNOCELLULOSIC BIOMASS -A RENEWABLE ENERGY SOURCE

Derived from plants, lignocellulosic biomass is an abundant carbon neutral renewable energy source composed of polysaccharides (cellulose and hemicellulose) and an aromatic polymer (lignin) holds immense promise as a substitute for fossil fuels, enabling the production of biofuels and biochemicals without posing a threat to global food security [23]. Common sources of lignocellulosic biomass include agricultural residues, energy crops, forest residues, grass, etc. [24]. The arrangement of these biopolymers in lignocellulosic biomass forms non-uniform three-dimensional structures at different degrees as illustrated in Figure 1.2.1. Cellulose, the primary carbohydrate in the lignocellulosic cell wall, creates long and oriented microfibrils that can further assemble into longer and larger fibrils [25]. Hemicelluloses, on the other hand, are amorphous, branched and single-chain heterogeneous polysaccharides that link to adjacent cellulose fibrils through non-covalent cross-links [26]. In contrast, lignin, a complex crosslinked macromolecule, plays a crucial role in binding the lignocellulose matrix and reinforcing cell walls [27].

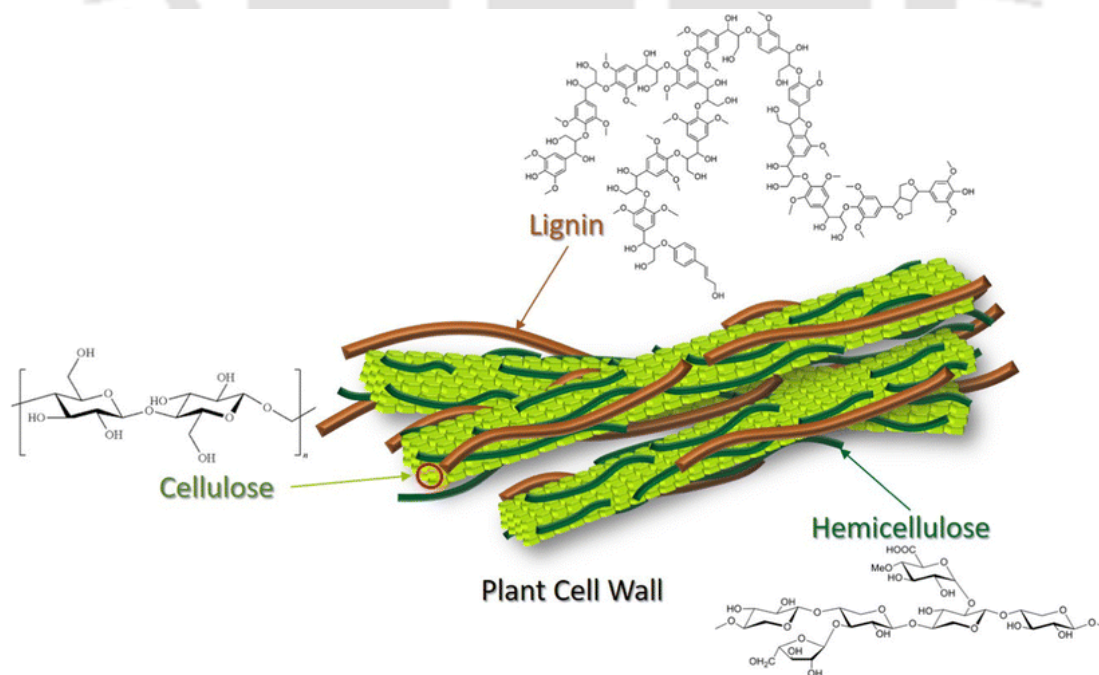


Figure 1.2.1 Representative structure of lignocellulosic biomass [28].

In this study, *Erythrina indica* (EI) and *Azadirachta indica* (AI) commonly referred to as Modar and Mahaneem in India, respectively, has been employed as feedstocks to produce biofuels. EI is a medium-sized, spiny deciduous tree native to India and South Asia, commonly found in the low altitude regions. The tree is also cultivated in specific areas of Malaysia, Myanmar and Thailand. EI is a multipurpose tree used for ornamental purposes and fencing due to its thorny bark. The leaves are used in cooking, while the bark has medicinal applications, including neuromuscular blocking and smooth muscle relaxation [29,30]. Despite being a softwood, EI timber is also used to make small curved articles. The tree also serves as shady tree in coffee plantations and contributes to the natural enrichment of soil nitrogen content. In contrast, AI is a fast-growing evergreen tree belonging to Meliaceae family of mahogany trees. AI is cultivated in over 30 countries worldwide, including Central and South America, Africa and Asia, with a few small-scale plantations in Europe and the USA [31]. Similar to EI, AI also has multipurpose utility. Young twigs, blossoms, fruits and leaves are commonly consumed as vegetables. Extractives of these trees are used to protect grains from insects. Medicinal practitioners from Siddha and Ayurveda believe that AI compounds possess sedative, contraceptive, antiviral, antifungal, antibiotic and antibacterial properties [32]. Bark, leaves and fruits have also been used to treat rheumatism, leprosy, syphilis and skin issues. Wood from AI trees are often used to make doors, knobs, furniture, etc. Despite having multipurpose utility their application does not confine to one user. A small portion of the tree becomes useful for one user while the remaining portion is treated as waste. Thus, there is a high chance that a huge amount of waste will also be generated from these trees. Proper collection of these waste can make both these feedstocks a sustainable source. Moreover, this study utilizes the branches as the feedstock which does not have any potential use. However, specific data on the availability of the waste generated from these trees is not available. According to reports made by National Research Centre for Agroforestry, India is home to more than 18 million *Azadirachta indica* trees [33]. Similar, is the growth of *Erythrina indica* tree. Thus, the proper collection of waste generated from the two trees may be considered as a potential feedstock for producing biofuels on industrial scale. Despite their potential to generate significant amounts of waste, neither EI nor AI has been considered as feedstocks for producing biofuels. Thus, the idea behind this study is to explore the bioenergy potential of these two feedstocks and bridge the existing knowledge gap surrounding their utilization for biofuel production.

1.3 BIOMASS TO ENERGY CONVERSION PATHWAYS

The utilization of biomass for the production of green energy focuses on the transformation of biomass waste to useful energy products such as: transportation fuels, direct combustion to generate heat or co-firing with other fossil fuels for power generation. Given its versatile nature, biomass can undergo diverse energy transformations through various energy conversion pathways. The resulting energy form is contingent on factors such as feedstock type, availability, intended energy form, end use and prevailing environmental and economic conditions. Broadly classifying biomass to energy conversion pathways can be divided into three categories—physiochemical, biochemical and thermochemical conversion [34]. Figure 1.3.1 provides an overview of the various biomass conversion pathways employed to transform biomass into different types of value-added products.

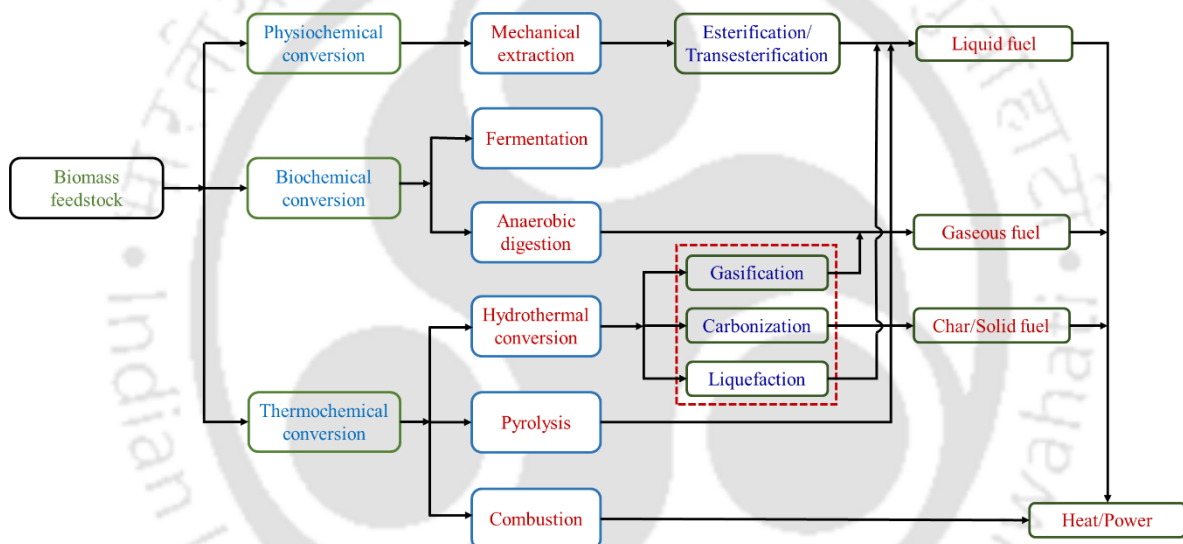


Figure 1.3.1 Biomass conversion pathways to value-added products [34].

1.3.1 Physiochemical conversion

The physiochemical conversion, also known as mechanical extraction, is a process utilized to extract oil from various biomass sources like oilseeds, vegetables and flowers [35]. The extracted oils, characterized by high viscosity contains free fatty acids which makes them unsuitable for direct use in diesel engines. To make these oils suitable for use in diesel engines, the extracted oil undergoes a transesterification reaction in the presence of a catalyst, resulting in the formation of fatty acid methyl ester, commonly referred to as biodiesel. The transesterification reaction involves mixing of alcohols, catalyst and purification of methyl ester [36]. This process also generates a solid residue as a by-product which is commonly used

as animal fodder [37]. The biodiesel produced is as a transportation fuel and is often blended with petroleum-derived diesel.

1.3.2 Biochemical conversion

Biochemical conversion pathway involves breakdown of biomass by microorganisms such as bacteria and yeast into valuable bio-based products such as bioethanol and biomethane along with other high-value biochemicals [34]. In this process microorganisms break down complex organic compounds within the biomass into simpler products through various biochemical processes. Fermentation and anaerobic digestion are two main biochemical conversion techniques.

1.3.2.1 Fermentation

Fermentation is a two-step anaerobic biochemical conversion technique which employs microorganisms such as yeast to convert starch and sugars to alcohol and carbon dioxide through enzymatic hydrolysis followed by fermentation. Subsequently, ethanol separation from other components is achieved by distillation process. Optimum temperatures for fermentation and hydrolysis are 30 and 50 °C, respectively, maintaining a pH range of 4.5–6.0. Commonly used microorganisms for enzymatic saccharification include *Saccharomyces cerevisiae*, *Trichoderma reesei*, *Candida brassica* and *Clostridium*. Sugarcane, corn, sweet potatoes, wheat, barley, oat and rice are the most common feedstocks used for fermentation [34]. Bioethanol produced through fermentation is most commonly used as a blend with commercial gasoline. The solid residue obtained as a by-product after fermentation can be used as cattle-feed or used as a fuel in boilers or used for subsequent gasification [37].

1.3.2.2 Anaerobic digestion

Anaerobic digestion is another biological process that uses bacteria and other microorganisms to convert organic matter into biogas and nitrogen rich liquid digestate in the absence of oxygen. The degradation process involves four important steps which includes hydrolysis, acidogenesis, acetogenesis and methanogenesis, which are primarily dependent on the type of bacteria employed [34]. The biogas produced is a mixture of methane, carbon dioxide and traces of hydrogen sulphide which vary depending on the feedstock. Organic non-lignocellulosic waste or energy crops grown for feeding in anaerobic digestion plants are the common feedstocks used in anaerobic digestion process [35]. Biogas produced from anaerobic

digestion can be used to produce electricity or fed to gas grid. The liquid digestate obtained as a by-product contains essential plant nutrients useful for plant growth.

1.3.3 Thermochemical conversion

Thermochemical conversion involves breakdown of biomass into energy products under application of heat and/or pressure. Depending on working circumstances and environment, thermochemical conversion can be further classified into combustion, pyrolysis and hydrothermal processes [38–41]. Thermochemical conversion offers a wide array of feedstocks including feedstocks with high moisture content. The conversion of such feedstock can be achieved under temperatures of 180–360°C and pressures 4–22 MPa [42]. Hydrothermal conversion can be further classified into gasification, carbonization and liquefaction.

1.3.3.1 Combustion

Biomass combustion is the simplest thermochemical conversion technique. Combustion refers to direct burning of biomass in the presence of excess oxygen to generate energy in the form of heat [43]. Combustion yields heat, power or combination of heat and power as its primary products. Biomass combustion involves four stages drying, pyrolysis, volatile combustion and char combustion. Biomass combustion process generates gaseous products at 800–1000°C that can directly be used to produce electricity [34]. Woody biomass and agricultural crop residues are the most common feedstocks used for combustion.

1.3.3.2 Pyrolysis

Pyrolysis is a thermochemical conversion technique which works on the principle of disintegration of complex organic compounds of biomass to lighter hydrocarbons under inert conditions at moderate temperatures and atmospheric pressure. Hemicellulose, cellulose and lignin are the three biopolymers that are involved in the breakdown of biomass during pyrolysis. Hemicellulose and cellulose begin to break down between 180–200°C and 240–350°C, respectively, whereas lignin begins to break down at temperatures beyond 400°C [11]. Feedstock, reactor type, heating rate, residence time, catalysts, additives and pressure greatly affect the pyrolysis process and the products. Liquid bio-oil (condensable vapours), non-condensable py-gas and solid biochar are the three main products obtained from biomass pyrolysis [44–46]. The liquid product, or bio-oil, can be further divided into two phases: fuel phase, which is the desired fuel product and the non-fuel phase, which is primarily constituted of water with traces of non-combustible hydrocarbons. The liquid product is currently a focal

point of interest due to its ability to be stored, transported and utilized for various purposes, including energy, transportation fuels, chemicals or as an energy carrier. The by-products, biochar, serves as a dependable solid fuel and it also finds applications in areas such as bio-fertilizer and wastewater treatment, whereas the py-gas can be utilized as a source for synthesis gas or green hydrogen for heating requirements of any chemical plant.

1.3.3.3 Hydrothermal carbonization

Hydrothermal carbonization is a thermochemical conversion technique employed to process biomass in the presence of water, typically at temperatures ranging between 180-250°C and pressure 20-40 bar, with a residence time ranging from 5 to 240 minutes, resulting in the production of hydrochar with characteristics similar to that of low rank coal [47]. Both wet and dry biomass can serve as feedstocks for hydrothermal carbonization. The process involves three main steps: dehydration, polymerization and carbonization, resulting in formation of spherical particles which can have a calorific value ranging from 20-29 MJ/kg [34]. Factors such as moisture content, biomass particle size, heating rate, operating temperature, precursor concentration and reaction time significantly impact the carbonization process.

1.3.3.4 Gasification

Gasification is another thermochemical conversion process that transforms biomass into useful energy in the form of combustible gases, consisting of CO, H₂, CH₄ and CO₂, with calorific values ranging from 0.4-10 MJ/m³ with tar and ash as by-products. The gasification process involves vaporization, devolatilization, pyrolysis, cracking of tars, reduction and reaction steps occurring at temperatures between 700-1200°C, utilizing air, oxygen, steam and other gasifying agents. Factors influencing the gasification process include the type of biomass feedstock, moisture content, particle size, temperature and steam-to-biomass ratio. Various reactor configurations, such as fixed-bed (updraft and downdraft), fluidized-bed, entrained flow, spouted-bed, rotary kiln, plasma and dual fluidized-bed (bubbling and fluidized-bed) reactors, are commonly used [34]. Wood and coal are widely used as feedstocks to produce gaseous fuels. These gaseous fuels produced through gasification show potential for various applications, including combustion in boilers, electricity generation through reciprocating engines or gas turbines, conversion into liquid biofuels, or as a synthetic natural gas (SNG) for injection into gas grids [35].

1.3.3.5 Hydrothermal liquefaction

Hydrothermal liquefaction is a thermochemical conversion process which works similar to hydrothermal carbonization process. However, the hydrothermal liquefaction works at higher temperatures and pressures of 250-375°C and pressures up to 180 bar and produces a liquid biocrude [48]. The biocrude can be upgraded to a wide range of petroleum derived products by catalytic hydro-treatment [49]. The hydrothermal liquefaction process demands high temperature to separate maximum moisture content and reduce the oxygenates. At normal temperature and pressure conditions, fats and strong peptide chains of amino acids are highly insoluble in solvents, thus demanding for higher temperature and pressure scenarios. At higher temperatures, the lipid content gradually turns into biocrude.

1.4 PYROLYSIS: A PROMINENT AND EFFICIENT TECHNOLOGY

Amongst various biomass conversion pathways pyrolysis has achieved considerable attention in recent years and has been extensively used to produce biofuels and valuable chemicals due to its unique set of benefits [50]. Notably, the pyrolysis process is inexpensive and works at moderate conditions as compared to other thermochemical conversion processes like gasification and liquefaction, while it also has the advantage of consuming substantially less time as compared to biochemical conversion processes like anaerobic digestion [51]. Furthermore, pyrolysis produces a range of valuable products, such as oil, char and non-condensable gases which strongly depend on the reaction conditions [11,44–46]. These products can be utilized in a wide range of industrial applications as a fuel or feedstock to produce valuable chemicals. Bio-oil produced through pyrolysis can be upgraded to transportation fuels and other value-added chemicals while the char and gaseous products can be used to provide energy to the pyrolysis reaction or produce heat or generate power [52]. The technology of pyrolysis has reached a level of maturity with established processes and commercial applications for e.g., Shirke Energy, Pune, India (feedstock: agricultural residue), Charm Industrial, USA (feedstock: waste biomass), Standard Biocarbon, USA (feedstock: organic residues), ArSta Eco Pvt. Ltd. in Tumkur, India (feedstock: multiple feedstocks). Techno-economic analysis of biofuels produced through pyrolysis also revealed economic advantages over other conversion pathways [53–55]. This provides a reliable and scalable pathway for biofuel production, with ongoing advancements improving its efficiency and cost-effectiveness. Another significant advantage of pyrolysis is that the technique can be used for continuous production of biofuels. The pyrolysis process also has flexibility in terms of reactor

design to handle different types of feedstocks like agricultural residues, forestry waste, household waste, municipal waste and other energy crops [44,56–58]. However, the physiochemical properties, especially the moisture content of a feedstock greatly affects the pyrolysis process as it demands more energy for converting the biomass and also have negative effects on the physiochemical properties of the bio-oil [59,60]. Thus, it is recommended to have a low moisture content feedstock for carrying out pyrolysis. Proximate analysis results indicated *Erythrina indica* and *Azadirachta indica* biomass to have low moisture contents of 11.226 and 14.179 wt.% on wet basis which makes them preferable feedstock for producing biofuels through pyrolysis.

Despite having significant advantages, pyrolysis is not without its challenges. Negative aspects, including a tendency to produce unstable bio-oil, limited product yield, low calorific value, high density and the need for higher reaction temperatures are a few of present hurdles to its widespread implementation [61]. Nevertheless, these shortcomings can be addressed to some extent through co-pyrolysis or introducing a catalyst, or combining both [62]. The co-pyrolysis approach combines two or more feedstocks to improve the quality and yield of the biofuels. The co-pyrolysis of biomass alongside other hydrogen rich waste materials presents a distinct advantage as it facilitates hydrogen transfer within a single reactor, eliminating the need for supplementary units. The presence of multiple feedstock can lead to synergistic effects promoting more efficient decomposition and release of volatiles including hydrogen which could promote hydrodeoxygenation reactions resulting in better bio-oil yield. Combining various feedstocks in the pyrolysis process has been observed to yield beneficial synergistic effects, enhancing the quality of the resulting oil while concurrently delivering a secure and efficient method for waste treatment. In contrast, in the case of catalytic pyrolysis, a catalyst is used which promotes specific desired reactions, including cracking, hydrodeoxygenation and aromatization. Employing sophisticated synthesis techniques allows for the manipulation and improvement of shape selectivity, thereby influencing the course of the reaction and promoting the generation of the desired compounds [63]. However, the cost of producing biofuels increases due to the cost of catalysts involved in the process and in addition, produces large fraction of non-fuel liquid as a detrimental effect. Thus, the process of co-pyrolysis is found to be advantageous as compared to catalytic pyrolysis as it is simple but without any additional financial burden. Co-pyrolysis offers advantages in terms of product diversification, feedstock versatility and enhanced overall process efficiency. Both EI and AI possesses a high volatile matter contents of 79.734 wt.% and 82.727 wt.%, respectively on dry basis. Further, EI and AI

biomass possesses a high H/C ratio of 1.824 and 1.888, respectively indicating a high amount of liquid and gaseous products are expected upon pyrolysis. However, the O/C ratio of 0.780 for EI biomass is slightly higher than AI biomass which has an O/C ratio of 0.525. The lower oxygen content of AI biomass suggests that it is a superior feedstock compared to EI biomass. Co-feeding AI biomass with EI may aid in producing biofuels with improved physiochemical properties. Similar studies reported by Chen et al. [64], Kawale and Kishore [65], Hua and Li [66] and Chang et al. [67] indicated significant synergistic effects in the pyrolysis products which were discussed in Chapter 2 of this thesis. Thus, the co-feed pyrolysis of EI and AI has also been considered in this study.

1.5 KINETICS AND THERMODYNAMICS OF BIOMASS PYROLYSIS

The process of biomass waste pyrolysis is extremely complex, involving multiple reactions within a short time frame [41]. The presence of cellulose, hemicellulose and lignin in biomass adds to the complexity, as their pyrolysis is not a homogeneous reaction. A comprehensive understanding of the reaction kinetics in biomass pyrolysis is essential for various reasons. Most importantly, it provides insights into the fundamental mechanisms governing this vital renewable energy conversion process. This information is essential for optimizing pyrolytic processes, improving energy efficacy, and reducing waste, all of which are pivotal for transitioning to sustainable energy sources. Moreover, a profound understanding of reaction kinetics contributes to the design of efficient reactors and process control strategies, influencing the scalability and economic viability of biomass pyrolysis technologies. Therefore, a detailed investigation into the reaction kinetics of the biomass pyrolysis process is essential for effectively designing pyrolysis processes and reactors for industrial applications, especially for biofuel and biochar production [68].

Thermogravimetric analysis (TGA), a certified thermal analysis technique, is commonly employed by various researchers to explore the kinetics and thermodynamics of biomass pyrolysis [69–72].

The foundation of chemical kinetics originated from empirical studies primarily focussed on homogeneous reactions in the gas phase. These principles, later found application in solution phase processes, which eventually extended to solid-state reactions. The development of chemical kinetic concepts for solid-state did not occur separately; instead, their application in solid-state was justified based on the similarities with certain homogeneous reactions. For instance, the Arrhenius equation was initially derived empirically which later

gained theoretical justification in gases through collision theory and in solutions through transition-state theory. A similar rationale was applied to justify the use of this equation in solid-state kinetics [73]. Therefore, the principles of solid-state kinetics evolved from homogeneous kinetic principles. However, their applications differ due to the distinct nature of solids, solutions and gases. There are numerous methods to study solid-state kinetics [74]. However, these methods can be broadly classified into two categories—experimental and calculation methods as illustrated in Figure 1.5.1.

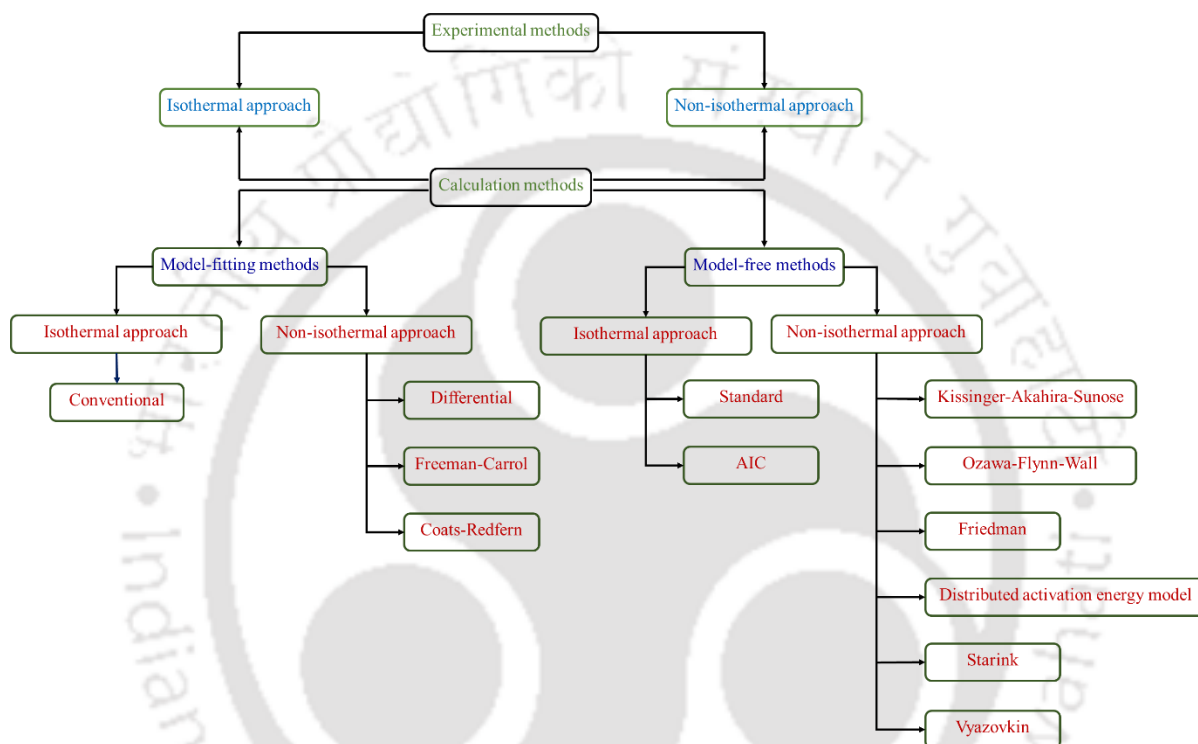


Figure 1.5.1 Methods for studying solid-state kinetics of biomass pyrolysis.

1.5.1 Experimental methods

Thermogravimetric analysis (TGA) is commonly used to obtain solid-state kinetic data for biomass pyrolysis [69–72]. TGA provides valuable insights into the thermal decomposition behavior of biomass under varied operating conditions, facilitating to analyze the kinetic parameters and its associated thermodynamic properties [75–78]. TGA data can be obtained through isothermal and non-isothermal approaches [79–81]. In isothermal approach, a sample undergoes changes at a controlled temperature, with real-time monitoring of its weight loss concerning with time. Conversely, in non-isothermal approach, the sample is subjected to a controlled variable temperature environment. However, the non-isothermal approach is favored over the isothermal approach due to its shorter duration and avoids drawbacks like mass loss during heating and non-zero degree of transformation during heating [80,82].

1.5.2 Calculation methods

The solid-state kinetic data obtained from isothermal or non-isothermal study can be analysed using model-fitting and model-free methods. Model-fitting methods strive to identify the model offering the best statistical fit for computing kinetic parameters, encompassing apparent activation energy and pre-exponential factor. In contrast, the model-free method calculates the apparent activation energy by incorporating various components, including the model and pre-exponential factor, into the linear equation's intercept, with the gradient used to compute the apparent activation energy. Model-free approaches have become more popular in recent times due to their reliability, efficiency and accuracy [41,83]. The shift is driven by the fact that the model-free approach does not require assumptions about the reaction mechanism while fitting the model, unlike the model-fitting method. Additionally, the model-fitting method assumes constant kinetic parameters and attempts to fit these parameters using a single heating rate and a single run, which is an inadequate approach. Conversely, the model-free method employs multiple heating rates at identical conversion levels to determine the kinetic parameters and are often referred to as iso-conversional methods [84]. Iso-conversional methods, offer a straightforward way to analyze complex reactions, minimizing the risk of selecting an inappropriate kinetic model or obtaining inaccurate kinetic parameters. These methods are particularly valuable for investigating the kinetics of solid feedstocks in the pyrolysis process, as they do not assume any specific reaction mechanism and allow for the quantification of activation energy concerning the conversion level [72].

1.6 ORGANIZATION OF THE THESIS

The research work embedded in this thesis is broadly divided into eight chapters.

Chapter 1: Introduction- This chapter offers an extensive insight into the research context of this thesis, exploring the background of the study, highlighting the significance of biomass waste as a renewable energy source. The various biomass-to-energy conversion pathways, with a focus on pyrolysis as an efficient technology, are discussed in this chapter. Additionally, this chapter explains the various methods used for studying solid-state kinetics for biomass pyrolysis, establishing the foundation for the subsequent chapters. The chapter concludes with a brief outline of the thesis structure.

Chapter 2: Literature Review- In this chapter, an extensive review of relevant literatures on lignocellulosic biomass pyrolysis and the challenges associated with bio-oil obtained from pyrolysis are presented. It covers studies related to single-feed and co-feed pyrolysis of

lignocellulosic biomass, as well as various techniques of upgrading bio-oil with a focus on the extraction of fuel phase of bio-oil using various solvents. In addition to these, this chapter also covers studies related to kinetics and thermodynamics of single-feed and co-feed biomass pyrolysis. This chapter concludes with a summary that highlights key insights gleaned from the literature.

Chapter 3: Motivation and Objectives- This chapter addresses the research gaps and the motivation behind conducting this research work. It outlines the broad objectives of this research study aimed at addressing the identified knowledge gaps, providing a clear path for future research.

Chapter 4: Materials and Methods- Providing details on the foundational aspects of this research study, this chapter outlines the materials and methods used to carry out this research work. It introduces the feed materials and solvent used in this study as well as their characterization. It provides details on the experimental procedures used to carry out the pyrolysis processes, calculating yields of pyrolysis products, methods for fuel phase extraction from bio-oil, along with the characterization techniques employed to analyse the pyrolysis products. Additionally, it includes an economic analysis of setting up a pyrolysis plant, examining the costs and financial feasibility associated with establishing and operating such a facility.

Chapter 5: Kinetics and Thermodynamics Study- This chapter furnishes details on the methods used to conduct the kinetics and thermodynamics study of the single and co-feed pyrolysis processes. It explains the non-isothermal approach employed for conducting the thermogravimetric analysis. Additionally, it provides details on the evaluation of the kinetic triplets and thermodynamics involved in the pyrolysis processes.

Chapter 6: Results and Discussions- Presenting the empirical outcomes of this study, this chapter covers characterization results of the feedstocks and properties of the solvents. It provides details of the outcomes of the single-feed and co-feed pyrolysis processes, followed by an in-depth analysis of the pyrolysis products and an evaluation of the economic analysis for setting up and operating a pyrolysis plant, to examine the financial viability and cost implications. Following this, a detailed analysis of the kinetics and thermodynamics of the pyrolysis processes are also presented. The chapter concludes with a summary highlighting the key findings of this research work.

Chapter 7: Conclusions- Summarizing the entire research work, this chapter highlights the key findings and their interpretations. It provides a brief description of the conclusions drawn from the empirical outcomes of this research work.

Chapter 8: Future scope of this work

In the final chapter, the thesis looks forward, suggesting future scope of this research work and potential commercialization based on the current findings. It suggests potential extensions or applications of the study to improve the quality of the products and their utilization in various industries, contributing to the continuous evolution of knowledge in the field.





Chapter 2: Literature Review

The study of pyrolysis of lignocellulosic biomass is extensive, with numerous research efforts dedicated to producing biofuels from these materials [51,85–87]. Despite having tremendous potential, the commercialization of the pyrolysis process has not reached the desired level. A critical challenge lies in the quality of bio-oil produced through pyrolysis.

2.1 CHALLENGES WITH BIO-OIL OBTAINED FROM PYROLYSIS

Figure 2.1.1 illustrates the negative characteristics of bio-oil along with the limitations/problems and causes obtained through pyrolysis. These challenges include low pH, high viscosity, high density, high water content, low calorific value, high oxygen content and aging problem which make bio-oil less suitable for direct use as fuel, requiring extensive refining and upgrading, which increases the complexity and cost of the process and hinders the market penetration of pyrolysis based-technologies. Bio-oil obtained from pyrolysis exhibits several challenging characteristics that impact its usability. Its low pH can cause corrosion of system parts and pipelines, primarily due to the degradation of organic acids present in the feedstock. High viscosity of bio-oil leads to phase separation, driven by factors such as, high ash content in feedstocks, increased water content in the bio-oil and the rise in molecular mass of the liquid. The high density of bio-oil causes flowability and pumping issues, attributed to the presence of complex and heavy molecules. Additionally, high water content affects the viscosity and stability of bio-oil, reducing its calorific value, a result of the pyrolysis reaction and the initial water present in the feedstock. The low calorific value itself denotes low-grade fuel, exacerbated by increased water and oxygen content. High oxygen content results in poor stability and non-miscibility with hydrocarbons, linked to the inherent biomass composition. Furthermore, bio-oil's aging leads to an increase in viscosity, restricting long-term storage in open air due to the continuation of secondary reactions, including polymerization. While co-feed pyrolysis has shown promise in enhancing product quality and yield, the resultant liquid product still falls short of the standards set by commercial fossil fuels. To provide a comprehensive understanding of the limitations of bio-oil, a few relevant studies on single and co-feed pyrolysis of lignocellulosic biomass are discussed in the following sub-sections.

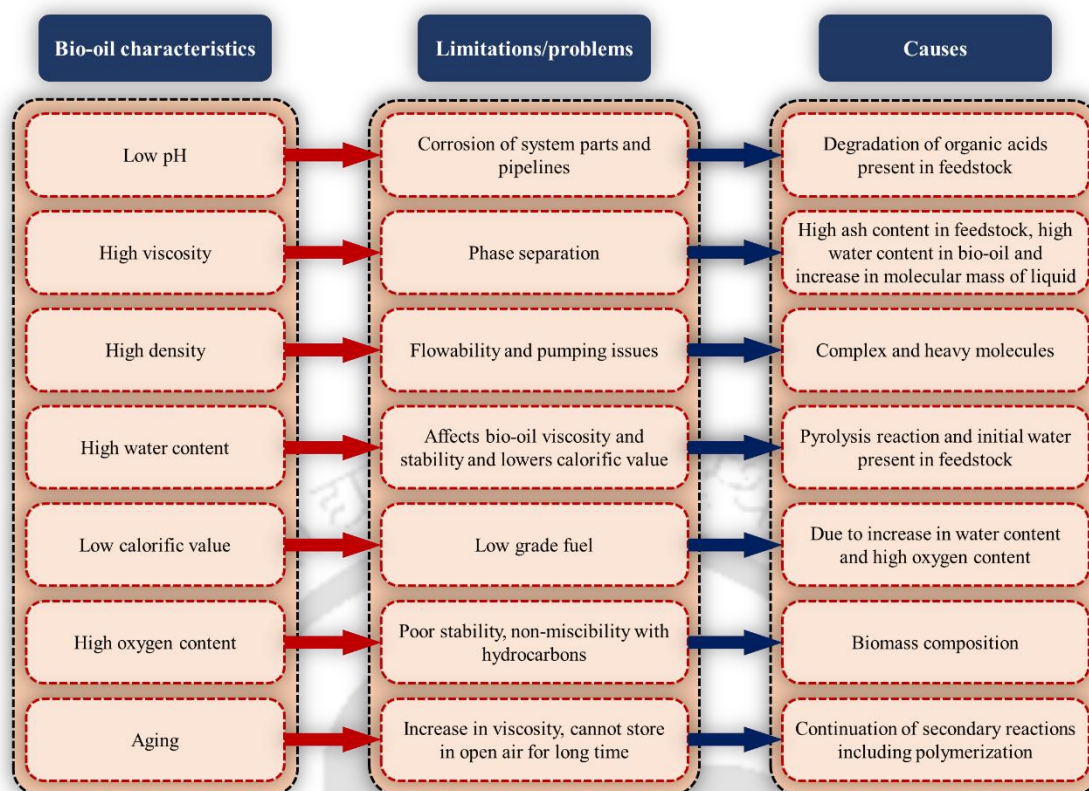


Figure 2.1.1 Limitations and causes of negative characteristics of bio-oil obtained through pyrolysis [88].

2.1.1 Single-feed pyrolysis

Şensöz [89] conducted slow pyrolysis of *Pinus brutia* bark residues using an externally heated fixed-bed reactor, with reaction temperatures ranging from 300 to 500°C. To separate the fuel phase of the bio-oil, the bio-oil was dissolved in dichloromethane and then extracted using a rotary evaporator. The maximum yield of bio-oil, 33.25 wt.%, was obtained at 450°C. The bio-oil had a calorific value of 31.03 MJ/kg and a density of 1.2 g/mL, and it primarily composed of oxygenated compounds, with minor quantities of hydrocarbons. Similarly, Baghel et al. [90] conducted a study on the slow pyrolysis of *Prosopis juliflora* wood using a mild steel fixed-bed reactor. The experiments were performed at temperatures between 300 and 600°C, with a residence time of 1 hour for each reaction, and nitrogen gas was used as an inert atmosphere at a flow rate of 1500 cm³/min. They achieved the highest yield of bio-oil, 38.5%, at 500°C, while the maximum calorific value of 20.87 MJ/kg was recorded at 600°C. The bio-oil produced at 500°C contained the highest concentration of phenolic compounds, reaching 35.54%. Furthermore, Ahmed et al. [91] investigated the pyrolysis of *Acacia* timber sawdust using an auger reactor, with reaction temperatures ranging from 400 to 600°C under a nitrogen atmosphere at a flow rate of 300 cm³/min. They observed that the bio-oil yield increased with

temperature within the range of 400 to 500°C, peaking at 45.10 wt.% at 500°C, attributed to the higher decomposition rates of cellulose and hemicellulose in the feedstock. However, further increasing the temperature from 500 to 600°C resulted in a decrease in bio-oil yield to 31.81 wt.% but with improved physiochemical properties. The bio-oil produced at 600°C had the lowest density of 1.043 g/mL, but the highest calorific value of 29.871 MJ/kg and a pH of 3.40, with its chemical composition including phenols, nitrogen-containing compounds, guaiacols, organic acids, ketones, anhydrous sugars, esters and aldehydes.

Yorgun and Yildiz [92] carried out pyrolysis of paulownia wood (*P. tomentosa*) in a fixed-bed reactor made of 316 stainless-steel. The experiments were performed at temperatures ranging from 350 to 600°C, utilizing nitrogen as the inert gas, and examined heating rates of 10 and 50°C/min. The highest yield of 54 wt.% of liquid product was achieved at 500°C with a heating rate of 50°C/min, and the calorific value of the bio-oil was measured at 28.6 MJ/kg. The bio-oil was a complex mixture of oxygenated aliphatic and aromatic hydrocarbons. Kawale and Kishore [93] conducted pyrolysis of *Delonix regia* biomass in a fixed-bed reactor made of SS Inconel material, with reaction temperatures ranging from 500 to 700°C and nitrogen as the inert medium at a flow rate of 0.3 cm³/min. They found that the maximum liquid yield of 38 wt.% was achieved at 500°C, while the highest calorific value of 25.70 MJ/kg was observed at 700°C. The bio-oil produced at 700°C had the minimum values of density 0.88 g/mL and viscosity 1.22 mPa.s, with a wide range of organic compounds including alkanes, alkenes, ketones, aldehydes, aromatics, esters and ethers.

Morali & Şensöz [94] performed pyrolysis of hornbeam shell (*Carpinus betulus* L.) waste from the furniture industry using a 316 stainless steel fixed-bed reactor, with reaction temperatures ranging from 400 to 600°C. The residence time was set to 30 minutes once the desired temperature was reached. Liquid products were recovered through dichloromethane washing. The oil phase was initially treated with anhydrous sodium sulphate, followed by the separation of bio-oil and solvent using a rotary evaporator. The highest bio-oil yield of 24.67% and a calorific value of 30 MJ/kg was achieved at 550°C. The bio-oil produced mostly consisted of oxygenated aliphatic and aromatic compounds. Das et al. [95] conducted pyrolysis of *Jatropha curcas* shells using a stainless-steel fixed-bed reactor, with temperatures ranging from 300 to 600°C. The reactions were performed over a residence time of 4 hours. Bio-oil was extracted using diethyl acetate, achieving a maximum yield of 31.4 wt.% at 400°C, with a calorific value of 30.04 MJ/kg. The bio-oil had a density of 1.021 g/mL and a viscosity of 1.11

mPa.s, and in addition to various oxygenated compounds, it contained 40% carbonyl derivatives.

Sultana et al. [96] utilized rubber seed cake as a feedstock for biofuel production via pyrolysis in a horizontal reactor, employing nitrogen as the inert gas at a flow rate of 50 cm³/min. The pyrolysis reactions were conducted at temperatures ranging from 480 to 520°C, with residence times between 45 and 90 minutes. The highest bio-oil yield of 59.94 wt.% was obtained at 500°C with a residence time of 75 minutes, and the bio-oil had a calorific value of 29.86 MJ/kg.

2.1.2 Co-feed pyrolysis

Co-feed pyrolysis of bamboo waste was studied with *Nannochloropsis sp.* at co-feed ratios of 1:3, 1:2, 1:1, 2:1, 3:1 by Chen et al. [64]. The studies were carried out at 600°C in a quartz basket using argon as inert gas with a flow rate of 200 cm³/min. The residence time for carrying out the reactions was set at 30 mins. Substantial enhancement in the fuel property of bio-oil was evident following the co-feed pyrolysis reactions, resulting in a notable increase in bio-oil yield, reaching 66.63% by weight when the co-feed ratio was 1:1. Co-pyrolysis directed to a significant rise in bio-oil production and a concurrent decrease in gas yield. However, the pH value depicted an increasing trend as the percentage of *Nannochloropsis sp.* increased. The pH value of the bio-oil ranged between 2.5 to 4.0 while the co-feed ratio of 1:1 depicted a pH value of 3.6. The bio-oil produced from the co-feed pyrolysis indicated the presence of various compounds including acetic acid, long-chain fatty acids, phenols, aliphatics, aromatics, alcohols, furans, aldehydes, ketones, esters and other nitrogenated compounds. Kawale and Kishore [65] performed an investigation on the co-feed pyrolysis study of *Delonix regia* and pine wood saw dust for producing biofuels. The study was carried out at co-feed ratios of 1:3, 1:1 and 3:1 at a temperature of 600°C using nitrogen as inert gas using a SS 316 tubular batch reactor while the residence time was considered to be 2 hours after reaching the pyrolysis temperature. Notably, it was observed that the co-feed ratio of 1:1 resulted in the lowest biochar yield at 28.4% by weight, while concurrently, it yielded the highest amount of non-condensable gases, standing at 35.6% by weight. Among various bio-oil produced, the one resulted by co-feeding in 1:1 ratio exhibited the peak calorific value, measuring at 20.3 MJ/kg with a pH value of 4.5 and density of 0.966 g/mL. The bio-oil produced from the co-feed pyrolysis reactions indicated the presence of various functional groups including polymeric OH and water impurities, ketones, aldehydes, carboxylic acids, alkenes, aromatics, alkanes, esters, primary,

alcohols and phenols. Correspondingly, the biochar yield of 28.4 wt.% was found to be minimum for the co-feed ratio of 1:1 while it depicted the minimum calorific value of 29.8 MJ/kg.

Another co-feed pyrolysis study involving sugarcane bagasse and *Enteromorpha prolifera* was studied by Hua and Li [66]. The study was carried out in a cylindrical quartz reactor at co-feed ratios of 70:30, 60:40, 50:50, 40:60, 30:70 along with their individual counterparts at a temperature of 550°C using nitrogen as inert atmosphere with a flow rate of 250 cm³/min. It was observed that at 50:50 co-feed ratio, the liquid product exhibited its peak yield at 56.12% by weight, and the bio-oil had a higher heating value of 26.4 MJ/kg. The bio-oil produced composed of hydrocarbons, acids, ketones, aldehydes, alcohols, esters, phenols, amines, pyridines, indoles furans, etc. It was observed that the co-pyrolysis of sugarcane bagasse and *Enteromorpha prolifera* resulted in the formation of new compounds such as decyloxirane, 2,3-anhydro-D-mannosan and 1-heptyl acetate. Chang et al. [67] carried out an investigation of co-feed pyrolysis study of palm kernel shell and *Nannochloropsis sp.* at co-feed ratios of 9:1, 7:3, 1:1, 2:3, 3:7 and 1:9 using a quartz reactor at a temperature of 600°C using nitrogen as inert gas and residence time of 15 mins. The individual pyrolysis of *Nannochloropsis sp.* and palm kernel shell resulted in relative amounts of aromatic substances at 11.79 area% and 3.01 area%, respectively. However, a higher aromatic content of 30.39 area% was achieved at 600°C when the mass ratio of *Nannochloropsis sp.* to palm kernel shell was 1:1. During the co-feed pyrolysis of *Nannochloropsis sp.* and palm kernel shell, a synergistic effect was evident, leading to increased production of aromatic compounds.

These studies highlight that the characteristics of bio-oil produced through single and co-feed pyrolysis often do not compare favourably to conventional fossil fuels like gasoline, diesel and furnace heating oil. Consequently, the bio-oil requires upgrading to enhance its properties for practical applications.

2.2 TECHNIQUES FOR UPGRADING BIO-OIL

Bio-oil obtained through pyrolysis can undergo various upgradation processes to enhance its quality and usability. Figure 2.2.1 illustrates the operating conditions, reaction, advantages and disadvantage of the existing techniques available for upgrading bio-oil. Broadly, these upgradation techniques can be categorized into physical and chemical techniques [97]. Physical upgradation includes techniques such as distillation, supercritical fluid processing, extraction and emulsification. These methods focus on improving the physical properties of bio-oil,

making it more suitable for direct use or further processing. Chemical upgradation encompasses pathways like hydrotreating, catalytic cracking, hydrocracking and steam reforming. Hydrotreating, catalytic cracking, hydrocracking and steam reforming leverage catalysts and hydrogen to facilitate chemical reactions that remove unwanted components and improve the overall composition and stability of the bio-oil, whereas esterification involves a process that modifies the chemical structure of the bio-oil to enhance its properties. By converting organic acids and other reactive components into esters, esterification can improve the fuel characteristics and storage stability of the bio-oil [98].



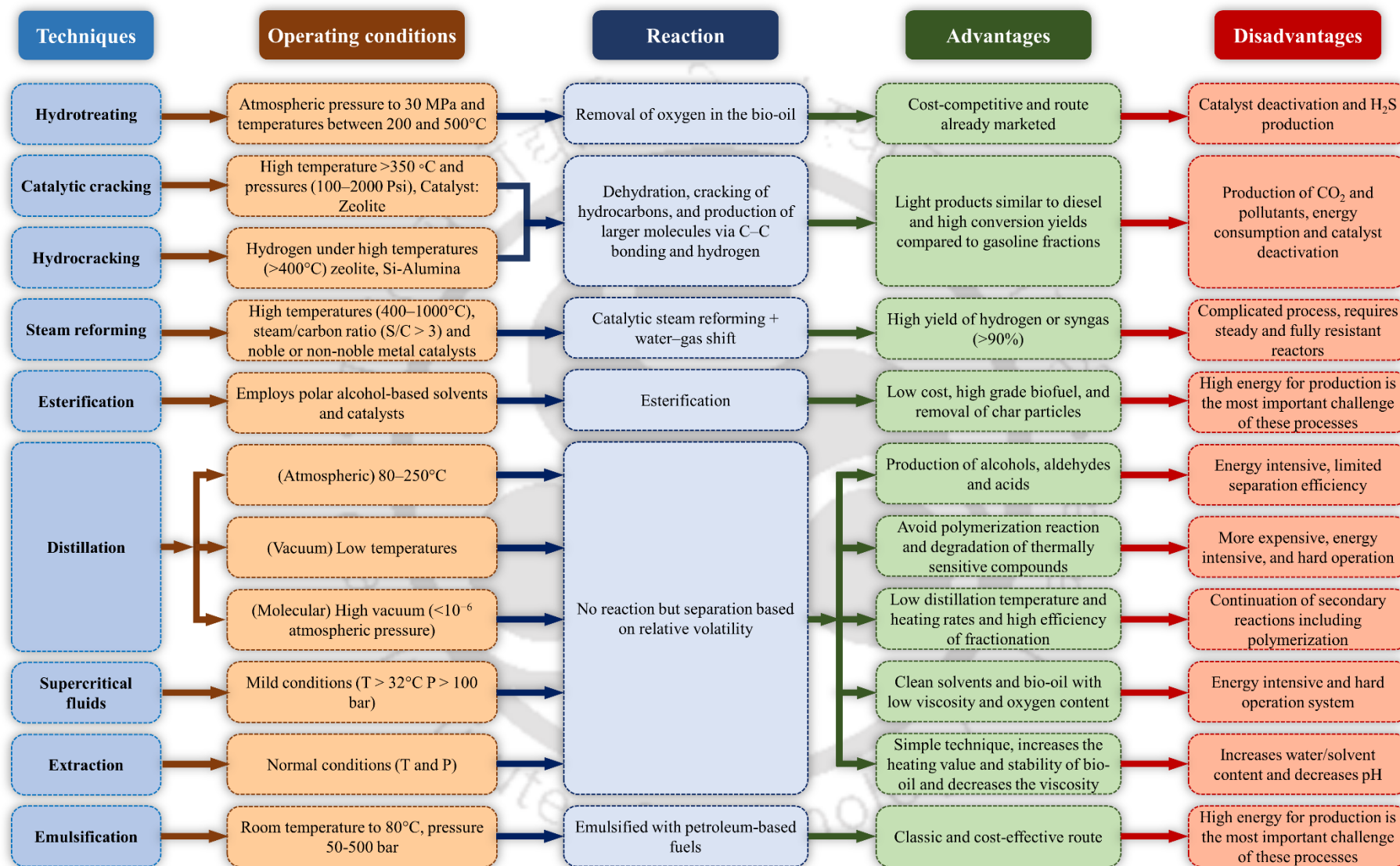


Figure 2.2.1 Operating conditions, reaction, advantages and disadvantages of existing bio-oil upgrading techniques [97].

Amongst various upgradation techniques, solvent extraction emerges as a potential solution to address these challenges associated with bio-oil. By selectively removing undesirable components from bio-oil, it enhances the quality and applicability of bio-oil. Further, the technique is simple to operate and works under milder conditions compared to other upgrading techniques [97]. The process works on the relative solubilities of two immiscible liquids or phases. Furthermore, solvent extraction contributes to reducing energy consumption and operational costs, making it energy-efficient option. Researchers have extensively studied and reported the extraction and fractionation of bio-oil to produce value-added chemicals based on solubility properties using various solvents. However, there has been limited research on separating the fuel phase of bio-oil from a fuel perspective. A few relevant literatures on extraction of fuel phase of bio-oil produced through pyrolysis has been discussed below.

2.2.1 Fuel phase extraction

Ucar and Ozkan [99] performed the pyrolysis of rapeseed (*Brassica napus* L.) oil cake in a stainless-steel fixed bed reactor across temperatures ranging from 400 to 900°C, using nitrogen as an inert atmosphere. The fuel phase of the bio-oil was extracted with diethyl ether, with the extracted fraction subsequently dried over anhydrous sodium sulfate, filtered and evaporated using a rotary evaporator to remove the ether. The highest bio-oil yield of 18.58 wt.% was obtained at 500°C, with a calorific value of 33.17 MJ/kg. Oleic acid was the predominant component in the bio-oil across all pyrolysis temperatures. Additionally, the bio-oil contained significant amounts of 1H-indole, 2,3,5-trimethoxy toluene, toluene, (Z)-9-octadecanamide, psoralene, phenol and various phenol derivatives. Wei et al. [100] conducted the pyrolysis of Douglas fir pellets in a microwave oven at 450°C, with a reaction time of 25 minutes. They extracted the organic components from the pyrolysis oil using ether, hexane and chloroform, with chloroform proving to be the most effective solvent, especially at a solvent-to-water phase ratio of 1:1. When comparing the chloroform-extracted phase to the raw bio-oil, they found higher concentrations of phenol and guaiacol and lower levels of alcohols. Ren et al. [101] carried out the pyrolysis of switchgrass (*Panicum virgatum* L.) in a semi-pilot scale auger pyrolysis reactor at 500°C, with nitrogen as the inert gas at a flow rate of 20 L/min. The process yielded bio-oil between 50-54 wt.%. The bio-oil was then mixed with deionized water at a 1:4 weight ratio to separate it into aqueous and organic phases. Organic compounds in the aqueous phase were extracted using ethyl acetate and chloroform at solvent-to-aqueous phase ratios of 1:1 and 2:1, respectively. Approximately 60 wt.% of the chemicals were transferred to the

aqueous phase, which has potential for further enhancement to hydrocarbon fuels. The highest organic extraction efficiency, reaching 70 wt.%, was achieved with diethyl acetate at a 2:1 solvent-to-aqueous phase ratio.

Li et al. [102] extracted the organic phase from rice straw pyrolysis oil using dichloromethane as solvent and water as anti-solvent. The highest extraction efficiency was achieved with a 10:10:3 volume ratio of oil, dichloromethane and water. This process removed 46.62 wt.% of the flowable organic phase from the pyrolysis oil. Compared to the raw bio-oil, the extracted organic phase had lower sugar and water content and a higher concentration of phenolic chemicals. Kanaujia et al. [103] extracted the fuel phase of bio-oil derived from *Jatropha Curcas* seed cake using a variety of solvents, including benzene, ethyl acetate, carbon tetrachloride, chloroform, dichloromethane, iso-octane, diethyl ether, hexane, xylene and cyclohexane. Optimal recoveries for different functional groups were 3.79 wt.% with ethyl acetate and 3.63 wt.% with dichloromethane. The separation of the bio-oil phase and solvents was based on their polarity. Das and Goud [104] conducted bio-oil extraction using hexane, ethyl acetate and acetone in a 1:1 ratio by volume. Ethyl acetate yielded the highest bio-oil recovery of 35.5%, with a calorific value measured at 14.56 MJ/kg. Solvent extraction significantly enhanced the bio-oil quality by reducing its water content from 55% to 25.8%. Aravind et al. [40] conducted the pyrolysis of *Delonix regia* in a fixed bed tubular reactor at 600°C, using nitrogen as the inert gas, with a reaction residence time of 2 hours. The bio-oil produced was extracted using dichloromethane and n-hexane at a 1:10 solvent-to-bio-oil volume ratio. The bio-oil extracted with n-hexane exhibited superior physical properties, including a density and calorific value that were 23% higher than those obtained with dichloromethane.

In summary, different solvents were used to separate out fuel phase from bio-oil and varying yields and calorific value of fuel phase were reported. Thus, there is a need to optimize the type and vol.% of solvent required for better results of fuel phases.

2.3 KINETICS AND THERMODYNAMICS OF BIOMASS PYROLYSIS

As discussed in section 1.5, understanding the reaction kinetics of biomass pyrolysis is essential as it provides valuable insights into the fundamental mechanisms governing the pyrolysis process. This information helps in optimizing pyrolytic processes, improving energy efficacy, reducing waste, designing efficient reactors and process control strategies which influences the scalability and economic viability of biomass pyrolysis technologies. Kinetics and

thermodynamics of pyrolysis for various lignocellulosic biomasses have been studied extensively by various researchers revealing significant insights into the process [38]. A few relevant literatures providing insights on the activation energy required and the associated thermodynamic properties of single-feed and co-feed pyrolysis of lignocellulosic biomass using iso-conversional methods have been discussed in the following paragraphs.

2.3.1 Single-feed pyrolysis kinetics and thermodynamics

Balogun et al. [105] investigated the pyrolysis of *Delonix regia* pods over a temperature range of 29 to 900°C using nitrogen at a flow rate of 30 mL/min, with heating rates of 5, 10, 20 and 50°C/min. The activation energies obtained ranged from 196-277 kJ/mol using DFM, 194-234 kJ/mol using OFW and 194-236 kJ/mol using STK. The thermodynamic properties determined using DFM indicated values of ΔH at 214 kJ/mol, ΔG at 143 kJ/mol and ΔS at 0.116 kJ/mol·K. Similarly, Chandrasekaran et al. [106] investigated the pyrolysis of *Prosopis juliflora* biomass in the temperature range of 30 to 600°C using argon at a flow rate of 60 mL/min. The heating rates considered for this study were 2, 5, 10, 15, 20 and 25°C/min. The activation energies using the KAS, OFW and DFM models were found to be 204.0, 203.2 and 219.3 kJ/mol, respectively. Another study by Balogun et al. [105] focused on pyrolysis of *Moringa oleifera* husk, conducted over a temperature range of 29 to 900°C using nitrogen at a flow rate of 30 mL/min. The heating rates for the study were considered to be 5, 10, 20 and 50°C/min. The activation energies using DFM, OFW and STK varied in the range of 201-364, 292-296 and 199-200 kJ/mol. The thermodynamic properties using DFM indicated values of ΔH of 233 kJ/mol, ΔG of 135 kJ/mol and ΔS of 0.152 kJ/mol·K. Wang et al. [107] studied the pyrolysis of *Gracilaria lemaneiformis* over a temperature range of 25 to 700°C, at heating rates of 10, 20, 30, 50 and 80°C/min using nitrogen at a flow rate of 30 mL/min. An activation energy of 153.79 kJ/mol was obtained using OFW. Gupta and Mondal [108] analysed the pyrolysis of maize cob from 25 to 900°C under nitrogen at 60 mL/min at heating rates of 5, 10 and 20°C/min. The activation energies using DFM, OFW, KAS and STK were found to be 197.63, 186.06, 185.39 and 185.80 kJ/mol, respectively. The thermodynamic properties were ΔH of 192.83 and 180.58 kJ/mol, ΔG of 176.49 and 176.76 kJ/mol and ΔS of 0.027 and 0.006 kJ/mol·K using DFM and KAS, respectively. Ceylan and Kazan [109] focused on the pyrolysis of *Tetraselmis* sp. over a temperature range of 25 to 800°C with nitrogen at 80 mL/min and heating rates of 5, 10 and 20°C/min. They reported an activation energy of 334 kJ/mol using DAEM.

Singh et al. [110] investigated the pyrolysis of corncob within a temperature range of 25 to 900°C using nitrogen at 50 mL/min at heating rates of 10, 20 and 30°C/min. The activation energies were 240, 238, 241 and 248 kJ/mol using KAS, OFW, STK and DFM, respectively. The thermodynamic properties indicated ΔH of 236 and 243 kJ/mol, ΔG of 181 kJ/mol and ΔS of -0.137 and -0.162 kJ/mol·K, using STK and DFM, respectively. Rasool et al. [111] performed pyrolysis of almond shells between 30 and 1000°C with nitrogen at 200 mL/min at heating rates of 10, 25 and 50°C/min. The activation energies were 153.0, 152.02 and 152.73 kJ/mol using KAS, OFW and STK, respectively. The thermodynamic properties indicated ΔH of 147.76, 149.71 and 149.70 kJ/mol, ΔG of 180.55, 181.73 and 181.81 kJ/mol, and ΔS of -0.054, -0.052 and -0.052 kJ/mol·K using KAS, OFW and STK, respectively. Damartzis et al. [112] examined the pyrolysis of cardoon stems over a range of 25 to 850°C using nitrogen at 60 mL/min at heating rates of 5, 10, 20 and 30°C/min. The activation energies were 224.51 and 229.70 kJ/mol using KAS and OFW, respectively. Lee et al. [113] conducted pyrolysis of *Hibiscus cannabinus* L. from 25 to 900°C under nitrogen at 100 mL/min at heating rates of 5, 10, 20, 30, 40 and 50°C/min. The activation energy was evaluated to be 180.51 kJ/mol using DAEM, while the thermodynamic properties using DAEM were ΔH of 175.65 kJ/mol, ΔG of 172.96 kJ/mol and ΔS of 0.443 kJ/mol·K. Li et al. [114] studied the pyrolysis of poplar sawdust within a temperature range of 25 to 900°C using nitrogen at 100 mL/min at heating rates of 5, 10, 20 and 40°C/min. The activation energies were 159, 157, 159 and 157 kJ/mol using DFM, STK, OFW and KAS, respectively. The thermodynamic properties indicated ΔH ranging from 140.7 to 230.6 kJ/mol and ΔG from 162.0 to 164.5 kJ/mol. Rammohan et al. [115] conducted the pyrolysis of *Delonix regia* over a range of 25 to 1000°C using nitrogen at 40 mL/min at heating rates of 5, 10, 20, 35 and 55°C/min. The activation energies using DFM, KAS, OFW, STK and DAEM were 202, 206, 205, 206 and 206 kJ/mol, respectively. The thermodynamic properties indicated ΔH of 197.14 and 204.7 kJ/mol and ΔG of 181.52 and 181.01 kJ/mol using DFM and DAEM, respectively.

2.3.2 Co-feed pyrolysis kinetics and thermodynamics

Sharma et al. [116] conducted kinetics and thermodynamics study on the co-pyrolysis of poplar and eucalyptus sawdust at temperatures ranging from room temperature to 1000°C, using nitrogen as the inert gas with a flow rate of 100 mL/min. The heating rates considered were 5, 10 and 20°C/min. The activation energies determined through OFW and KAS methods were found to be 203.25 kJ/mol and 203.70 kJ/mol, respectively. The thermodynamic properties were as follows: for OFW, ΔH ranged from 198.15 to 198.32 kJ/mol and ΔG ranged from

179.53 to 198.15 kJ/mol; for KAS, ΔH ranged from 198.59 to 198.76 kJ/mol and ΔG ranged from 179.52 to 198.59 kJ/mol. Muigai et al. [117] conducted co-pyrolysis of biomass blends consisting of water hyacinth (WH), sugarcane bagasse (SCB) and *Thevetia peruviana* (TP) in a 1:1 ratio, at heating rates of 8, 10, 15 and 30°C/min. The activation energies for the biomass blends (WH:SCB, WH:TP and TP:SCB) ranged between 122.90 to 237.53, 127.93 to 272.92 and 124.80 to 235.94 kJ/mol, respectively. The thermodynamic properties for WH:SCB, ΔH ranged from 188.24 to 227.51 kJ/mol, ΔG from 91.81 to 137.85 kJ/mol and ΔS from 71.42 to 161.2 J/mol·K; for WH:TP, ΔH ranged from 243.79 to 267.67 kJ/mol, ΔG from 72.80 to 144.97 kJ/mol and ΔS from 107.69 to 285.86 J/mol·K; for TP:SCB, ΔH ranged from 123.8 to 232.53 kJ/mol, ΔG from 105.52 to 140.38 kJ/mol and ΔS from 30.55 to 154.05 J/mol·K.

Kazawadi et al. [118] conducted co-feed pyrolysis of rice husk (RH) with cashew nut shells (CNS) and coconut shells (CCS) at ratios of RH:CNS-30%:70%, 60%:40% and RH:CCS-30%:70%, 60%:40%. The studies were carried out at heating rates of 10, 15 and 20°C/min using nitrogen as an inert medium at a flow rate of 400 L/hr. The activation energies for RH:CNS-30%:70%, 60%:40% and RH:CCS-30%:70%, 60%:40% were determined using OFW and found to be 72.418, 78.230, 76.435 and 81.253 kJ/mol, respectively. Using KAS, the activation energies were 60.458, 66.145, 63.619 and 71.454 kJ/mol, respectively. The thermodynamic properties ΔH , ΔG and ΔS for RH:CNS-30%:70%, 60%:40% 54.45 kJ/mol, 218.99 kJ/mol, -0.23 kJ/mol·K; 59.97 kJ/mol, 245.11 kJ/mol, -0.25 and RH:CCS-30%:70%, 60%:40% are 57.53 kJ/mol, 222.67 kJ/mol, -0.23 kJ/mol·K; 65.07 kJ/mol, 233.53 kJ/mol, -0.22 kJ/mol·K, respectively.

These studies demonstrate the significant variability in the activation energy and thermodynamic properties across different lignocellulosic biomasses during pyrolysis. These findings highlight the complex nature of biomass pyrolysis and underscore the importance of selecting appropriate kinetic and thermodynamic models to optimize pyrolysis processes for specific feedstocks.

2.4 SUMMARY OF THIS CHAPTER

From the literature review, it is clear that numerous studies have investigated biomass pyrolysis for producing biofuels. However, researchers have reported that the quality of bio-oil produced through pyrolysis often falls short of fossil fuel standards and requires upgrading before it can be used directly in the existing fuel combustion technologies. Among the existing techniques for bio-oil upgrading, solvent extraction stands out as a promising method due to its simple

technique and milder operating conditions. Despite this, there remains a significant research gap in the efficient separation of the fuel phase of bio-oil, particularly from a fuel quality perspective. Specifically, limited research has focused on using different solvents at various ratios relative to the volume of bio-oil, followed by extensive characterization of the separated phases.

Considering the existing research gap and the potential scope of this study, two underexplored lignocellulosic biomasses: *Erythrina indica* and *Azadirachta indica* were chosen as feedstocks for this study. Despite having tremendous potential, none of them been considered as feedstocks for biofuel production through pyrolysis. Additionally, no research has been reported on the kinetics and thermodynamics of the pyrolysis processes for these two specific biomasses.

To address these gaps, two solvents, dichloromethane and n-hexane were used to study their efficacy in separating the fuel phase from bio-oil. Various ratios of solvent to bio-oil volume were explored, followed by comprehensive characterization of the resulting phases. This approach aims to optimize the separation process and improve the quality of the fuel phase.

The objectives of this research, which are elaborated in the subsequent chapter, aim to fill these gaps by providing new insights into the pyrolysis of *Erythrina indica* and *Azadirachta indica*, and the subsequent separation and characterization of bio-oil fuel phases using selected solvents. By focusing on these underexplored biomasses and optimizing solvent extraction techniques, this research has the potential to significantly advance the field of biofuel production from lignocellulosic biomass. In addition, kinetics and thermodynamics of pyrolysis of these feedstocks are also aimed in the later part of the investigation.



Chapter 3: Motivation and Objectives

3.1 RESEARCH GAPS AND MOTIVATION

The literature review in the preceding chapter highlighted numerous studies on biomass pyrolysis for biofuel production. However, an in-depth study on effective separation of fuel phase of bio-oil using solvents at various ratios and their subsequent characterization is found to be limited. Ineffective separation of the fuel phase from the bio-oil significantly affects the physiochemical properties of the fuel phase, which greatly hinders the commercial application of the pyrolysis process for producing biofuels. The choice of solvent plays a crucial role in the separating the fuel phase and it greatly affects the physiochemical properties such as density, viscosity, pH, water content, calorific value and optimum extraction of the fuel phase from the bio-oil. Additionally, solvent selection greatly affects the stability of the separated fuel phase. Thus, the first part of this thesis work focusses on an extensive study on extraction of the fuel phase of bio-oil using two distinct solvents dichloromethane (DCM) and n-hexane at various ratios of solvent relative to the volume of bio-oil. The purpose of choosing DCM and n-hexane for extraction is due to their good solubilizing properties, low and narrow boiling points, high volatility and widespread use as extraction solvents [119,120]. Further the use of solvents also serves the purpose of enhancing the physiochemical properties of the fuel phase.

Two scarcely researched lignocellulosic biomass *Erythrina indica* (EI) and *Azadirachta indica* (AI) were considered as feedstocks for pyrolysis in this study. Both EI and AI are widely grown in the Indian subcontinent due to their multipurpose utility. AI and EI are one of those essential trees which are widely grown for food, medicine, wood, etc. These trees are also highly valuable for ornamental purposes. Thus, it is obvious that the wide use of these trees for various purposes would also lead to generation of huge amount of waste. The priority of selecting EI and AI biomass for this study is justified by:

- The superior calorific value of the fuel phase and the biochar.
- Moderate density and viscosity of the fuel phase.
- Fair flowability and combustion indices of the biochar which makes it comparable to conventional coal.
- Better hydrogen, methane and carbon monoxide yield in the non-condensable gases.

In addition to the single-feed pyrolysis study, this study also delineates the synergistic effect of co-feed pyrolysis of aforementioned selected biomass at various co-feed ratios. Understanding the kinetics and thermodynamic properties of the pyrolysis processes also becomes very much essential. Hence the second part of this thesis work delineates the kinetics and thermodynamic properties of single and co-feed pyrolysis processes at various heating rates.

3.2 OBJECTIVES

Based on the literature and available research gaps EI and AI biomass have been rarely utilized as resources for renewable energy generation. Thus, this work considered these two feedstocks and carried out extensive studies on production of biofuels, biochar and non-condensable gases followed by kinetics and thermodynamics of the processes. The main objectives of this research work are broadly classified as below.

- Fuel phase extraction of bio-oil obtained from single-feed pyrolysis of *Erythrina indica* and *Azadirachta indica* biomass using dichloromethane and n-hexane at four different ratios of bio-oil to solvent followed by subsequent characterization of the products.
- Synergistic effect of co-feed pyrolysis of *Erythrina indica* and *Azadirachta indica* biomass at seven different ratios.
- Elucidation of kinetics and thermodynamic properties of *Erythrina indica* and *Azadirachta indica* biomass single-feed pyrolysis at four different heating rates.
- Synergistic effect on kinetics and thermodynamic properties of co-feed pyrolysis of *Erythrina indica* and *Azadirachta indica* biomass at four different heating rates.

Chapter 4: Materials and Methods

4.1 FEEDSTOCK COLLECTION AND CHARACTERIZATION

To conduct this research study dry branches of *Erythrina indica* (EI) and *Azadirachta indica* (AI) trees were gathered from the plantation areas of the IIT Guwahati campus, where they were cultivated primarily for aesthetic purposes. The collected dry branches underwent a series of procedures to ensure their suitability for the study. Initially, the dry branches were manually chopped into smaller pieces to reduce their size and then exposed to sunlight to eliminate the extra moisture present in them. Subsequently, the dried pieces underwent further processing using a motorized woodcutter (Make: Nutech Eng. Corporation, India) which operates on the principle of a hammer mill to further reduce the size of the feed material, making it suitable for subsequent milling in a mixer grinder. The resulting milled biomass was sorted through a standard test sieve (Make: Ikon Instruments) of size 600-micron mesh, and subsequently subjected to overnight drying in a hot air oven (Make: Relitech, India) to eradicate the residual moisture. The resulting dry and moisture-free feed material was then ready for further study. Figure 4.1.1 (a) and (b), respectively illustrate the size-reduced, dry and moisture-free EI and AI biomass.



Figure 4.1.1 (a) *Erythrina indica* biomass and (b) *Azadirachta indica* biomass.

To check the feasibility of EI and AI biomass for pyrolysis, the proximate, ultimate and calorific value analyses of these biomasses were carried out to study the physiochemical properties. For a more comprehensive understanding of the process and in the event of scaling up for a continuous process, other properties apart from its physiochemical properties, various

types of densities (which include bulk, tapped and particle density), porosity, flowability indices and combustion indices were also explored. The studies were conducted according to ASTM procedures which are explained in the following sections.

4.1.1 Physiochemical characterization

The proximate analysis reveals the moisture, ash, volatile matter and fixed carbon contents of a sample. For determining the moisture content (MC) on wet basis, ASTM E871-82 [121] method was followed. For this method, approximately 10 g of raw biomass sample underwent drying in a hot air oven (Make: Relitech, India) at a temperature set to 103°C for 24 hours followed by weighing at 30-minute intervals. The weighing process persisted until a constant weight was achieved, signifying the removal of all moisture. Equation (4.1.1) below illustrates the mathematical formula for determining the moisture content.

$$\text{Moisture content, } MC_{wb} \text{ (wt. \%)} = \frac{W_i - W_f}{W_i - W_c} \times 100 \quad (4.1.1)$$

Where W_c indicates the weight of empty crucible, W_i indicates the initial weight of crucible and sample and W_f indicates the final weight of crucible and sample after drying.

To determine the ash content (AC) on dry basis, ASTM E1755-01 [122] method was followed. In this approach, approximately 2 g of oven-dried sample was subjected to heating in a muffle furnace (Make: Ikon Instruments, India) at a temperature set to 600°C for six hours to eliminate all moisture and volatiles (as vapour) and organics (as carbon dioxide and oxides of nitrogen). Equation (4.1.2) below illustrates the mathematical formula for determining the ash content.

$$\text{Ash content, } AC_{db} \text{ (wt. \%)} = \frac{W_1 - W_{sc}}{W_2 - W_{sc}} \times 100 \quad (4.1.2)$$

Where W_{sc} indicates the weight of the empty silica crucible, W_1 indicates the final weight of the silica crucible and ash and W_2 indicates the initial weight of silica crucible and oven-dried sample.

To determine the volatile matter content (VM) on dry basis, ASTM E872-82 [123] method was followed. This involved subjecting 1 g of the oven-dried sample to heating in a muffle furnace (Make: Ikon Instruments, India) for 7 minutes at a temperature set to 950°C to eliminate the volatiles. Equation (4.1.3) below illustrates the mathematical formula for determining the volatile matter content.

$$\text{Volatile matter content, } VM_{db} \text{ (wt. \%)} = \frac{W_3 - W_4}{W_3 - W_{qc}} \times 100 \quad (4.1.3)$$

Where W_{qc} indicates the weight of empty quartz crucible, W_3 indicates the weight of the quartz crucible and oven-dried sample and W_4 indicates the weight of quartz crucible and residue left after removal of volatiles. Finally, fixed carbon content (FC) of the samples were assessed by the difference.

The ultimate analysis reveals the elemental composition of carbon, hydrogen, nitrogen and sulphur of a sample. For this analysis, a CHNS elemental analyser (Model: EuroEA3000, Make: Euro Vector, Italy) was utilized. A schematic diagram of the CHNS elemental analyser used for conducting the ultimate analysis is presented in Figure 4.1.2. The analysis involved combusting approximately 10 mg of the oven-dried sample using pure oxygen gas to produce carbon dioxide, water vapour, nitrogen and sulphur dioxide gases. The makeup of carbon, hydrogen, nitrogen and sulphur was then determined by analysing the product gases using a gas chromatograph (GC) column with peaks detected by thermal conductivity detector (TCD). The difference allows for the calculation of the oxygen content [124].

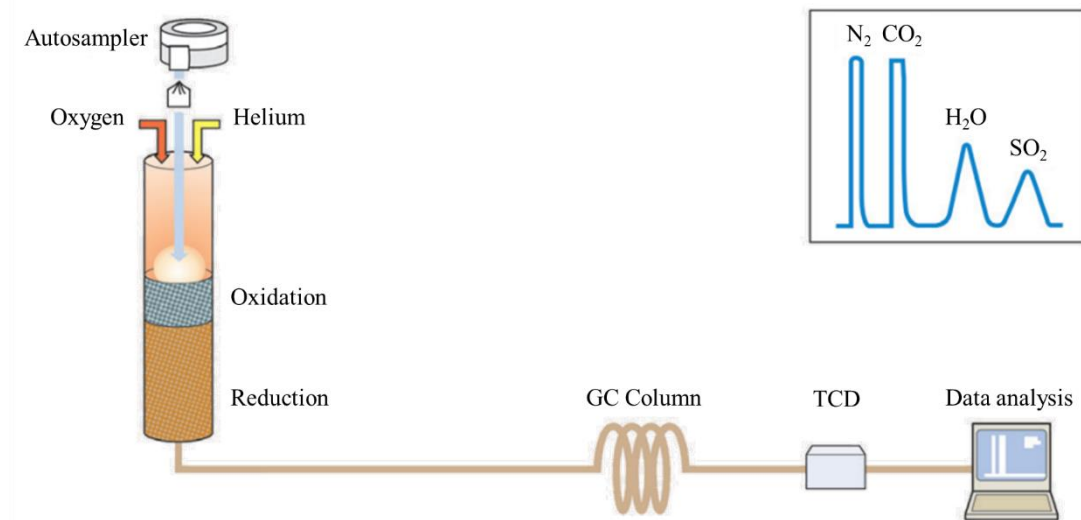


Figure 4.1.2 Schematic diagram of CHNS elemental analyser [125].

The hydrogen to carbon ratio (H/C) is determined by the ratio of (weight percentage of hydrogen by atomic weight of hydrogen) to (weight percentage of carbon by atomic weight of carbon). Similarly, the oxygen to carbon (O/C) ratio is the ratio of (weight percentage of oxygen by atomic weight of oxygen) to (weight percentage of carbon by atomic weight of carbon). Higher H/C ratios and lower O/C ratios indicate better fuel characteristics and less carbon dioxide emission from the fuel [126]. Furthermore, it is desirable to have a low O/C

ratio for pyrolysis feed, as a high O/C ratio could foster the production of oxygenated molecules during pyrolysis.

The calorific value analysis was conducted using a bomb calorimeter (Make: Hindustan Apparatus Manufacturing Company, India). A schematic diagram of the bomb calorimeter used for determining the calorific value is presented in Figure 4.1.3. For this analysis, approximately 1 g of the oven-dried sample underwent controlled combustion within a bomb pressurized with oxygen (purity 99.995%) to 30-bar, all surrounded by deionized water. This controlled combustion process occurred within the confines of deionized water, resulted in the release of heat and a subsequent elevation in the water temperature. Equation (4.1.4) below provides the mathematical formula for determining the calorific value which uses the change in water temperature for calculating it.

$$\text{Calorific value, } CV_S (\text{MJ/kg}) = \frac{\Delta T \times W - (CV_T + CV_W)}{M} \times 0.004187 \quad (4.1.4)$$

Where ΔT indicates the change in temperature of water expressed in °C, W indicates the water equivalent expressed in cal/°C, CV_T and CV_W indicate the respective calorific values for thread and wire expressed in cal and M indicates the mass of the sample expressed in g.

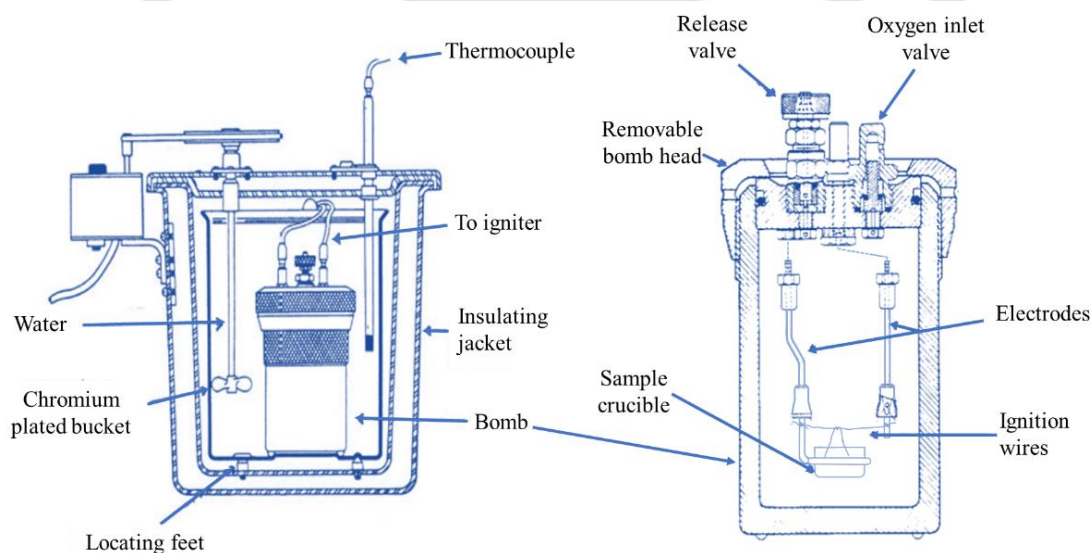


Figure 4.1.3 Schematic diagram of bomb calorimeter [127].

4.1.2 Density and porosity analysis

Solid matter exhibits three distinct densities: bulk, tapped and particle. The computation of these densities is detailed as follows. To determine the bulk density, ASTM E873-82 [128] method was followed. In this method, a known quantity of the oven-dried sample is loaded into

a measuring cylinder. The bulk density is given by the ratio of the mass to the volume occupied by the sample. Tapped density, on the other hand, is established by tapping the cylinder until the volume reaches a constant value. Particle density of the sample was assessed by loading four grams of the material in a measuring cylinder containing fifty millilitres of deionized water, followed by one minute of shaking to achieve uniform particle dispersion. An additional, three millilitres of water was poured through the inner walls of the cylinder to dislodge any sample adhering to the walls. The mixture was then shaken for an additional five minutes, and the final volume was recorded. Subtracting the amount of water from the total volume, yielded the volume of the test sample. The weight of the sample divided by this volume provides the particle density value. Equations (4.1.5), (4.1.6) and (4.1.7) below illustrates the mathematical formulations for determining bulk, tapped and particle density, respectively.

$$\text{Bulk density, } \rho_b (g/ml) = \frac{m_{gs} - m_g}{V_L} \quad (4.1.5)$$

$$\text{Tapped density, } \rho_{Tb} (g/ml) = \frac{m_{gs} - m_g}{V_T} \quad (4.1.6)$$

$$\text{Particle density, } \rho_p (g/ml) = \frac{m_p}{V_m - V_w} \quad (4.1.7)$$

Where in equation (4.1.5) and (4.1.6) m_g and m_{gs} indicate the mass of the empty graduated cylinder and mass of the cylinder plus sample, respectively, whereas V_L and V_T indicate the untapped and tapped volume of the sample, respectively. Further, in equation (4.1.7) m_p indicates the mass of the sample and V_m and V_w are the respective volume of the mixture and water.

Porosity is defined as the ratio of the difference of particle density and bulk density to particle density. Equation (4.1.8) below illustrates the mathematical formula for determining the porosity.

$$\text{Porosity, } \varepsilon_o = \frac{\rho_p - \rho_b}{\rho_p} \quad (4.1.8)$$

Where ρ_p and ρ_b indicate the particle and bulk density of the sample, respectively.

4.1.3 Flowability indices

Flowability indices are parameters used to assess the ability of a material to flow or move under the influence of gravity. These indices provide insights into the powder or granular material's behaviour during handling, storage and processing. As mentioned by Lumay et al. [129], the

angle of repose, Hausner ratio and Carr compressibility index are the common flowability indices to determine the flowability characteristics of a powdered material.

The angle of repose is a crucial parameter in the design of material storage and handling equipment as it offers insights into the flowability characteristics of a powder. The funnel test, conducted following the ASTM C1444 [130] method, was employed to determine the angle of repose. Figure 4.1.4 illustrates the schematic diagram for calculating the angle of repose. In this method, the sample is poured through a funnel over a horizontal surface until the flow from the triangular heap remains constant without slumping. The angle of repose is then determined by the angle of inclination of the resulting pile. A lower angle of repose indicates better flowability. Equation (4.1.9) below illustrates the mathematical formula for determining the angle of repose.

$$\text{Angle of repose } (\theta) = \tan^{-1} \left(\frac{H}{R} \right) \text{ where } R = D/2 \quad (4.1.9)$$

Where R indicates the radius of the base of the pile and H is the height of the pile.



Figure 4.1.4 Schematic diagram for calculating angle of repose.

The Hausner ratio is a parameter which provides the measure of interparticle friction of a powder. It is determined by the ratio of tapped density to the bulk density. A lower Hausner

ratio (< 1.18) indicates good flowability [131]. Equation (4.1.10) below illustrates the mathematical formula for determining the Hausner ratio.

$$\text{Hausner ratio (HR)} = \frac{\rho_{Tb}}{\rho_b} \quad (4.1.10)$$

Where ρ_{Tb} and ρ_b indicate the tapped and bulk density of the sample, respectively.

The Carr compressibility index is a parameter which provides the measure of powder bridge strength and stability of a powder. It is determined by the ratio of the difference of tapped density and bulk density to the tapped density, multiplied by 100. A low Carr compressibility index (< 15) indicates good flowability [131]. Equation (4.1.11) below provides the mathematical formula for determining the Carr compressibility index.

$$\text{Carr compressibility index (CCI)} = \frac{\rho_{Tb} - \rho_b}{\rho_{Tb}} \times 100 \quad (4.1.11)$$

Where ρ_{Tb} and ρ_b indicate the tapped and bulk density of the sample, respectively.

4.1.4 Combustion indices

The combustion indices are parameters used to assess the fuel potential of a material. These indices provide insights into the combustion behaviour of a material. As mentioned by Conag et al. [132], fuel ratio, combustibility index and volatile ignitability are the common combustion indices.

The fuel ratio (FR) provides insights into the composition of the fuel and its propensity to release energy during combustion. Specifically, it helps evaluate the balance between the combustible elements (fixed carbon) and the elements that undergo rapid combustion (volatile matter). FR values of the coal used in coal-based power plant ranges between of 0.5-2.0. Fuels with FR values more than 2.0 have been found to have encountered with issues of ignition and flame stability [131]. Equation (4.1.12) below illustrates the mathematical formula for determining the fuel ratio.

$$\text{Fuel ratio, FR} = \frac{FC_{db}}{VM_{db}} \quad (4.1.12)$$

Where VM_{db} and FC_{db} indicate the volatile matter and fixed carbon content of the material on dry basis.

The combustibility index provides a measure of how easily a substance can burn. It indicates a material's susceptibility to combustion. Materials with higher combustibility indices are more prone to ignition and sustain combustion under specific conditions. It is recommended

to have a minimum combustibility index value of 23 MJ/kg [131]. Equation (4.1.13) below illustrates the mathematical formula for determining the combustibility index.

$$\text{Combustibility index, } CI(\text{MJ/kg}) = \frac{CV_{db}}{FR} \times (115 - AC_{db}) \times \frac{1}{105} \quad (4.1.13)$$

Where FR , CV_{db} and AC_{db} indicate the fuel ratio, calorific value and ash content of the sample on dry basis.

The volatile ignitability pertains to the likelihood of volatile components within a substance to undergo ignition. The ease with which these volatile components initiate combustion can influence the efficiency of combustion processes. It is recommended to have a minimum volatile ignitability value of 14 MJ/kg [131]. Equation (4.1.14) below illustrates the mathematical formula for determining the volatile ignitability.

$$\text{Volatile ignitability, } VI(\text{MJ/kg}) = \left[\frac{CV_{db} - 0.338FC_{db}}{VM_{db} + MC_{db}} \right] \times 100 \quad (4.1.14)$$

Where CV_{db} , FC_{db} , VM_{db} and MC_{db} indicate the calorific value, fixed carbon, volatile matter and moisture content of the sample on dry basis.

In addition to these, the feedstocks have also been characterized using thermogravimetric analysis, powder X-ray diffraction analysis and field emission scanning electron microscopy to understand the thermal stability, crystallinity and surface morphology of the feedstocks which have been explained in the following sections.

4.1.5 Thermogravimetric and differential thermogravimetric analysis

The thermogravimetric analysis (TGA) technique is a thermal analysis method used to study the thermal stability of a material. The analyses of the feed materials were studied using a thermogravimetric analyser (Model: TG 209 F1 Libra, Make: Netzsch, Germany). A schematic diagram of the thermogravimetric analyser used to carry out the thermal analysis is also presented in Fig. 4.1.5. The thermogravimetric analyser operates based on the principle where the mass of a sample is monitored over temperature or time under a controlled temperature program and atmosphere. The TGA apparatus consists of an alumina crucible positioned on a precise thermobalance inside a furnace. During the analysis, the crucible is heated, and concurrently, the mass of the sample is recorded. To control the environment within the TGA chamber, a purge gas is utilized based on the requirement [133]. To carry out the thermogravimetric analysis, approximately 8 mg of sample underwent heating, at temperatures ranging from 30 to 800°C under a controlled heating rate of 10°C/minute. Nitrogen was served as the purge as well as the protective gas, with flow rates set at 40 and 20 mL/min, respectively.

The use of nitrogen as the purge gas aimed to create an inert environment, preventing oxidation of the sample and the occurrence of secondary reactions within the TGA chamber. Prior to the analysis, the thermobalance was purged with nitrogen gas and underwent 10-minute stabilization process to eliminate any potential instrumental error.

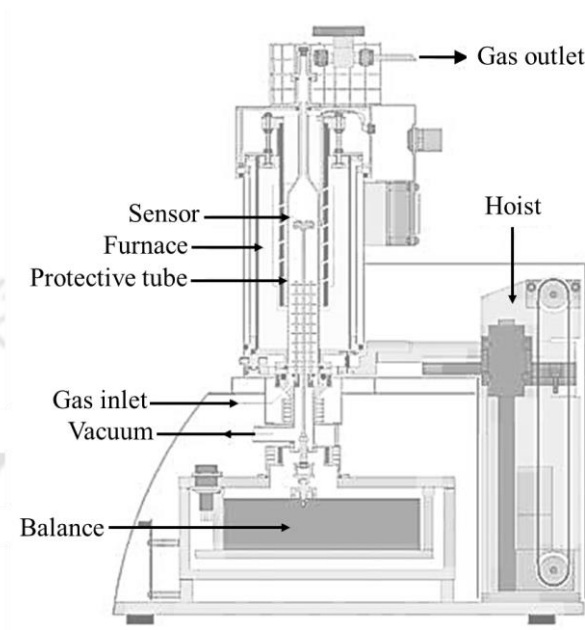


Figure 4.1.5 Schematic diagram of thermogravimetric analyser [134].

4.1.6 X-ray diffraction analysis

The X-ray diffraction (XRD) analysis technique is used to study the crystal structure of a material. The crystal structures of the feed materials were analyzed using a powder X-ray diffraction system (XRD, Make: Rigaku, Japan). A schematic diagram of the system used to carry out the X-ray diffraction analysis is also presented in Fig. 4.1.6. The X-ray diffraction analysis works on the principle of wave interference. When a beam of known wavelength is directed onto a powdered sample, the X-ray interacts with the crystalline structure of the material and undergo diffraction according to Bragg's law illustrated by equation (4.1.15). The resulting diffraction pattern, consisting of bright peaks and dark areas, is captured by a detector. Analyzing the positions and intensities of these peaks reveals information about the sample's crystal structure.

$$n\lambda = 2d \sin \theta_i \quad (4.1.15)$$

Where n is a positive integer which indicates the order of reflection, λ indicates the wavelength of X-ray source which has a value of $1.54056 \text{ \AA}$, d indicates the spacing between crystal lattice planes and θ_i is the angle of incidence of X-ray.

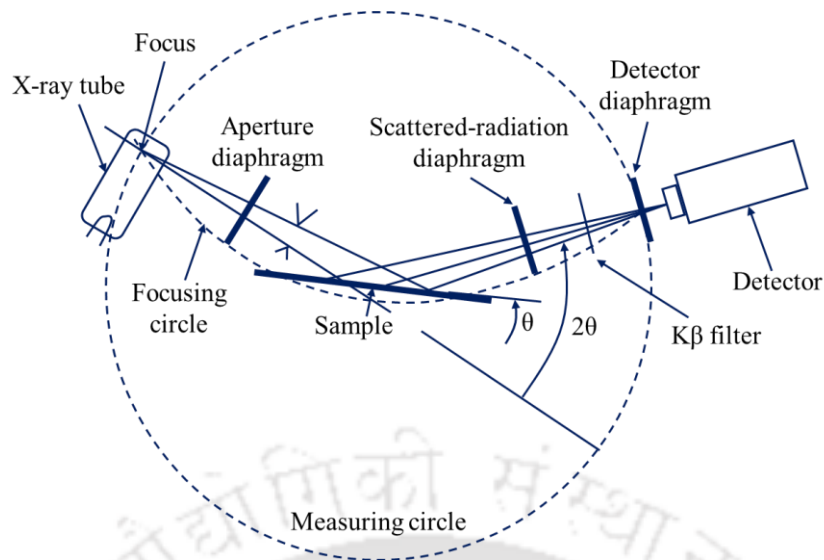


Figure 4.1.6 Schematic diagram of powder X-ray diffraction system [135].

The Debye-Scherrer technique was employed to determine the crystallite size of the samples. This technique utilizes equation (4.1.16) below to calculate the crystallite size:

$$L = k\lambda / \beta \cos\theta_d \quad (4.1.16)$$

Where k indicates the Scherrer constant which have a value of 0.9, λ indicates the wavelength of X-ray source which have a value of $1.54056 \text{ \AA}$, θ_d indicates the diffraction angle of the peak having the extreme height and β indicates the full width at half of the maximum (FWHM).

4.1.7 Field emission scanning electron microscopy

The field emission scanning electron microscopy (FESEM) is used to study the surface morphology of a material using accelerated electrons. In this technique a field emission gun produces accelerated electrons towards a high electrical field gradient. Primary electrons focus in a high vacuum column, where an electronic lens deflects electrons bombarding into the objects. Consequently, the objects emit secondary electrons, and their surface features impact the velocity and angle of these electrons. A detector captures emitted electrons, producing an electronic signal which is then converted into a video-scan image. The image can be viewed on a monitor and saved for analysis [136]. Using a field emission scanning electron microscope (Model: Gemini, Make: Carl Zeiss, Germany), the surface morphology of the feed materials were investigated. A schematic diagram of the setup has been illustrated in Figure 4.1.7.

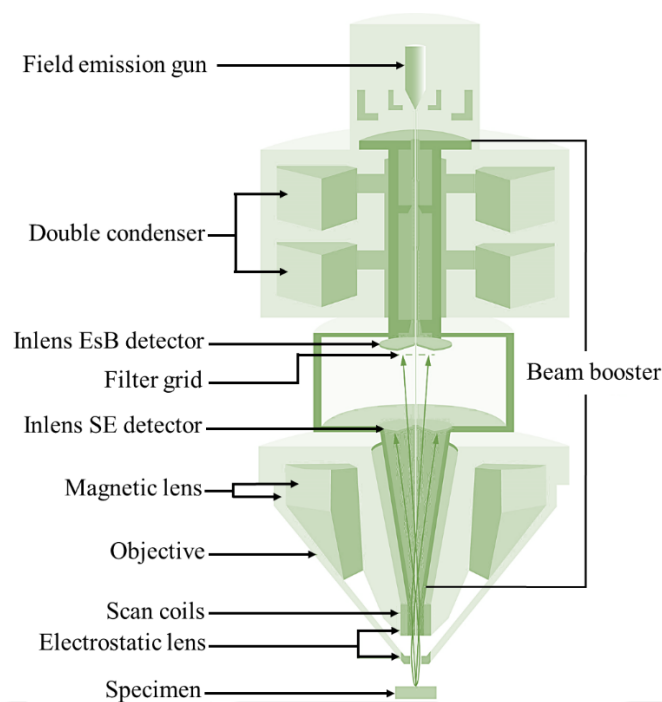


Figure 4.1.7 Schematic diagram of field emission scanning electron microscope [137].

4.2 SOLVENTS

The solvents employed for extracting the fuel phase of bio-oil in this research study include dichloromethane (EMPLURA®, Merck) and n-hexane (EMPARTA® ACS, Merck), supplied by Jaldhara & Co., India.

4.3 EXPERIMENTAL PROCEDURE OF PYROLYSIS

The single-feed and co-feed pyrolysis of *Erythrina indica* and *Azadirachta indica* biomass was studied in a stainless-steel tube batch type reactor (Make: Lelesil Innovative Systems, India) mounted vertically on an iron structure. The reactor had an inner diameter of 50 mm, a depth of 45 cm and a 1 litre water capacity which could hold approximately 300-350 g of pulverized biomass depending upon the bulk density. The system's temperature was elevated using a single-zone heating furnace. To extract the gas and liquid products separately, the system was also equipped with additional accessories such as vapour cooling condenser, gas liquid separator and liquid collecting vessel (which are also placed on the iron frame). A PID (Proportional-Integral-Derivative) controller was used to manage the furnace temperature, which aids in maintaining reactor temperature. Two thermocouples (K-type) were employed to monitor the reactor and the furnace temperature. The experimental procedure for the single-feed reactions involved introducing 300 g of the prepared feed material to the reactor. For co-feed reactions, the feed material was prepared by thoroughly mixing dry-grounded EI and AI

biomass at co-feed ratios of 1:4, 1:3, 1:2, 1:1, 2:1, 3:1 and 4:1. Subsequently, the reactions were carried out separately by feeding the prepared feed material. Nitrogen served as the inert medium for all the reactions and the reactions were carried out at a temperature of 600°C under an initial pressure of 1 bar. It is presumed that the reactions will proceed at a heating rate of 10°C per minute and that they will remain in situ for 2 hours after reaching the desired temperature. When biomass is pyrolytically converted, vapours made up of both condensable as well as non-condensable gases are produced. The condensed vapours that flow through the condenser were converted into bio-oil, the liquid product. The non-condensable gases were isolated out from the liquid product in the gas-liquid separation vessel and collected through the gas outlet after cooling. A fuel phase and a non-fuel phase make up the bio-oil that is produced. Methane, hydrogen, carbon monoxide and carbon dioxide are the primary elements that make up the non-condensable gases. Carbon is the primary component of the solid by-product known as biochar [87,138–140]. A schematic illustration of the setup utilised for the pyrolysis reactions is depicted in Figure 4.3.1.

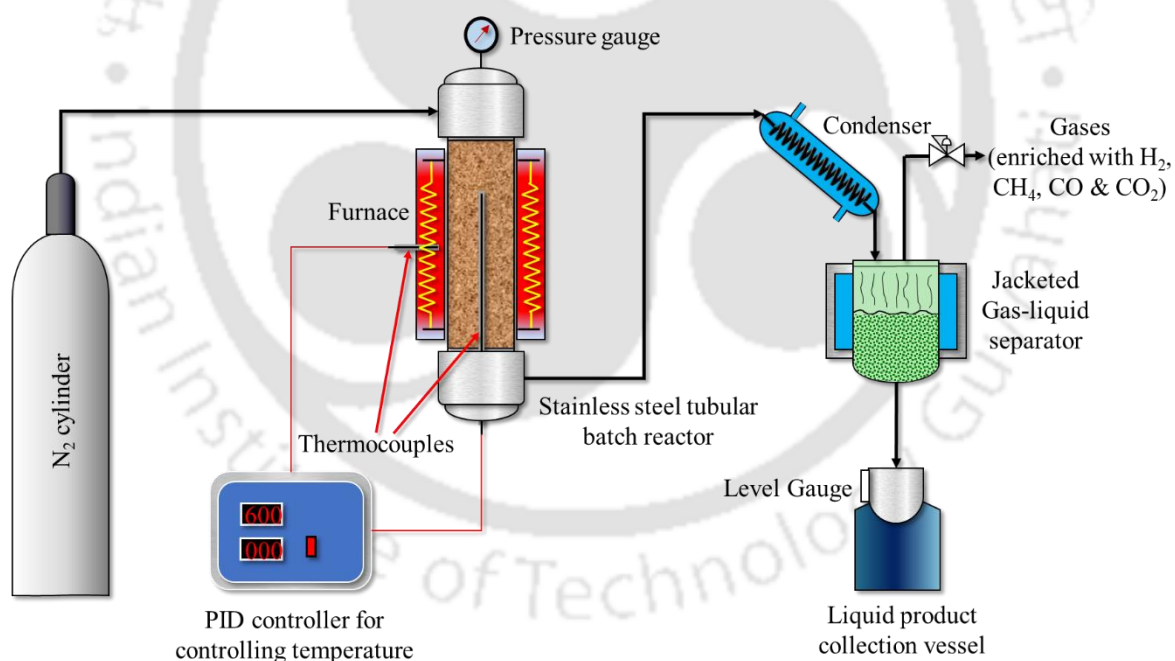


Figure 4.3.1 Schematic representation of the tubular reactor system used for pyrolysis reactions.

4.4 DISTRIBUTION OF PYROLYSIS PRODUCTS

Following completion of the pyrolysis reactions, the yield estimates in wt.% for each of the three products were determined. Equations (4.4.1), (4.4.2) and (4.4.3) described below provides the mathematical formulations for determining yield estimates of the pyrolysis products.

$$\% \text{ Yield of bio - oil} = \frac{\text{Weight of liquid product}}{\text{Weight of biomass fed}} \times 100 \quad (4.4.1)$$

$$\% \text{ Yield of biochar} = \frac{\text{Weight of biochar obtained}}{\text{Weight of biomass fed}} \times 100 \quad (4.4.2)$$

$$\% \text{ Yield of non - condensable gases} = 100 - \% \text{ Yields of (bio - oil + biochar) } \quad (4.4.3)$$

4.5 SOLVENT EXTRACTION OF FUEL PHASE OF BIO-OIL

The extraction of the fuel phase of bio-oil produced from the single-feed reactions were conducted using dichloromethane and n-hexane at four different volume percentages of solvent (10%, 20%, 30% and 40%) relative to the volume of raw bio-oil. The solvent was added to the raw bio-oil in a separating funnel, followed by rigorous shaking, allowing the fuel phase to separate from the non-fuel phase due to solubility and density differences. Once both phases were separated, they were collected individually for further analysis. The physicochemical and fuel properties of the fuel phase and non-fuel phase were then compared to those obtained without using a solvent, followed by subsequent characterization. Similarly, the extraction of the fuel phase of bio-oil produced from the co-feed reactions were performed using n-hexane at 10 volume percentage of solvent relative to the volume of bio-oil.

4.6 PYROLYSIS PRODUCT CHARACTERIZATION

4.6.1 Characterization of bio-oil

4.6.1.1 Physiochemical properties and calorific value

After phase separation, the physiochemical properties namely pH, density and viscosity were determined for both the phases. A 10 mL specific gravity bottle was used to measure density while a Eutech benchtop pH meter (Model: pH 700, Model: Thermo Fischer Scientific, India) was utilised to determine pH (Make: Borosil, India). Utilizing an Ostwald viscometer, the sample's viscosities were calculated. The calorific values of the fuel phases were determined using the bomb calorimeter as explained in Section 4.1.1.

4.6.1.2 Fourier transform infrared spectroscopy

The Fourier transform infrared (FTIR) spectroscopy is an analytical technique used to determine the chemical functional groups of a sample. FTIR spectrometer (Model: IRAffinity-1, Make: Shimadzu, Japan) facilitated the identification of chemical functional groups present in both phases within the 4000-400 cm^{-1} wavenumber range. The scanning was considered to be thirty scans with four cm^{-1} spectrum resolution. The software used to perform the baseline

correction and frequency variation was IR solution 1.5, was provided by Shimadzu. A schematic diagram of the setup used to carry out the FTIR analysis has been illustrated in Figure 4.6.1. The analysis works on the principle that infrared light is absorbed by all molecules except monoatomic and homopolar diatomic molecules. The chemical bond absorbs infrared radiation at a precise wavelength radiation when infrared radiation interacts with it thereby helping in identifying the functional groups. For e.g., the ketonic groups absorb infrared light at 1700-1720 cm^{-1} so if any infrared light is absorbed within this range will confirm the presence of ketone in the sample. Similarly, they would validate the presence of the C-H group of aromatic chemicals in the sample if it absorbs infrared light between 1180 and 1280 cm^{-1} .

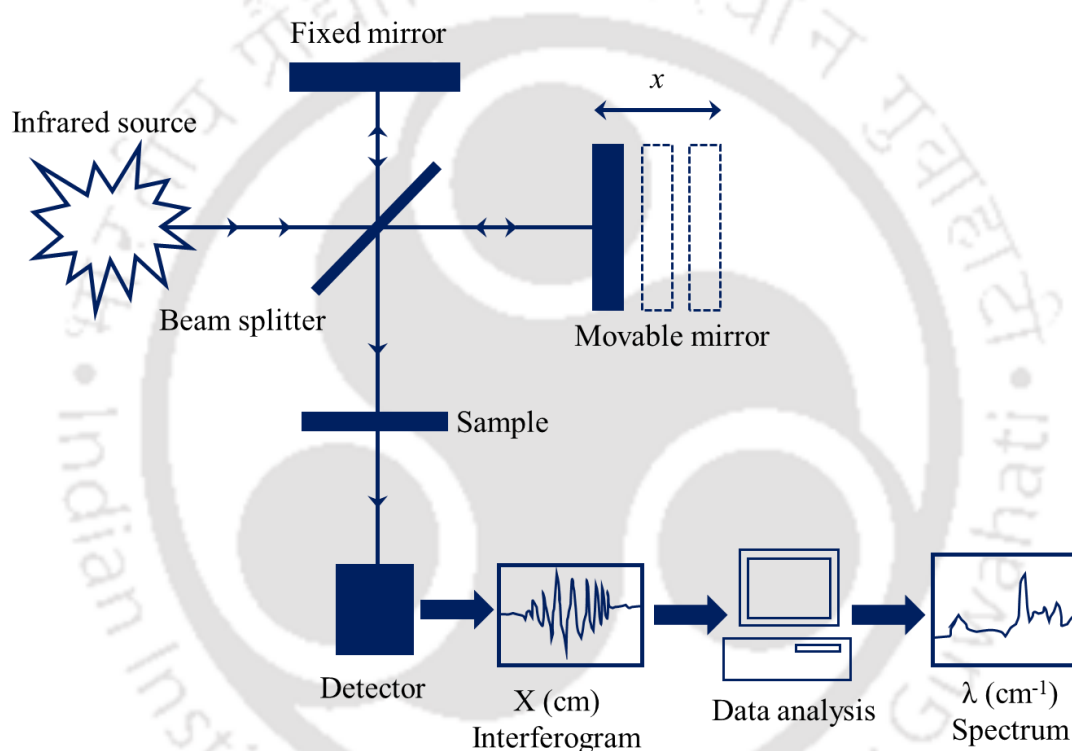


Figure 4.6.1 Schematic diagram of Fourier transform infrared spectrometer [141].

4.6.1.3 Proton nuclear magnetic resonance spectroscopy

The potential structure of the chemical compounds present in the fuel phase was ascertained using the proton nuclear magnetic resonance spectroscopy (^1H NMR, 600 MHz, Make: Bruker, USA). When a radio wave strikes a sample of hydrogen, it absorbs the energy and moves to a higher energy level, where it becomes stable after releasing the energy. The compound structure was identified by the help of energy released. For instance, the CH_3 protons at 1715 Hz and the OH proton at 1830 Hz, both of which would be recorded downfield from TMS, would be assigned to the radio wave signals from methanol. Similarly, for 1,2-

dimethoxyethane, 1017 Hz and 1065 Hz signals will be present downfield from TMS. The solvent used for this study is chloroform-D and the number of scans was considered to be 16 for the proton ^1H NMR analysis. A schematic diagram of the setup used to carry out the ^1H NMR analysis has been illustrated in Figure 4.6.2.

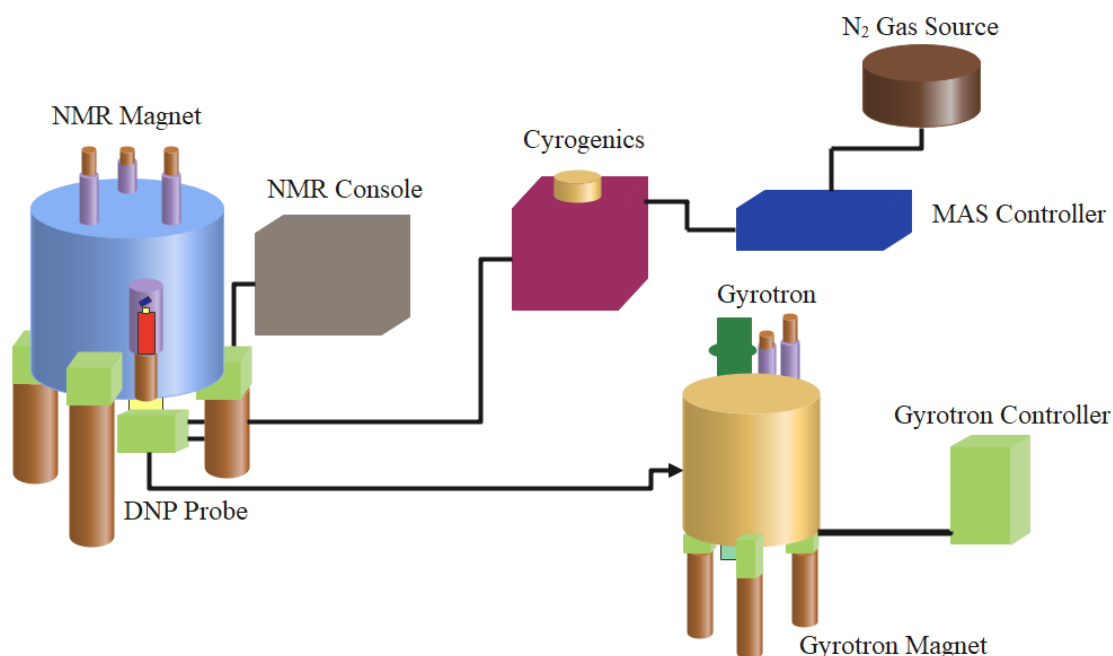


Figure 4.6.2 Schematic diagram of proton nuclear magnetic resonance spectrometer.

4.6.1.4 Gas chromatography and mass spectrometry

The gas chromatography and mass spectrometry (GC-MS) is a combination of two analytical tools to identify and quantify the probable compounds present in a sample. The principle behind how the gas chromatograph (GC) operates is that heating a mixture causes it to split the sample into distinct compounds. Through a column, the hot gases are transported with an inert gas (such as helium). The separated components flow into the mass spectrometer (MS) as they leave the opening of the column for identification [142]. A schematic diagram of the setup used to carry out the GC-MS analysis has been illustrated in Figure 4.6.3. Using the National Institute of Standards and Technology (NIST) library, the identification of the likely chemicals contained in the samples is performed. The fuel phase samples were characterized using a gas chromatography and mass spectrometer (PerkinElmer Clarus680 GC/600C MS, USA). A capillary column (Elite-5MS, diameter of 250 μm and a length of 60 m composing phase 5% diphenyl and 95% dimethyl polysiloxane) was used for the GC analysis. At 280°C, a split injector with a 20:1 split ratio was employed. One millilitre per minute of 99.5% pure helium

was allowed to flow. The temperature of the GC oven was first set at 50°C for a 2-minute hold period before ramping up by 5°C/min to 280°C. The solvent used for preparing the samples for the GC-MS analysis is acetone of spectroscopic grade, manufactured by Merck.

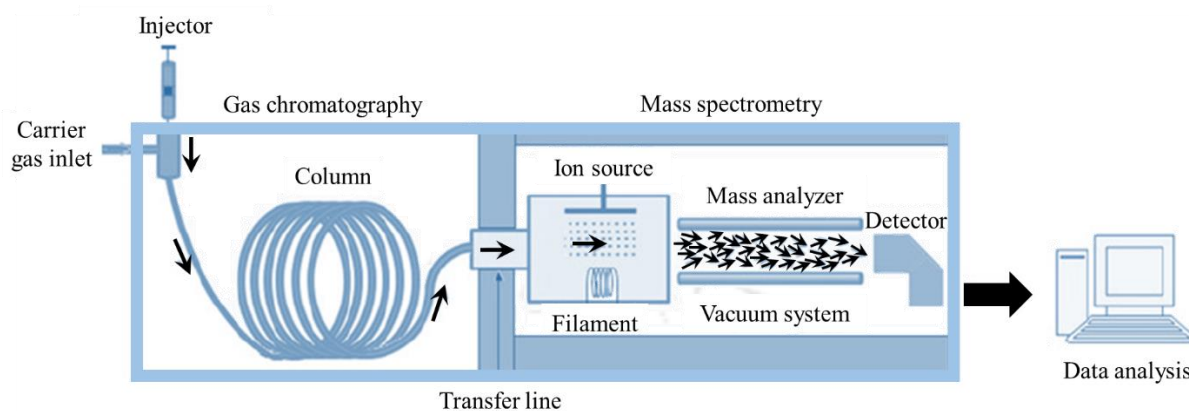


Figure 4.6.3 Schematic diagram of gas chromatography-mass spectrometer [142].

4.6.2 Characterization of biochar

As the pyrolysis process produces biochar as a solid fuel, therefore it is very much necessary to make a comparative study of the physiochemical properties along with flowability and combustion indices of biomass and the biochar to check the improvement in the solid product obtained. The flowability and combustion indices would be helpful in designing continuous feed processes. Hence, the flowability and combustion indices were determined for both the biomass and biochar. The proximate and ultimate along with calorific value analyses of the biochar samples were carried out using the same ASTM methods as described for the feed material. Other properties such as flowability indices and combustion indices were also determined for the biochar samples to obtain a much-detailed picture. Similar to the methods followed for the feed material, the TGA, XRD and FESEM procedures were also used to examine the thermal stability, crystal structure and surface morphology of the biochar samples. In addition to these the biochar samples were also characterized with energy-dispersive X-ray analysis to study the essential element present in the biochar necessary for soil conditioning.

4.6.2.1 Energy-dispersive X-ray spectroscopy

The energy-dispersive X-ray (EDX) spectroscopy provides quantitative information on the elements that are present within a sample. A field emission scanning electron microscope (Model: Gemini, Make: Carl Zeiss, Germany) was used to carry out the EDX study. In EDX analysis, the electron beam strikes an atom's inner shell, ejecting an electron and creating a positively charged electron hole. This displacement attracts an outer shell electron to fill the

vacancy. As the electron transitions from the outer higher-energy to the inner lower-energy shell, the energy difference releases an X-ray. The X-ray energy corresponds to the characteristic of the element and transition. A silicon drift detector collects the emitted X-rays and interprets the signal through software. This analysis helps in identifying and quantifying each element within a sample [143]. Figure 4.6.4 illustrates the working principle of EDX analysis.

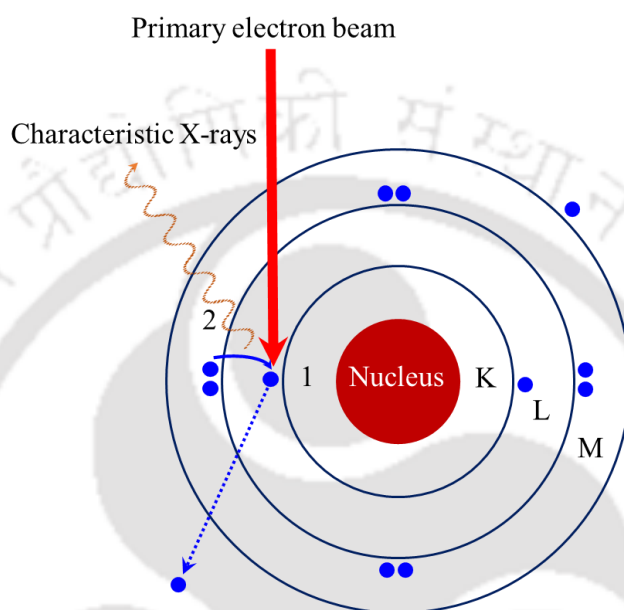


Figure 4.6.4 Working principle of energy-dispersive X-ray analysis [143].

4.6.3 Characterization of non-condensable gases

4.6.3.1 Gas chromatography

To analyse the composition of various gases, present in the gaseous product, samples of non-condensable gases were collected in tedlar bags and analysed using a gas chromatograph (GC, Model: Trace 1110, Make: Thermo Scientific, USA). A schematic diagram of the setup used to carry out the GC analysis has been illustrated in Figure 4.6.5. The analysis of non-condensable gas samples involved injecting 1 mL of gas into the column using a syringe. A thermal conductivity detector (TCD) was employed to detect the gases in the packed bed column used for this investigation. TCD detection relies on the difference in thermal conductivity between the sample and the carrier gas [144]. Helium is often utilized as the carrier gas due to its high constant value for thermal conductivity. However, when helium and hydrogen are target compounds nitrogen or argon is used as the carrier gas. Each compound has a distinct thermal conductivity constant. The thermal conductivity values for argon, carbon monoxide, carbon dioxide, hydrogen and methane are 17.7, 16.0, 25.0, 186.6 and 34.4,

respectively [145]. A peak is detected as a negative value when the thermal conductivity of the target chemical exceeds that of the carrier gas. TCD can effectively detect various chemicals, excluding the carrier gas, though it possesses lower sensitivity compared to other detectors. Argon served as the carrier gas in this investigation, with a set flow rate of 12 mL/min. The analysis runtime for this procedure is 15 minutes. Considering the vol.% of gases, the calorific value of the non-condensable gases were determined using equation (4.6.1) below by Xiao et al. [146]:

$$CV, (kJ/Nm^3) = (CO\% \times 3018 + H_2 \times 3052 + CH_4\% \times 9500) \times 0.01 \times 4.1868 \quad (4.6.1)$$

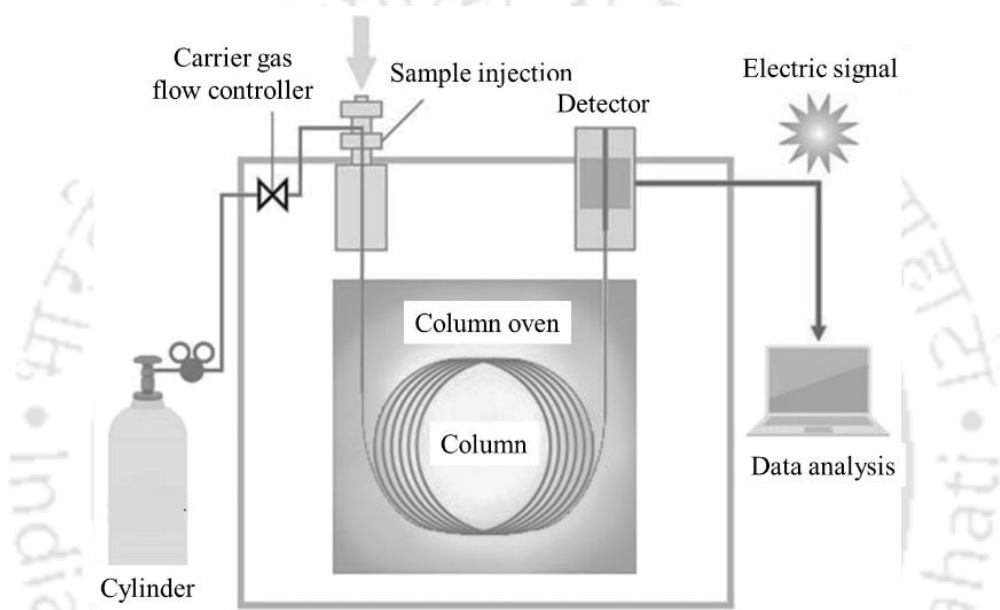


Figure 4.6.5 Schematic diagram for gas chromatograph [147].

4.7 ECONOMIC ANALYSIS

Economic analysis is a crucial tool for assessing the feasibility of any process by evaluating the associated costs without physically constructing the plant. This analysis helps in identifying the risks involved in building the plant and assesses its profitability potential. To evaluate the economic feasibility of scaling up the pyrolysis process, the methodology outlined by Yahya et al. [148] was employed. This approach considers the initial investment in the pyrolysis plant, as well as the fixed and variable costs associated with its operation. Several bases were made to estimate the fixed costs involved in running the pyrolysis plant to study its economic feasibility, as detailed in Table 4.7.1. These include the source of capital, annual availability of the pyrolysis unit, depreciation period and the capacity of the pyrolysis unit.

Table 4.7.1 Bases for pyrolysis unit to study economic feasibility.

Parameters	Assumptions	Reference
Financing	100% owned capital	-
Pyrolysis unit availability	312 days/year	[149]
Pyrolysis unit depreciation period	15 years	Shree Balaji Engineering Works, Jaipur, India
Capacity of the pyrolysis unit	10 tons per day	[148]

The purchase equipment cost for the 10-ton capacity reactor batch type is determined by scaling up the cost of a 5-ton capacity batch reactor, as provided by Shree Balaji Engineering Works, Jaipur, India. The estimated equipment cost for the scaled up pyrolysis unit is calculated by using equation (4.7.1) provided by Peters and Timmerhaus [150]. Figure 4.7.1 presents a schematic diagram detailing the essential components of the pyrolysis unit. The additional equipment including the shredder, biomass dryer, additional storage tank, backhoe loader, DG set, transformer, installation cost, shed and civil work and other miscellaneous equipment were quoted from various local vendors.

$$\text{Cost of equipment, } A = \text{Cost of equipment, } B \left(\frac{\text{Capacity of equipment, } A}{\text{Capacity of equipment, } B} \right)^{0.6} \quad (4.7.1)$$

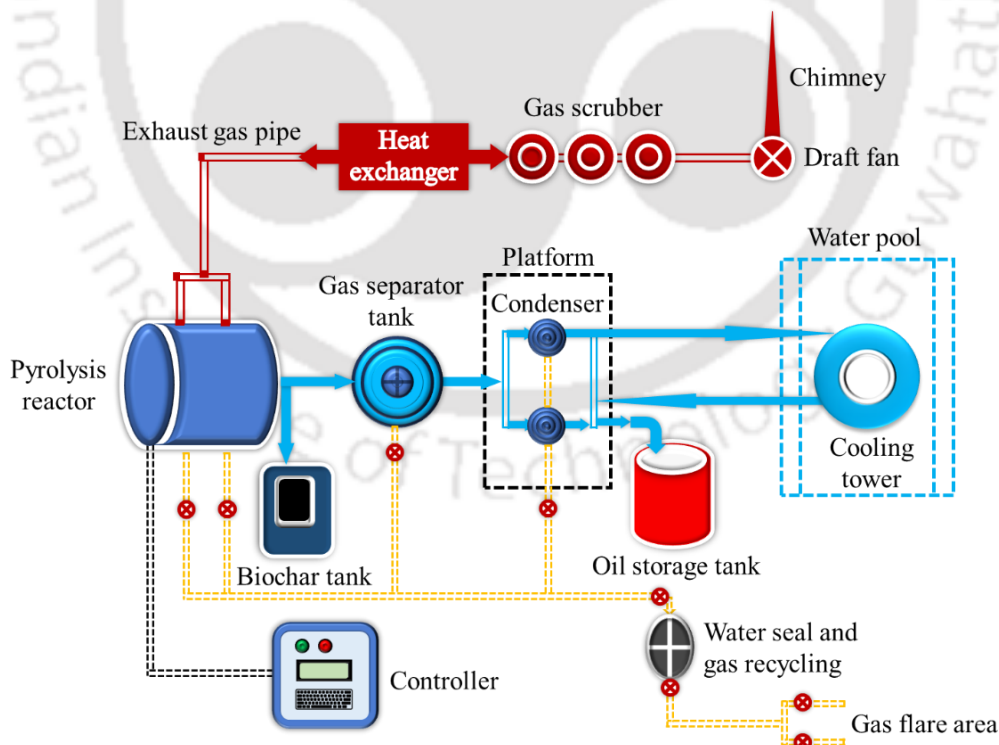


Figure 4.7.1 Schematic diagram of the scaled-up pyrolysis unit [151].

The sources for calculating the fixed and variable costs, which encompass depreciation rate, interest on investment, land rent, insurance rate, repair and maintenance expenses, labor cost, feedstock purchasing and transportation cost, electricity and fuelwood for biomass pre-processing and initial heating of the reactor, packaging and marketing and miscellaneous chemicals for fuel phase extraction and cleaning, are detailed in Table 4.7.2.

Table 4.7.2 Sources for calculating the fixed and variable costs to operate the pyrolysis plant.

Item	Cost factors	Reference
Fixed cost	Depreciation rate	11.25% of initial cost of investment per annum [148]
	Interest on investment	10% of initial cost of investment per annum [149]
	Land rent	INR 1,00,000 per annum Agreement
	Insurance rate	2% of initial cost of investment per annum [148]
Variable cost	Repair and maintenance cost	2% of initial cost of investment per annum [148]
	Labor cost (01 highly skilled, 02 semi-skilled and 09 unskilled workers)	INR 17,73,648 per annum As per Assam govt. rules, India
	Feedstock purchasing and transportation cost	INR 5 per kg Jay Bio Fuel, Nadiad, India
	Cost of electricity for biomass pre-processing and fuel wood for initial heating of reactor	INR 1,70,000 per annum Ragaanvaya India Pvt. Ltd., Guwahati, India
	Packaging and marketing cost	INR 40,000 per annum Ragaanvaya India Pvt. Ltd., Guwahati, India
	Acetone for cleaning (20 litres per day)	INR 45 per litre Valia Industries, Bharuch, India
	n-hexane for extraction of fuel phase of bio-oil	INR 58 per litre Siddhi Vinayak Industries, Ahmedabad, India

The minimum fuel selling price of the fuel phase of the bio-oil was calculated based on the total operating cost, revenue generated from biochar and quantity of bio-oil produced. Equation (4.7.2) below illustrates the mathematical formula for determining the minimum fuel selling price of fuel phase.

$$\text{Minimum fuel selling price} = \frac{\text{Annual operating cost} - \text{Revenue generated from biochar per annum}}{\text{Fuel phase of bio-oil produced per annum}} \quad (4.7.2)$$

4.7.1 Break-even analysis

The break-even analysis is a financial tool used to determine the sales volume necessary to cover all costs and the duration needed to recover the initial investment. The break-even point signifies the sales level at which total revenues equal total costs, resulting in no profit or loss. Calculating this point helps businesses understand the minimum performance needed to avoid financial losses. When the concept of the payback period is incorporated, break-even analysis gains additional utility by pinpointing the time required for an investment to repay itself through generated cash flows. The payback period is the duration needed for cumulative net cash flow to match the initial investment. This metric is vital for evaluating the financial viability and risk associated with new projects, products or business expansions. By evaluating both the break-even point and the payback period, businesses can make more informed decisions regarding pricing, cost management and investment strategies. This analysis allows them to determine the timeframe required to recoup their investment and begin generating profits, which is essential for effective financial planning and resource allocation. This integrated approach provides a thorough understanding of financial dynamics, enabling businesses to strategize more effectively and mitigate potential risks. The break-even point, in terms of cost and revenue, can be determined using equation (4.7.3) illustrated below.

$$\text{Break even point} = \frac{X}{Y-Z} \quad (4.7.3)$$

Where X indicates the total fixed cost invested at the inception of the plant, Y indicates the gross revenue generated by the pyrolysis plant per annum and Z indicates the total fixed and variable costs incurred annually to operate the plant.

4.7.2 Net present value

Net present value is a financial tool used to evaluate the profitability of a project. It is calculated by taking the difference between the present value of cash inflows and the present value of cash outflows over the life of the project. The salvage value at the end of the project was considered to be 10% of the initial investment. To determine the net present value, future cash flows are discounted to their present value using a specific discount rate that generally reflects the project's risk and the cost of capital. In this study a discount rate of 10% was assumed. A positive net present value suggests that the project is likely to be successful, while a negative net present value indicates that the project may not be financially viable.

4.7.3 Internal rate of return

The internal rate of return is a financial tool used to assess the viability of an investment. It represents the discount rate at which the net present value of all future cash flows from the investment equals zero. In simpler terms, internal rate of return is the rate at which the present value of a project's cash inflows matches the present value of its cash outflows. This rate indicates the potential profitability of the investment over its useful life. A higher internal rate of return suggests a more lucrative investment. Widely used in capital budgeting, internal rate of return helps compare and prioritize different investment opportunities. An investment is deemed worthwhile if its internal rate of return surpasses the required rate of return or the cost of capital.



Chapter 5: Kinetics and Thermodynamics Study of Pyrolysis Process

The kinetics of pyrolysis process can be obtained by using TGA data at different heating rates and kinetics, in turn, are useful in obtaining the thermodynamics of the process.

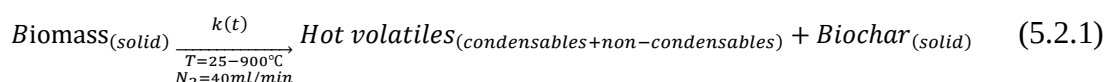
5.1 THERMOGRAVIMETRIC AND DIFFERENTIAL THERMOGRAVIMETRIC ANALYSIS

The non-isothermal study of single and co-feed pyrolysis processes of *Erythrina indica* and *Azadirachta indica* biomass was studied using thermogravimetric analyzer discussed in section 4.1.5, while the analyses being performed at heating rates of 10, 20, 30 and 40°C/min. For this, approximately 9 mg of samples underwent heating in a TGA chamber, at temperatures ranging from 25 to 900°C. The TGA data generated was used to study the kinetics and thermodynamics associated to the pyrolysis processes which have been discussed in the following sections.

5.2 EVALUATION OF KINETIC TRIPLETS

The kinetic parameters, namely the apparent activation energy (E_a) expressed as kJ/mol, pre-exponential factor (k_o) expressed as min⁻¹ and the associated reaction mechanism (Z_a) are generally known as kinetic triplets. Iso-conversional techniques were applied to determine the apparent activation energy and pre-exponential factor at various conversion ratios. To deduce the inherent reaction mechanism, master plots including Criado's master plot and master plot based on integral form of kinetic data were employed.

As stated in the Introduction section that biomass pyrolysis is an intricate process which involves numerous reactions within a short period of time. Moreover, it is essential to note that the pyrolysis process can differ based on the type of pyrolysis employed. Thus, predicting and explaining the exact reaction mechanism is almost impossible. However, researchers have used the following generic equation (5.2.1) to explain the biomass pyrolysis process:



The generic expression for conversion (α) in a pyrolysis process is given by:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \quad (5.2.2)$$

Where m_i indicates the initial mass of the biomass sample at time $t = 0$, m_f indicates the final mass of the biomass sample at time $t = t_f$ and m_t indicates the mass of the biomass sample at any moment within the time interval $0 < t < t_f$.

The fundamental rate equation used to assess the kinetics of solid-state thermal decomposition is as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (5.2.3)$$

Where $\frac{d\alpha}{dt}$ indicates the reaction rate, $k(T)$ indicates the reaction rate constant which is temperature-dependent and $f(\alpha)$ expresses the differential form of reaction model contingent upon on degree of conversion.

The rate constant $k(T)$ is generally expressed using Arrhenius equation can be formulated as:

$$k(T) = k_0 \exp\left(-\frac{E_\alpha}{RT}\right) \quad (5.2.4)$$

Where k_0 indicates the pre-exponential factor expressed in terms of min^{-1} , E_α indicates the apparent activation energy expressed in terms of kJ/mol , R indicates the universal gas constant expressed in $\text{J/mol}\cdot\text{K}$ and T indicates the absolute temperature expressed in K .

Substituting equation (5.2.4) in (5.2.3), we get:

$$\frac{d\alpha}{dt} = k_0 \exp\left(-\frac{E_\alpha}{RT}\right) f(\alpha) \quad (5.2.5)$$

In non-isothermal studies, the sample weight varies with time due to change in temperature. Subsequently, the heating rate can be expressed as:

$$\beta = \frac{dT}{dt} \quad (5.2.6)$$

Now, introducing the heating rate (β) in equation (5.2.5) and rearranging, we get:

$$\frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \exp\left(-\frac{E_\alpha}{RT}\right) dT \quad (5.2.7)$$

Upon integrating equation (5.2.7), we get:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \int_0^T \exp\left(-\frac{E_\alpha}{RT}\right) dT = \frac{k_0 E_\alpha}{\beta R} \int_\infty^x \left(-\frac{e^{-x}}{x^2}\right) dx = \frac{k_0 E_\alpha}{\beta R} p(x) \quad (5.2.8)$$

Where $x = \frac{E_\alpha}{RT}$ with $g(\alpha)$ indicates the integral form of reaction rate and $p(x)$ indicates the temperature integral, and it lacks a straightforward analytical solution. Consequently, various approximation methods were devised to solve this equation, giving rise to the development of several integral equations.

5.2.1 Calculation of apparent activation energy (E_α) and pre-exponential factor (k_o)

Evaluation of two kinetic parameters of the kinetic triplets, specifically the apparent activation energy (E_α) and pre-exponential factor (k_o) were carried out using five distinct iso-conversional methods. The foundation of iso-conversional methods rests on the assumption that, at a specific conversion, the reaction rate is exclusively dependent on temperature and the kinetic parameters remain unaffected due to heating rate, as illustrated by equation (5.2.9) below [152].

$$\left[\frac{d \ln \left(\frac{d\alpha}{dt} \right)}{dT^{-1}} \right]_\alpha = -\frac{E_\alpha}{R} \quad (5.2.9)$$

The iso-conversional methods used to determine E_α and k_o are elucidated in the following sub sections.

5.2.1.1 Differential Friedman method

The differential Friedman method (DFM) [153], formed on the basis of the differential expression of rate law, is the simplest method to evaluate the kinetic parameters (E_α and k_o) as a function of conversion. This method avoids the application of any approximation to determine the kinetic factors, thus reducing the possibility of inaccuracy. Equation (5.2.10) below illustrates the generalized equation for DFM:

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln \left[\beta \left(\frac{d\alpha}{dT} \right) \right] = \ln [k_o f(\alpha)^n] - \frac{E_\alpha}{RT_\alpha} \quad (5.2.10)$$

The kinetic factors (E_α and k_o) were ascertained by analyzing the slope and intercept derived from plotting the graph of $\ln \left[\beta \left(\frac{d\alpha}{dT} \right) \right]$ against $\frac{1}{T_\alpha}$.

5.2.1.2 Kissinger-Akharia-Sunose method

Kissinger [154] and Akharia-Sunose [155] developed an integral method often referred to as the Kissinger-Akharia-Sunose (KAS) method to evaluate the kinetic parameters (E_α and k_o) using Coats-Redfern approximation in equation (5.2.8). Conferring to Coats-Redfern's approximation one can write $p(x)$ as:

$$p(x) = x^2 \exp^{-x} \quad (5.2.11)$$

Upon substituting, $p(x)$ from above equation in equation (5.2.8) and rearranging the terms, we obtain the general formula for KAS method, as illustrated below in equation (5.2.12):

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left[\frac{k_o R}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{RT_\alpha} \quad (5.2.12)$$

The kinetic parameters (E_α and k_o) were ascertained by analyzing the slope and intercept derived from plotting the graph of $\ln\left(\frac{\beta}{T_\alpha^2}\right)$ against $\frac{1}{T_\alpha}$.

5.2.1.3 Ozawa-Flynn-Wall method

Ozawa [156] and Flynn-Wall [157] proposed an iso-conversional approach often referred to as the Ozawa-Flynn-Wall (OFW) for investigating the kinetic parameters (E_α and k_o) by employing Doyle's approximation for $p(x)$ in equation (5.2.8). Conferring to Doyle's approximation the equation for $p(x)$ can be written as:

$$p(x) = \exp(-0.457x - 2.315) \quad (5.2.13)$$

Upon substituting the aforementioned equation of $p(x)$ into equation (5.2.8) and rearranging the terms, one can arrive at the general formula for OFW method, as illustrated in equation (5.2.14) below:

$$\ln(\beta) = \ln\left[\frac{k_o E_\alpha}{R g(\alpha)}\right] - 2.315 - 0.457 \frac{E_\alpha}{RT_\alpha} \quad (5.2.14)$$

The kinetic parameters (E_α and k_o) were ascertained by analyzing the slope and intercept derived from plotting the graph of $\ln(\beta)$ against $\frac{1}{T_\alpha}$.

5.2.1.4 Starink method

The Starink (STK) method uses Senum and Yang's approximation [158] as well as Coats-Redfern's approximation to determine the kinetic parameters (E_α and k_o). These were investigated by employing the approximation for $p(x)$ by Starink in equation (5.2.8).

$$p(x) = \exp(-1.0008x - 0.312)x^{1.92} \quad (5.2.15)$$

Substituting above equation of $p(x)$ in equation (5.2.8) and rearranging the terms, one can obtain the general formula for STK method as illustrated in equation (5.2.16) below:

$$\ln\left(\frac{\beta}{T_\alpha^{1.92}}\right) = \ln\left[\frac{k_o R^{0.92}}{E_\alpha^{0.92} g(\alpha)}\right] - 0.312 - 1.0008 \frac{E_\alpha}{RT_\alpha} \quad (5.2.16)$$

The kinetic parameters (E_α and k_o) were ascertained by analyzing the slope and intercept derived from plotting the graph of $\ln\left(\frac{\beta}{T_\alpha^{1.92}}\right)$ against $\frac{1}{T_\alpha}$.

5.2.1.5 Distributed activation energy model

The distributed activation energy model (DAEM) serves as a tool for examining intricate reaction mechanisms within the biomass pyrolysis process. DAEM postulates that the reactions taking place in pyrolysis process are first-order, potentially involving simultaneous, irreversible reactions with distinct activation energies and bond strength species. The equation representing the liberation of volatiles concerning reactant species and their mass balance can be expressed as follows:

$$1 - \alpha = \int_0^\infty \exp\left(-k_o \int_0^t \exp\left(\frac{-E_\alpha}{RT}\right) dt\right) f(E_\alpha) dE \quad (5.2.17)$$

Where $f(E)$ denotes the distribution of activation energy, which is satisfied by Miura's approximation [159] given below:

$$\int_0^\infty f(E_\alpha) dE = 1 \quad (5.2.18)$$

$$1 - \alpha = \int_{E_\alpha}^\infty f(E_\alpha) dE \quad (5.2.19)$$

$$\frac{0.545\beta E_\alpha}{k_o R T_\alpha^2} = \exp\left(\frac{-E_\alpha}{RT_\alpha}\right) \quad (5.2.20)$$

The kinetic factors (E_α and k_o) were investigated using Miura's approximation in equation (5.2.8). Equation (5.2.21) below illustrates the approximated equation using the Miura's approximation:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left[\frac{k_o R}{E_\alpha}\right] + 0.6075 - \left[\frac{E_\alpha}{RT_\alpha}\right] \quad (5.2.21)$$

The kinetic parameters (E_α and k_o) were ascertained by analyzing the slope and intercept derived from plotting the graph of $\ln\left(\frac{\beta}{T_\alpha^2}\right)$ against $\frac{1}{T_\alpha}$.

5.2.2 Reaction mechanism

To comprehend the intricate reaction mechanism inherent to the biomass pyrolysis process, it becomes imperative to employ diverse master plot techniques. These techniques, whether grounded in differential or integral formulations or a synthesis of both, serve to provide comparable outcomes for scrutinizing the kinetic facets of biomass decomposition. In this investigation, both Criado's master plot and master plot derived from the integral form of the

kinetic data were utilized to deduce the reaction mechanism associated to biomass pyrolysis process. The identification of the associated reaction mechanism was achieved by comparing the experimental plot with the corresponding theoretical plots.

5.2.2.1 Criado's master plot

To deduce the complex reaction mechanism (Z_α) involved in the pyrolysis process, Criado et al. [160] derived an expression for heterogenous reactions as illustrated in equation (5.2.22).

$$z(\alpha) = \frac{\left(\frac{d\alpha}{dt}\right)}{\beta} p(x) T \quad (5.2.22)$$

Where $p(x)$ is expressed as, $p(x) = \frac{e^{-x}}{x(x+4)(x^2+6x+6)}$

The theoretical (Z_α) curves were generated using below equation (5.2.23) and the corresponding functions has been detailed in Table 5.2.1.

$$z(\alpha) = f(\alpha) \times g(\alpha) \quad (5.2.23)$$

Whereas the experimental (Z_α) curve was derived using equation (5.2.22) based on thermogravimetric data, with the activation energy determined through the differential Friedman method.

Table 5.2.1 Expressions of different reaction models for solid state reactions.

Model name	Model code	Differential form $f(\alpha)$	Integral form $g(\alpha)$
Power law	P2	$2(\alpha)^{1/2}$	$(\alpha)^{1/2}$
Power law	P3	$3(\alpha)^{2/3}$	$(\alpha)^{1/3}$
Power law	P4	$4(\alpha)^{3/4}$	$(\alpha)^{1/4}$
Avrami-Erofeyev	A2	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
Avrami-Erofeyev	A3	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
Avrami-Erofeyev	A4	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
Contracting cylinder	R2	$2(1-\alpha)^{1/2}$	$1 - (1-\alpha)^{1/2}$
Contracting sphere	R3	$3(1-\alpha)^{2/3}$	$1 - (1-\alpha)^{1/3}$
1-D diffusion	D1	$\frac{1}{2\alpha}$	α^2
2-D diffusion	D2	$-\left[\frac{1}{\ln(1-\alpha)}\right]$	$[(1-\alpha) \ln(1-\alpha)] + \alpha$
3-D diffusion	D3	$\frac{3(1-\alpha)^{2/3}}{2(1-\alpha)[- \ln(1-\alpha)]^{1/3}}$	$(1 - (1-\alpha)^{1/3})^2$
Zero order	F0	1	α
1st order	F1	$(1-\alpha)$	$-\ln(1-\alpha)$
2nd order	F2	$(1-\alpha)^2$	$\left[\frac{1}{(1-\alpha)} - 1\right]$
3rd order	F3	$(1-\alpha)^3$	$\frac{1}{2}\left[\frac{1}{(1-\alpha)^2} - 1\right]$

5.2.2.2 Master plots based on the integral form of kinetic data

In this approach, the mathematical expression for determining $g(\alpha)$ is obtained by deriving equation (5.2.5), which is expressed in equation (5.2.24) below:

$$g(\alpha) = \frac{k_o E_\alpha}{\beta R} \int_{\infty}^x \left(-\frac{e^{-x}}{x^2} \right) dx = \frac{k_o E_\alpha}{\beta R} p(x) \quad (5.2.24)$$

Where $p(x) = \int_{\infty}^x \left(-\frac{e^{-x}}{x^2} \right) dx$ indicates the temperature integral and it lacks any analytical solution. However, the temperature integral can be approximated using Senum-Secondary Yang's rational approximation $p(x) = \frac{e^{-x}}{x(x+4)(x^2+6x+6)}$ which has a high accuracy for $p(x)$.

Here $x = \frac{E_\alpha}{RT}$, and the final equation for determining the reaction model through integral master plots is as follows:

$$\frac{g(\alpha)}{g(0.5)} = \frac{p(x)}{p(0.5)} \quad (5.2.25)$$

Where $g(0.5) = \frac{k_o E_\alpha}{\beta R} p(0.5)$.

Similar to the Criado's master plot, the plot of $g(\alpha)/g(0.5)$ against conversion is aligned with the theoretical values of various $g(\alpha)$ functions. For the experimental master plots of $p(x)/p(0.5)$ versus α , the E_α obtained from the differential Friedman method was employed. As per equation (5.2.25), in the case of an ideal kinetic model, the experimental $p(x)/p(0.5)$ and the theoretically calculated $g(\alpha)/g(0.5)$ values closely match. This integral master-plots technique can be harnessed for determining the kinetics of decomposition reactions.

5.3 THERMODYNAMIC PROPERTIES

The pyrolysis process encompasses both physical and chemical changes allowing to formulate quantitative connection between various forms of energy and their controlling factors. Analysis of these factors helps in identifying the spontaneity, equilibrium and the thermodynamic stability of the reaction. The scrutiny of the thermodynamic properties has been found to be crucial in understanding the conservation and energy quality during biomass pyrolysis. Hence, the thermodynamic properties, enthalpy change (ΔH) expressed in terms of kJ/mol, Gibbs free energy change (ΔG) expressed in terms of kJ/mol and entropy change (ΔS) expressed in terms of kJ/mol·K were also computed in this study. Equations (5.3.2), (5.3.3) and (5.3.4) illustrated

below were utilized to evaluate the thermodynamic properties involved in the pyrolysis process.

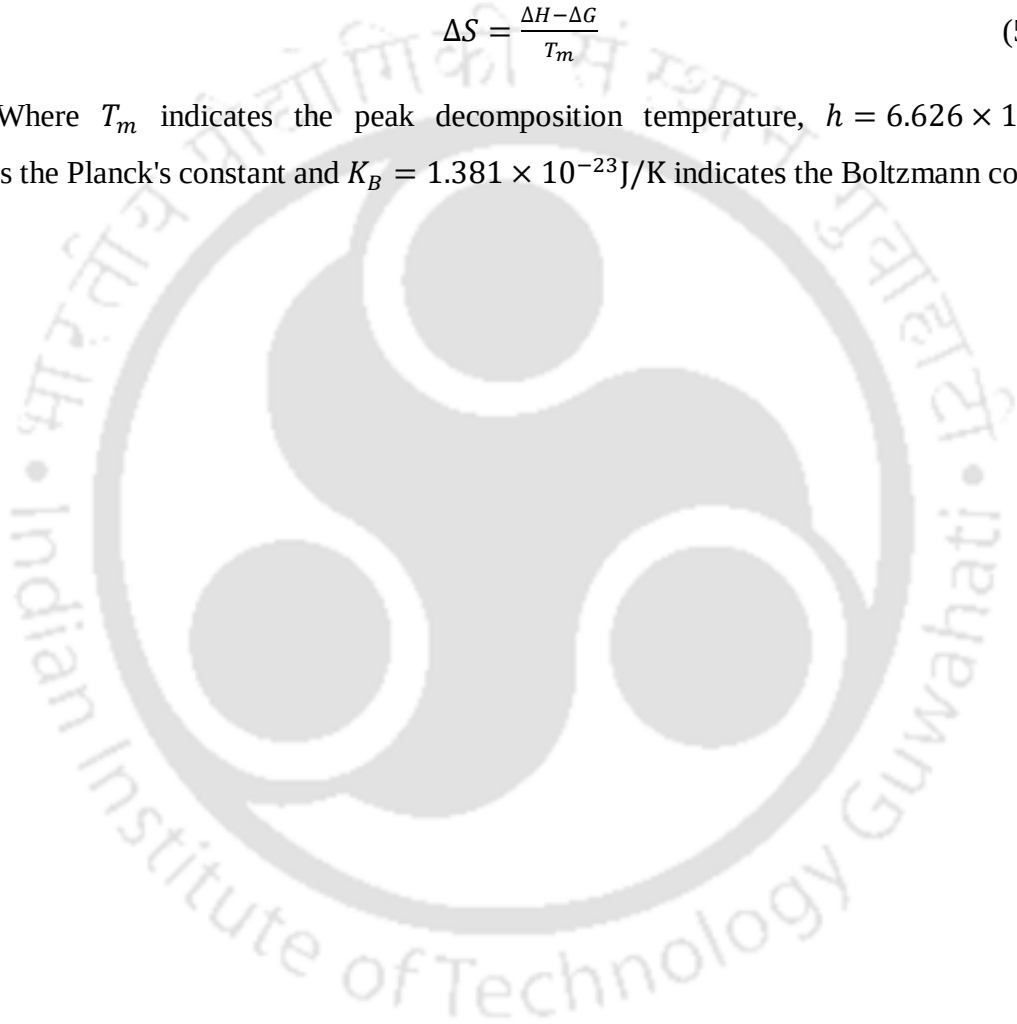
$$k_o = \frac{\beta \times E_\alpha \times e^{\left(\frac{E_\alpha}{RT_m}\right)}}{RT_m^2} \quad (5.3.1)$$

$$\Delta H = E_\alpha - RT_m \quad (5.3.2)$$

$$\Delta G = E_\alpha + RT_m \times \ln \left(\frac{K_B T_m}{h k_o} \right) \quad (5.3.3)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (5.3.4)$$

Where T_m indicates the peak decomposition temperature, $h = 6.626 \times 10^{-34}$ Js indicates the Planck's constant and $K_B = 1.381 \times 10^{-23}$ J/K indicates the Boltzmann constant.



Chapter 6: Results and Discussions

6.1 FEEDSTOCK CHARACTERIZATION

The physiochemical characterization results, encompassing the outcomes of proximate, ultimate and calorific value analyses of *Erythrina indica* (EI) and *Azadirachta indica* (AI) biomass has been presented in Table 6.1.1. To ensure the reliability of the results, each characterization was performed at least three times, and their average values are reported here. The proximate analysis results depicted that both EI and AI biomass possesses high volatile matter content (79.734 wt.% for EI and 82.727 wt.% for AI) implying comparatively higher yield of condensable and non-condensable gases anticipated by employing the right conversion process under suitable conditions. Additionally, both the biomasses had small contents of moisture (11.226 wt.% for EI and 14.179 wt.% for AI) and ash (4.753 wt.% for EI and 3.224 wt.% for AI). The ultimate analysis results depicted high values of H/C ratio of 1.824 for EI and 1.888 for AI, indicating high combustibility of the feed materials. Simultaneously, the high H/C ratio values also confirms the presence of more volatiles. Low nitrogen content and absence of sulphur in the feed materials would prevent the formation of nitrous and sulphurous compounds. Calorific value analyses indicate EI and AI biomass to have almost same values of 18.000 and 18.020 MJ/kg, respectively. The physiochemical characterization results highlight that both EI and AI biomass possess similar properties like other lignocellulosic biomasses used for pyrolysis, and suggest their potential application in producing biofuels through pyrolysis [11,93,161].

Table 6.1.1 also illustrate the different types of densities, porosity, flowability and combustion indices associated to EI and AI biomass. Higher densities are preferable for a good fuel as it offers higher energy density and reduced transportation cost [162,163]. However, in comparison to traditional coal, both EI and AI biomass lack strong flowability and combustion properties in addition to low densities as evidenced by the various types of densities, flowability and combustion indices [129,131,132]. Therefore, further processing of the waste generated from these trees using suitable conversion technology under optimal conditions may be helpful in achieving a fuel with better flowability and combustion characteristics, which could be used as a co-feed or substitute to conventional coal.

Table 6.1.1 Physiochemical properties, different types of densities, porosity, flowability and combustion indices of EI and AI biomass.

Properties		Feedstock	
		EI	AI
Proximate analysis	Moisture content (wet basis) (wt.%)	11.226	14.179
	Volatile matter content (dry basis) (wt.%)	79.734	82.727
	Ash content (dry basis) (wt.%)	4.753	3.224
	Fixed Carbon content ^a (dry basis) (wt.%)	15.513	14.050
	Carbon (wt.%)	45.114	50.788
Ultimate analysis	Hydrogen (wt.%)	6.856	7.991
	Nitrogen (wt.%)	1.123	5.660
	Sulphur (wt.%)	-	-
	Oxygen ^b (wt.%)	46.907	35.561
H/C ratio		1.824	1.888
O/C ratio		0.780	0.525
Calorific value (MJ/kg)		18.000	18.020
Densities	Bulk density, (ρ_b) (g/mL)	0.201	0.321
	Tapped density, (ρ_{tb}) (g/mL)	0.290	0.444
	Particle density, (ρ_p) (g/mL)	0.814	0.569
Porosity, (ε_o)		0.750	0.431
Flowability indices	Angle of repose (θ)	37.706	35.150
	Hausner ratio (HR)	1.445	1.383
	Carr compressibility index, (CCI)	30.700	27.545
	Fuel ratio, (FR)	0.195	0.170
Combustion indices	Combustibility index, (CI) (MJ/kg)	97.248	113.794
	Volatile ignitability, (VI) (MJ/kg)	14.025	13.692
^a calculated by difference		^b calculated by difference	

The thermogravimetric (TGA) and differential thermogravimetric (DTG) curves for EI and AI biomass are illustrated in Figure 6.1.1 (a) and (b), respectively. The TGA curves depicted that degradation of EI and AI biomass occurred in three stages and followed similar trends. The first stage of degradation involved drying and removal of minor amounts of lower molecular weight compounds, which occurred between 70 to 190°C for EI biomass and 70 to 200°C for AI biomass. The second stage, associated with devolatilization, occurred between 190 to 380°C for EI biomass and 200 to 390°C for AI biomass where the cellulose and hemicellulose were broken down. The last and final stage involved char formation, which started at around 380 and 390°C, respectively for EI and AI biomass and continued till the end of the analysis. It was noted that lignin degradation occurred over a wide temperature range,

owing to the complex structure of lignin, indicative of its relatively high thermal stability. Approximately, 25% of the material was left at the end of the analysis, which may be attributed to the presence of unconverted lignin or inorganic material, inherent to the biomass. Another possible reason could be due to the occurrence of secondary processes inside the TGA chamber [93]. The DTG curves also confirmed the similar degradation trend for EI and AI biomass. However, the peak degradation temperature for AI biomass was slightly higher than EI biomass. To be more precise, the peak degradation temperature for EI biomass was found to be between 310 to 330°C while for AI biomass the temperature was found to be between 340 and 360°C. However, the pyrolysis reactions were conducted at a higher temperature (600°C) to ensure optimal biomass conversion and improved product quality, as higher temperatures favor the production of thermally stable compounds [11,164–167]. The TGA-DTG curves for EI and AI biomass followed a similar pattern when compared to other biomasses reported by other researchers [11,65,93].

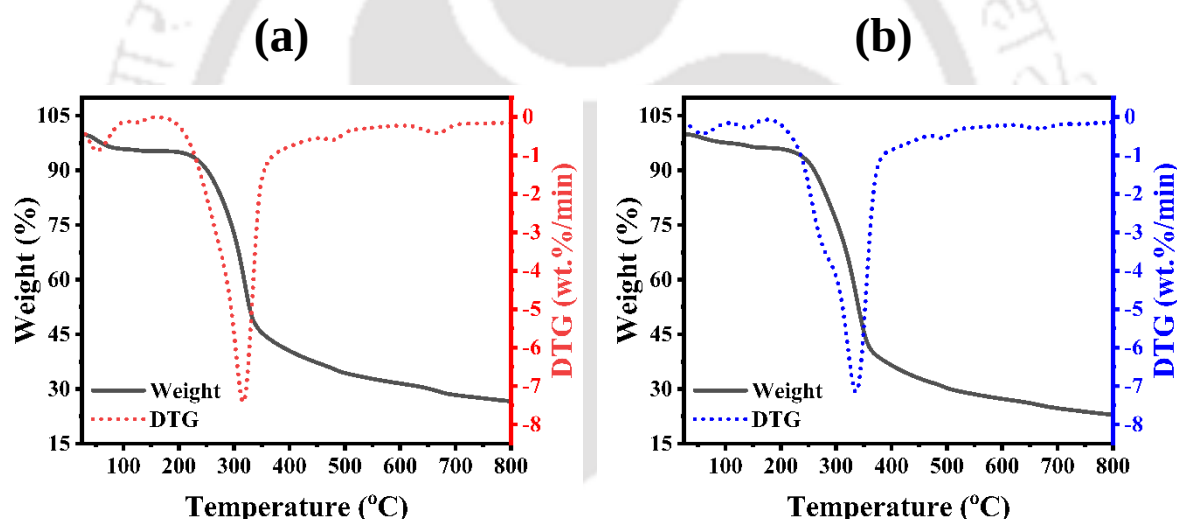


Figure 6.1.1 Thermogravimetric and differential thermogravimetric curves of (a) EI and (b) AI biomass.

6.2 SOLVENT CHARACTERIZATION

The physiochemical properties of the solvents, dichloromethane (DCM) and n-hexane used for extracting the fuel phase of bio-oil in this research study are presented in Table 6.2.1. Figure 6.2.1 (a) and (b) further illustrate the chemical structure of DCM and n-hexane, respectively.

Table 6.2.1: Physiochemical properties of dichloromethane and n-hexane.

Solvent	Density (g/mL)	pH	Dynamic viscosity (mPa.s)	Kinematic viscosity (mm ² /s)
Dichloromethane	1.319	4.44	0.886	0.672
n-hexane	0.657	3.89	0.490	0.746

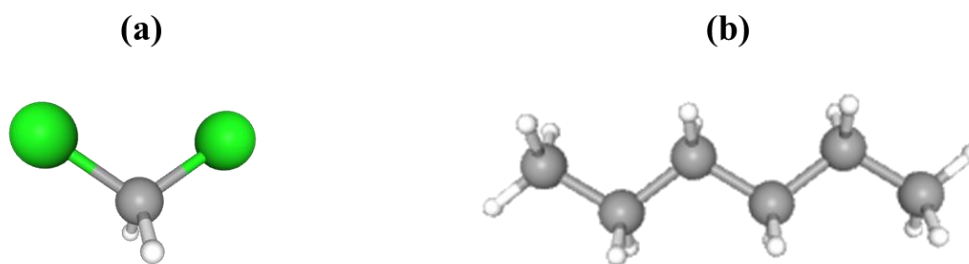


Figure 6.2.1 Chemical structure of (a) dichloromethane and (b) n-hexane.

6.3 SINGLE-FEED PYROLYSIS OF ERYTHRINA INDICA AND AZADIRACHTA INDICA BIOMASS

6.3.1 Yield analysis of products

The single-feed pyrolysis reactions of *Erythrina indica* (EI) and *Azadirachta indica* (AI) biomass waste were carried out at a temperature of 600°C under an initial pressure of 1 bar. The reactions were performed using nitrogen as inert atmosphere and the residence time of the reactions was set at 2 hours after reaching the pyrolysis temperature. The reactions have been repeated nine times to ensure repeatability and to carry out the fuel phase extraction study discussed in the subsequent section. The yield reports of pyrolysis products obtained from the single-feed pyrolysis reactions are comprehensively presented in Table 6.3.1. The table illustrates that for EI biomass the bio-oil yield ranged from 25.341 wt.% to 28.548 wt.%, while for AI biomass it varied between 25.020 wt.% and 29.831 wt.%. Additionally, the biochar yield showed variations between 40.567 wt.% and 44.490 wt.% for EI biomass and 38.433 wt.% and 43.967 wt.% for AI biomass, while the yield of non-condensable gases ranged between 28.552 wt.% and 31.987 wt.% for EI and 29.410 wt.% and 35.910 wt.% for AI biomass. The average yields of bio-oil, biochar and non-condensable gases for EI biomass were found to be 26.873 wt.%, 42.870 wt.% and 30.257 wt.%, respectively, with standard deviations of 1.204, 1.124 and 1.182, whereas for AI biomass the respective yields were found to be 27.286 wt.%, 41.053 wt.% and 31.622 wt.%, respectively, with corresponding standard deviations of 1.900, 1.535 and 2.001. These results demonstrate that both EI and AI biomass exhibit similar trends, comparable to other lignocellulosic biomass used for pyrolysis, indicating that EI and AI biomass can be considered as a dependable feedstock for producing biofuels [11,65,89,93,161,168].

Table 6.3.1 Pyrolysis product distribution (wt.%) of single-feed pyrolysis of EI and AI biomass.

Runs	Yield of bio-oil		Yield of biochar		Yield of non-condensable gases ^a	
	EI	AI	EI	AI	EI	AI
Run 1	28.227	25.020	43.000	39.070	28.773	35.910
Run 2	25.405	25.020	42.608	41.537	31.987	33.443
Run 3	26.175	28.319	42.720	39.854	31.105	31.827
Run 4	25.790	28.732	44.008	40.257	30.202	31.011
Run 5	26.559	27.494	44.469	40.057	28.945	32.449
Run 6	27.907	29.831	41.767	38.433	30.327	31.735
Run 7	28.548	26.624	42.900	43.900	28.552	29.476
Run 8	25.341	26.624	43.767	43.967	30.893	29.410
Run 9	27.907	27.907	40.567	42.400	31.527	29.693
Average	26.873	27.286	42.870	41.053	30.257	31.662
Std. dev.	1.204	1.535	1.124	1.900	1.182	2.001

^a calculated by difference

6.3.2 Fuel phase extraction of bio-oil

The extraction of fuel phase of bio-oil produced from the single-feed pyrolysis reactions of EI and AI biomass was carried out using DCM and n-hexane at four different volume percentages (10%, 20%, 30% and 40%) of solvent relative to the volume of bio-oil. Table 6.3.2 presents the vol.% distribution of the fuel and non-fuel phases of bio-oil obtained from EI and AI biomass, extracted without using any solvent, and with the use of DCM and n-hexane, considering the amount of solvent. It was observed that with an increase volume percentage of solvent for both feedstocks, the dispersion of fuel phase increased while the non-fuel phase decreased significantly. Furthermore, Table 6.3.2 also indicates that the pyrolytic liquid oil and the solvent do not form an ideal mixture as the total volume percent of the fuel and non-fuel phases do not add up to 100%, suggesting that there has been some volume change in the mixture. However, considering the physiochemical properties of the fuel phase, n-hexane was found to be the superior choice compared to DCM, which has been discussed in the subsequent sections.

Table 6.3.2 Fuel and non-fuel phase distribution (vol.%) of bio-oil obtained from single-feed pyrolysis of EI and AI after separation using DCM and n-hexane and without using any solvent.

Solvent %	Fuel phase (vol.%)		Non-fuel phase (vol.%)	
	EI	AI	EI	AI
Without solvent	6.667	7.692	93.333	92.308
10 vol.% DCM	15.840	12.821	78.512	78.089
20 vol.% DCM	26.348	29.935	68.627	67.961
30 vol.% DCM	29.851	30.180	65.442	65.513
40 vol.% DCM	39.855	38.571	57.971	58.571
10 vol.% n-hexane	16.719	13.685	83.595	83.089
20 vol.% n-hexane	22.472	19.076	75.843	76.305
30 vol.% n-hexane	24.975	23.170	70.929	70.436
40 vol.% n-hexane	29.557	32.020	64.039	68.144

6.3.3 Pyrolysis product characterization

6.3.3.1 Characterization of bio-oil

The physiochemical properties including the density, pH, dynamic viscosity, kinematic viscosity and calorific value of the fuel and non-fuel phases of bio-oil extracted without using any solvent, and those obtained using DCM and n-hexane at four different volume percentages of solvent relative to volume of bio-oil, resulting from the single-feed pyrolysis reactions of EI and AI biomass are presented in Table 6.3.3. It has been observed that with an increasing percentage of DCM, the density of the fuel phase showed a marginal increase from 1.018 to 1.128 g/mL for EI fuel phase and 1.053 to 1.143 g/mL for AI fuel phase. Conversely, when using n-hexane, the density of the fuel phase exhibited an opposite trend, decreasing from 0.912 to 0.684 g/mL for EI fuel phase and 0.870 to 0.722 g/mL for AI fuel phase. The density of the non-fuel phase remained almost constant with negligible variations, regardless of the solvent used. The density of the fuel phase recovered without the use of any solvent was 0.996 g/mL for EI fuel phase and 1.031 g/mL for AI fuel phase. The improvement in the density of the fuel phase extracted using n-hexane may be attributed to the addition of extra solvent to the fuel phases.

The pH of the fuel phase extracted from EI bio-oil increased with the increasing percentage of DCM up to 30 vol.% but decreased with the increasing percentage of n-hexane until 40 vol.% of it. However, the pH of the non-fuel phase displayed a mixed trend. The pH of the fuel phase extracted without using any solvent was found to be 4.200, while the pH of the fuel phase extracted using DCM and n-hexane varied in the range of 4.320-4.600 and 3.970-

4.440, respectively. The pH of the fuel and non-fuel phases extracted from AI bio-oil showed inconsistent trends when using DCM, with the pH of both phases rising with increasing percentages of the solvent until 20 vol.% and then falling as the solvent volume increased to 40 vol.%. Using n-hexane, the pH of the fuel phase decreased while the pH of the non-fuel phase increased with the increasing percentage of n-hexane. The pH of the fuel phase extracted using DCM ranged between 3.910 and 4.530, while the pH of the fuel phase extracted using n-hexane ranged between 4.000 and 4.230. The fuel phase recovered without using any solvent was found to have a pH of 3.940.

The dynamic viscosity of the fuel phase extracted from EI bio-oil decreased significantly with the increasing percentage of both DCM and n-hexane but followed a mixed trend for the non-fuel phase when using both solvents. The dynamic viscosity of the fuel phase obtained without adding any solvent was found to be 2.620 mPa.s, while the dynamic viscosity of the fuel phase extracted using DCM and n-hexane varied in the range of 0.904-1.088 and 0.543-1.694 mPa.s, respectively. For the fuel phase extracted from AI bio-oil, the dynamic viscosity of both the fuel and non-fuel phases showed a mixed trend with increasing amounts of DCM and n-hexane. The dynamic viscosity of the fuel phase extracted using DCM and n-hexane ranged between 0.911-1.034 and 0.627-1.295 mPa.s, respectively, while the dynamic viscosity of the fuel phase extracted without using any solvent was determined to be 6.282 mPa.s. The kinematic viscosity of the fuel phase extracted from EI bio-oil, obtained without using any solvent, was found to be 2.631 mm²/s. The kinematic viscosities of the fuel phases extracted using DCM and n-hexane ranged from 0.794 to 1.857 mm²/s and 0.801 to 1.069 mm²/s, respectively. For the fuel phases extracted from AI bio-oil, the kinematic viscosities of fuel phase using DCM and n-hexane varied from 0.801 to 0.928 mm²/s and 0.862 to 1.489 mm²/s, respectively. The kinematic viscosity of the fuel phase obtained without using any solvent was determined to be 6.093 mm²/s. This suggests a strong and positive influence of the solvent on fuel phase extraction.

The calorific value of the fuel phase extracted from both EI and AI bio-oil decreased with increasing vol.% of DCM, while it increased in the case of n-hexane. Without employing any solvent, the calorific value of the fuel phase extracted from EI bio-oil was discovered to be 18.480 MJ/kg, while the fuel phase extracted using DCM and n-hexane varied in the range of 14.360-23.670 and 26.290-39.730 MJ/kg, respectively. For AI, the calorific value of the fuel phase was 19.460 MJ/kg when no solvent was used, compared to a range of 15.060-19.620 and 29.110-37.110 MJ/kg for the fuel phase extracted using dichloromethane and n-hexane,

respectively. However, comparing to the fuel phase extracted without using any solvent, the fuel phase separated using n-hexane exhibited superior physiochemical and fuel properties, as indicated in Table 6.3.3. The calorific value of the fuel phases were comparable to those of bio-oil obtained from other lignocellulosic biomass feedstocks [91,95,168]. To compare with conventional gasoline, commercial gasoline was purchased from a local gas station, and its density, pH, viscosity and calorific value were determined which are also listed in Table 6.3.3. Notably, the fuel phase extracted using 30 vol.% and 40 vol.% n-hexane closely matched the physiochemical characteristics of commercial gasoline, especially from the viewpoints of density, viscosity and calorific value making it a significant achievement of this work and presents a promising alternative source of energy. The calorific value was found to be almost equivalent to that of conventional gasoline, which is a very positive indication from a fuel perspective. The observed decrease in the calorific value of the fuel phase separated using DCM, and the increase in the calorific value of the fuel phase separated using n-hexane, is attributed to the addition of extra solvent to the fuel phase. It is notable that the solvent was not separated from the fuel phase, as doing so has negative effects on the physiochemical properties and yield of the fuel phase. Upon solvent recovery, certain compounds were also transferred along with the solvent due to their lower boiling points, resulting in a viscous phase with a lower yield. Hence, it was considered that the solvent is being utilized for separating out the fuel phase.

Table 6.3.3 Density, pH, dynamic viscosity, kinematic viscosity and calorific value of fuel and non-fuel phases of bio-oil obtained from single-feed pyrolysis of EI and AI biomass.

Solvent %	Fuel phase										Non-fuel phase							
	Density (g/mL)		pH		Dynamic viscosity (mPa.s)		Kinematic viscosity (mm ² /s)		Calorific value (MJ/kg)		Density (g/mL)		pH		Dynamic viscosity (mPa.s)		Kinematic viscosity (mm ² /s)	
	EI	AI	EI	AI	EI	AI	EI	AI	EI	AI	EI	AI	EI	AI	EI	AI	EI	AI
Without solvent	0.996	1.031	4.200	3.940	2.620	6.282	2.631	6.093	18.480	19.460	0.995	1.003	3.890	3.660	1.691	1.714	1.699	1.709
10 vol.% DCM	1.018	1.053	4.550	3.910	1.088	0.933	1.069	0.886	23.670	19.620	1.004	1.002	4.150	3.810	1.314	1.240	1.309	1.238
20 vol.% DCM	1.081	1.114	4.440	4.530	0.969	1.034	0.896	0.928	19.410	16.620	1.004	1.008	4.250	4.480	1.336	1.232	1.331	1.222
30 vol.% DCM	1.113	1.137	4.600	4.250	0.912	0.911	0.819	0.801	14.820	15.100	1.006	1.007	4.410	4.290	1.271	1.217	1.263	1.209
40 vol.% DCM	1.128	1.143	4.320	3.990	0.904	0.936	0.801	0.819	14.360	15.060	1.001	1.010	4.310	3.990	1.251	1.220	1.250	1.208
10 vol.% n-hexane	0.912	0.870	4.440	4.230	1.694	1.295	1.857	1.489	26.290	29.110	0.998	1.004	4.450	3.820	1.354	1.403	1.357	1.397
20 vol.% n-hexane	0.791	0.758	4.250	4.210	0.791	0.723	1.000	0.954	33.120	33.240	1.003	1.002	4.150	3.950	1.415	1.386	1.411	1.383
30 vol.% n-hexane	0.710	0.727	3.980	4.130	0.593	0.627	0.835	0.862	35.630	34.210	1.001	0.998	4.100	3.990	1.303	1.376	1.302	1.379
40 vol.% n-hexane	0.684	0.722	3.970	4.000	0.543	0.652	0.794	0.903	39.730	37.110	1.001	1.000	4.140	4.090	1.247	1.398	1.246	1.398
Commercial Gasoline	0.763		6.200		0.623		0.817		43.740		-		-		-		-	

The stacked FTIR spectra of the bio-oil fuel phases extracted without using any solvent, and those obtained using DCM and n-hexane at four different volume percentages of solvent relative to volume of bio-oil, resulting from the single-feed pyrolysis of EI and AI biomass, are illustrated in Figure 6.3.1 (a) and (b) and Figure 6.3.2 (a) and (b), respectively. The functional groups identified in the fuel phase samples along with their class has been presented in Table 6.3.4. The FTIR spectrum revealed a similar trend, consistent with those obtained from other lignocellulosic biomass, confirming the presence of comparable functional groups [93,161,169]. The fuel phases extracted from EI bio-oil exhibited peak intensities of % transmittance at wavenumbers of 3400, 2967, 2923, 2850, 1707, 1607, 1507, 1453, 1362, 1267, 1226, 1108, 1026, 741, 591, 528 and 446 cm^{-1} using DCM, and 3385, 2954, 2922, 2863, 1707, 1607, 1512, 1457, 1367, 1267, 1222, 1108, 1026, 731, 591, 523 and 442 cm^{-1} using n-hexane. Similarly, the fuel phases extracted from AI bio-oil using DCM indicated peaks at wavenumbers 3406, 2976, 2934, 2854, 1707, 1607, 1512, 1454, 1373, 1262, 1226, 1108, 1026, 732, 606, 528 and 455 cm^{-1} , while those extracted using n-hexane showed peaks at 3403, 2960, 2927, 2854, 1707, 1607, 1507, 1457, 1371, 1272, 1222, 1108, 1026, 751, 595, 528 and 469 cm^{-1} . Peaks developing in the range of 3420–3250 cm^{-1} signifies the presence of polymeric OH and water impurities. Similar peaks were observed by Kawale et al. [93] for the bio-oil obtained from the pyrolysis of *Delonix regia* biomass. The intensities of peaks in the range of 3420–3250 cm^{-1} are flattened when extracted using a solvent, indicating proper separation of the fuel phase from the raw bio-oil. Peaks developing in the range of 2990–2850 cm^{-1} indicate the presence of methyl and methylene groups, belonging to the class of aliphatic compounds. Kumari et al. [161] identified similar peaks for the bio-oil obtained from the pyrolysis of *Polyalthia longifolia* leaves, confirming the presence of aliphatic compounds. Peaks developing between 1720 and 1700 cm^{-1} indicate the existence of C=O groups of ketones, while peaks between 1615 and 1590 cm^{-1} and 1515–1485 cm^{-1} indicate benzene rings in aromatic compounds [65]. Peaks developing in the range of 1475–1450 cm^{-1} confirm the presence of -CH₂ groups of aliphatic compounds, while peaks between 1380–1360 cm^{-1} confirm the existence of isopropyl groups. Similar peaks were observed by Ahmed et al. [11], confirming the presence of isopropyl and aliphatic compounds. C-H group of aromatic compounds are signified by the peaks developing in the range of 1280–1180 cm^{-1} , while aliphatic ethers are indicated by peaks in the 1150–1085 cm^{-1} range which were also observed by Kumari et al. [161]. Peaks developing in the range of 1065–1015 cm^{-1} confirm the presence of cyclic alcohols, and peaks at 760–740 cm^{-1} indicate the existence of o-benzenes in the class of aromatics [170]. Peaks in the 740–720 cm^{-1} range indicate the presence of -(CH₂)_n, a

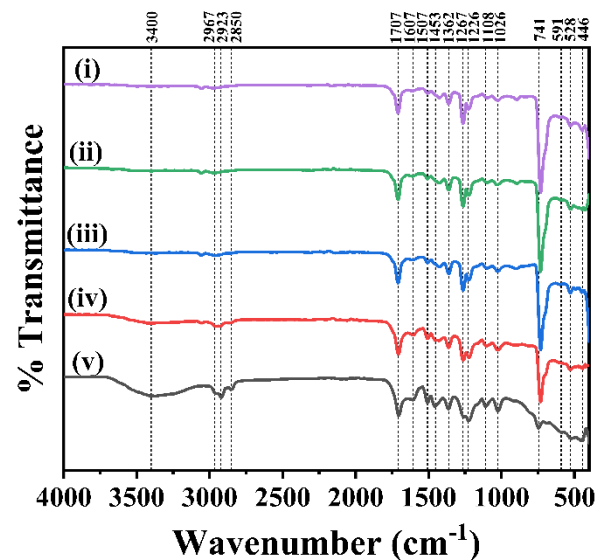
hydrocarbon, while peaks in the range of 700–590 cm^{-1} show O–C=O group in carboxylic acids. Faint peaks developing between 565 and 440 cm^{-1} indicate $\text{C}_n\text{H}_{2n+1}$ in alkyl groups [169].

Comparing the FTIR spectra of the fuel phases extracted using DCM and n-hexane with those of DCM and n-hexane alone in Figure 6.3.3, it was observed that the fuel phases extracted using DCM indicated the same peaks as obtained for DCM alone. Similar observations were made for samples separated using n-hexane, also with slight variations in certain intensities due to changes in solvent and its concentration. The intensities of % transmittance indicating the presence of DCM and n-hexane became stronger with increasing volume percentage of solvent. However, the intensity of the peaks obtained at 740–720 cm^{-1} for the DCM-extracted phases tended to increase with an increasing volume percentage of solvent, possibly due to the addition of DCM in the fuel phase. Similarly, for the n-hexane-extracted fuel phases, the peaks developing at 2990–2850 cm^{-1} showed slightly more significant intensity compared to the DCM-extracted phases, which could be due to the addition of n-hexane to the fuel phase. The broad peaks occurring between 3420 and 3250 cm^{-1} were highly diminished with increasing volume percentages of solvents, indicating proper extraction of the fuel phase and elimination of water impurities.

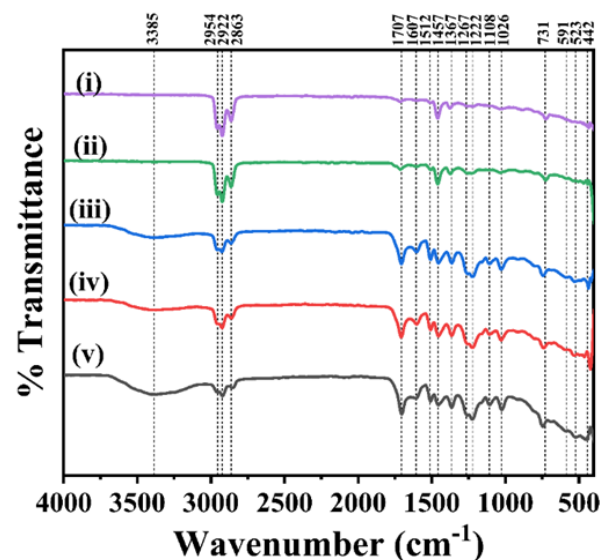
To identify the functional groups, present in the non-fuel phase of bio-oil obtained from EI and AI biomass, samples obtained using 10 vol.%-DCM and 10 vol.%-n-hexane were analyzed via FTIR spectroscopy, as illustrated in Figure 6.3.1 (c) and Figure 6.3.2 (c). The identified functional groups and their classes have also been represented in Table 6.3.4. Comparing the FTIR spectra of the non-fuel phases with the spectra of DCM and n-hexane, it was observed that the non-fuel phases lacked evidence of solvent presence for both DCM and n-hexane. Hence, the spectra for the non-fuel phases extracted using DCM and n-hexane were almost similar. It was confirmed that the change in solvent did not have a significant effect on the functional variations of the non-fuel phases. The FTIR spectrum showed intensities at wavenumbers 3335, 1644, 1377, 1277, 1014 and 616 cm^{-1} for the non-fuel phase extracted from EI bio-oil, while the non-fuel phase extracted from AI bio-oil showed intensities of % transmittance at 3358, 1700, 1644, 1373, 1277, 1101, 1018 and 616 cm^{-1} . The strong peaks developing in the range 3420–3250 cm^{-1} attributes to the presence of high-water impurities in the non-fuel phase, whereas the peaks in the range of 1720–1700 cm^{-1} and 1650–1620 cm^{-1} indicate the presence of C=O groups of ketones and N-H of primary amides in the non-fuel phase, respectively [170]. The strong peaks in the spectrum suggest that the non-fuel phase contains more water contaminants, and both spectra look alike without any significant

variations. The peaks developing within the range of 1380-1360 cm^{-1} and 1280-1180 cm^{-1} , respectively confirm the existence of the isopropyl group and C-H group of aromatic compounds, while the peaks occurring within the range of 1065-1015 cm^{-1} indicate the existence of cyclic alcohols [11]. The strong peaks developing between 700-590 cm^{-1} indicate the high presence of O-C=O groups of carboxylic acids in the non-fuel phase.

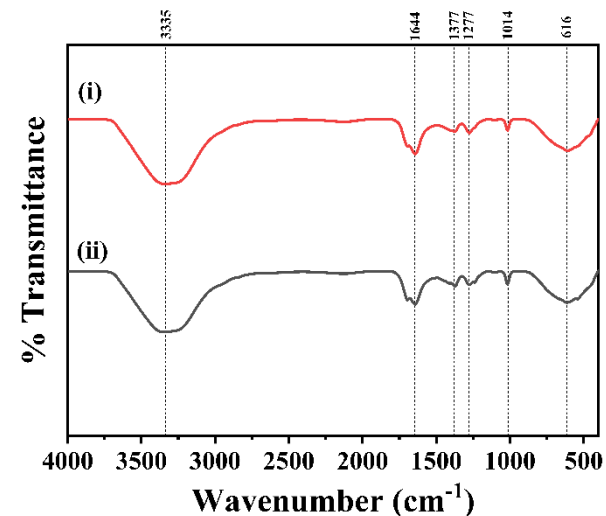




(a): (i) EI-fuel phase with 40 vol.%-DCM, (ii) EI-fuel phase with 30 vol.%-DCM, (iii) EI-fuel phase with 20 vol.%-DCM, (iv) EI-fuel phase with 10 vol.%-DCM, (v) EI-fuel phase without solvent.

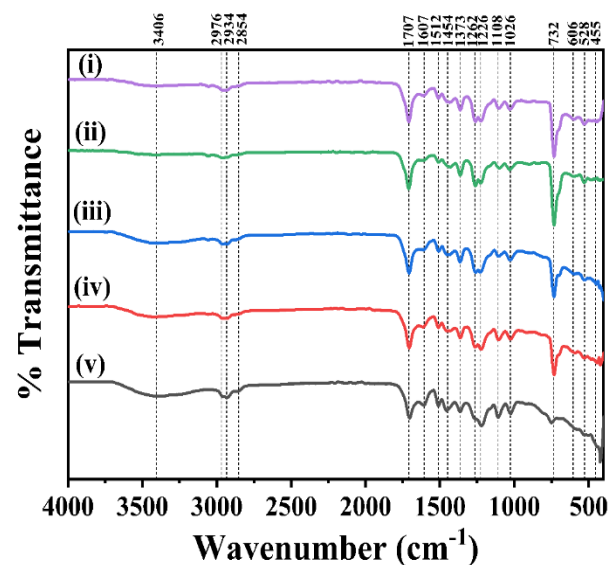


(b): (i) EI-fuel phase with 40 vol.%-n-hexane, (ii) EI-fuel phase with 30 vol.%- n-hexane, (iii) EI-fuel phase with 20 vol.%- n-hexane, (iv) EI-fuel phase with 10 vol.%- n-hexane, (v) EI-fuel phase without solvent.

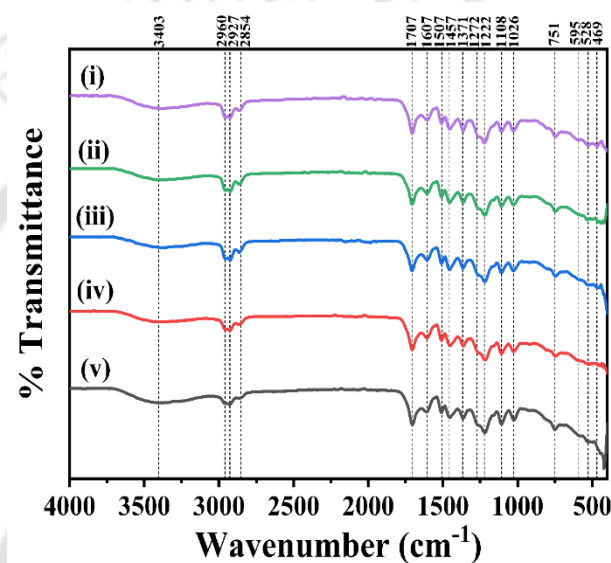


(c) (i) EI-non-fuel phase with 10 vol.%-DCM, (ii) EI-non-fuel phase with 10 vol.%-n-hexane.

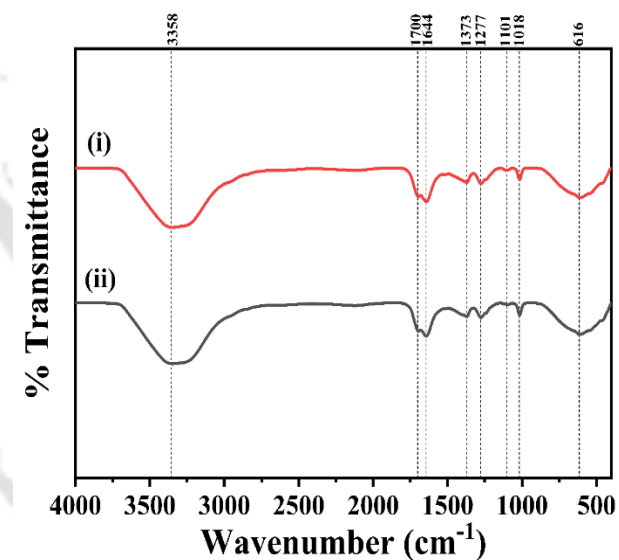
Figure 6.3.1 Fourier transform infrared spectra of fuel and non-fuel phases of bio-oil obtained from single-feed pyrolysis of EI biomass.



(a): (i) AI-fuel phase with 40 vol.-%-DCM, (ii) AI-fuel phase with 30 vol.-%-DCM, (iii) AI-fuel phase with 20 vol.-%-DCM, (iv) AI-fuel phase with 10 vol.-%-DCM, (v) AI-fuel phase without solvent.



(b): (i) AI-fuel phase with 40 vol.-%-n-hexane, (ii) AI-fuel phase with 30 vol.-%- n-hexane, (iii) AI-fuel phase with 20 vol.-%- n-hexane, (iv) AI-fuel phase with 10 vol.-%- n-hexane, (v) AI-fuel phase without solvent.



(c) (i) AI-non-fuel phase with 10 vol.-%-DCM, (ii) AI-non-fuel phase with 10 vol.-%-n-hexane.

Figure 6.3.2 Fourier transform infrared spectra of fuel and non-fuel phases of bio-oil obtained from single-feed pyrolysis of AI biomass.

Table 6.3.4 Functional groups present in the fuel and non-fuel phases of bio-oil obtained from single-feed pyrolysis of EI and AI biomass.

Wavenumber (cm ⁻¹)						Wavenumber range (cm ⁻¹)	Class of compound
EI fuel phase obtained using DCM	AI fuel phase obtained using DCM	EI fuel phase obtained using n-hexane	AI fuel phase obtained using n-hexane	EI non-fuel phase obtained using DCM and n-hexane	AI non-fuel phase obtained using DCM and n-hexane		
3400	3406	3385	3403	3335	3358	3420-3250	Polymeric OH and water impurities
2967, 2923, 2850	2976, 2934, 2854	2954, 2922, 2863	2960, 2927, 2854	-	-	2990-2850	Methyl and methylene groups of aliphatic compounds
1707	1707	1707	1707	-	1700	1720-1700	C=O group of ketones
-	-	-	-	1644	1644	1650-1620	N-H in primary amides
1607	1607	1607	1607	-	-	1615-1590	Benzene ring in aromatic compounds
1507	1512	1512	1507	-	-	1515-1485	Benzene ring in aromatic compounds
1453	1454	1457	1457	-	-	1475-1450	Methylene group of aliphatic compounds
1362	1373	1367	1371	1377	1373	1380-1360	Isopropyl group of isopropyl compounds
1267, 1226	1262, 1226	1267, 1222	1272, 1222	1277	1277	1280-1180	C-H group in aromatic compounds
1108	1108	1108	1108	-	-	1150-1085	Aliphatic ethers
1026	1026	1026	1026	1014	1101, 1018	1065-1015	C-OH groups of cyclic alcohols
741	-	-	751	-	-	760-740	o-benzenes of aromatics
-	732	731	-	-	-	740-720	-(CH ₂) _n - of hydrocarbons
591	606	591	595	616	616	700-590	O-C=O in carboxylic acids
528, 446	528, 455	523, 442	528, 469	-	-	565-440	C _n H _{2n+1} in alkyl groups

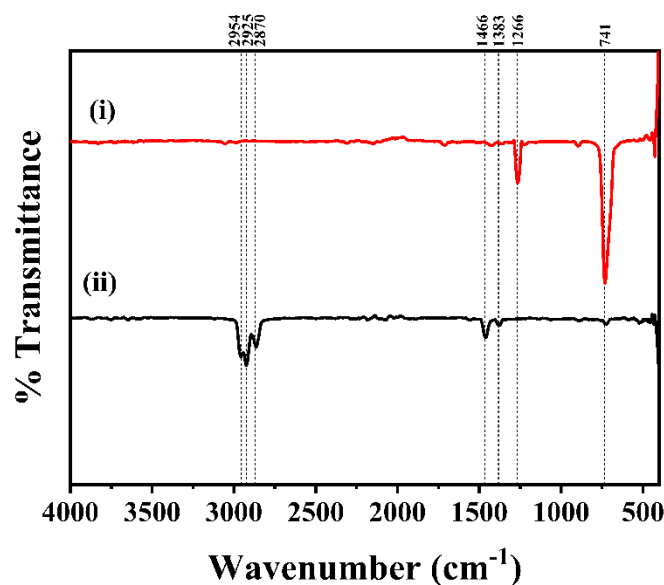


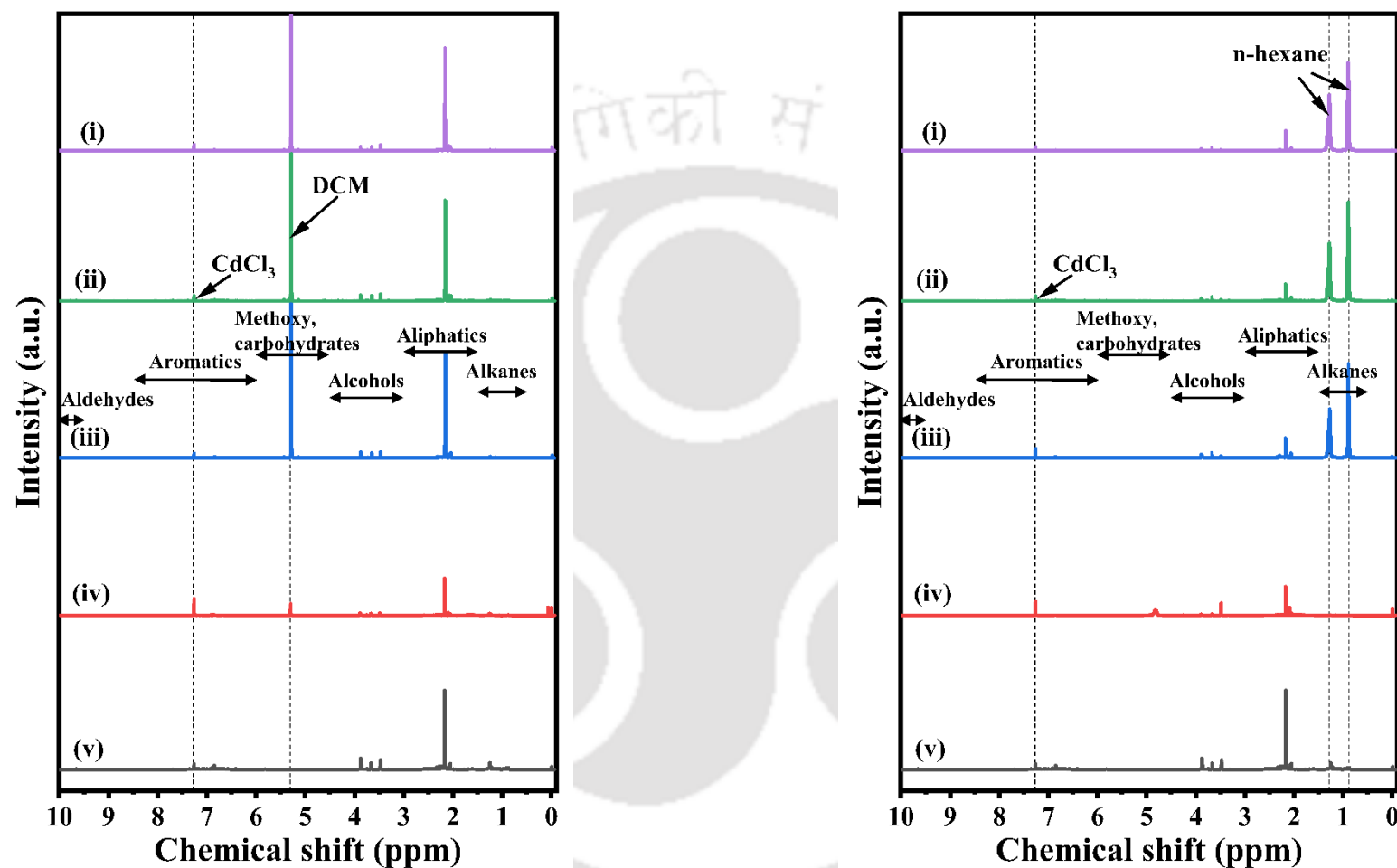
Figure 6.3.3 Fourier transform infrared spectra of (i) dichloromethane (ii) n-hexane.

FTIR functional groups and their assignments were cross-checked using proton nuclear magnetic resonance (^1H NMR) to confirm the functional groups present in the fuel phase of the bio-oil produced. The comparative ^1H NMR spectrum of the fuel phase without using any solvent and with the fuel phase obtained by using DCM and n-hexane at four different volume percentages of solvent relative to the volume of raw bio-oil, resulting from the single-feed pyrolysis of EI and AI biomass is illustrated in Figure 6.3.4 (a) and (b) 6.3.5 (a) and (b), respectively. The peak at 7.26 ppm represents chloroform-D, the solvent used for this analysis. The chemical makeup of the fuel phase is identified by comparing the peaks of the fuel phase with the literature available on pyrolysis oil [65,171–174]. The water impurity of the tetramethylsilane solvent is shown by the peak at 0 ppm. Alkanes were detected in the fuel phase by the peaks developing at 0.5–1.5 ppm. Peaks developing between 1.5–3.0 ppm signify aliphatic α to heteroatom. The peaks developing between 3.0–4.5 ppm indicate the presence of alcohols and methylene-dibenzene, while the peaks between 4.5–6.0 ppm confirm the presence of alkenes and methoxy carbohydrates. Peaks developing between 6.0–8.5 ppm and 9.5–10.0 ppm, respectively, demonstrate the presence of hetero-aromatics and aldehydes. DCM is indicated by the peak at 5.3 ppm, whereas n-hexane is indicated by the peaks at 0.88 ppm and 1.26 ppm [175]. The fuel phase obtained from other lignocellulosic biomass exhibited similar peaks, confirming the presence of the attributed compounds [11,93,161].

The ^1H NMR spectrum obtained for the fuel phases (originated from both feedstock) without using any solvent and those extracted using DCM and n-hexane indicate the presence of similar functional groups but the corresponding peaks in the case of ^1H NMR of fuel phases

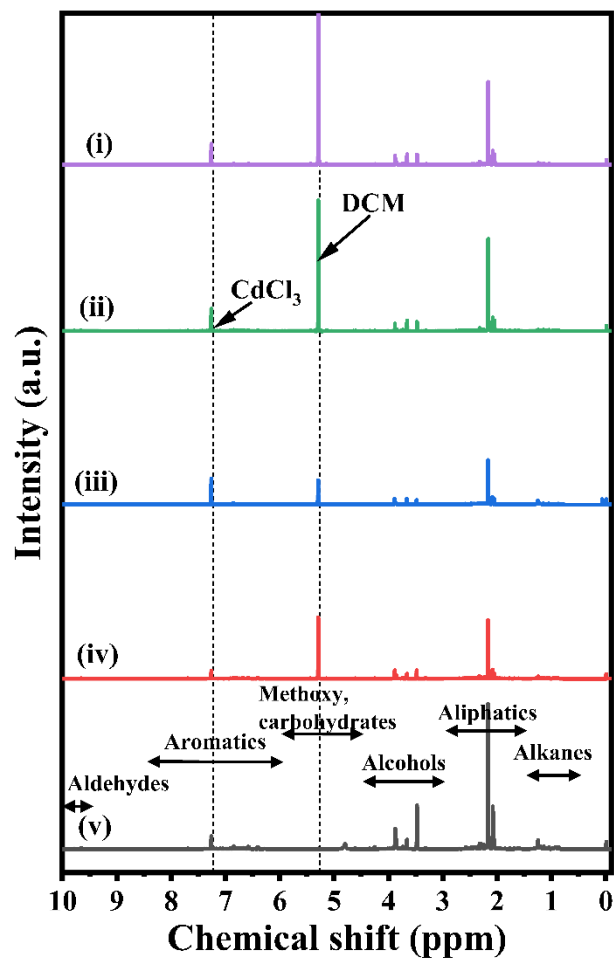
from AI biomass showed higher intensities. However, the addition of n-hexane and DCM is evident from the ^1H NMR spectrum of the fuel phases extracted using 20, 30 and 40 vol.% of solvent. This was confirmed after conducting the ^1H NMR analysis of the non-fuel phases, which indicated the absence of solvents even at 40 vol.% of solvent. Thus, this suggests that excess solvent is being added to the fuel phase. The peak was found to almost disappear for the fuel phase extracted with 10 vol.% of n-hexane but was visible for the fuel phase extracted using 10 vol.% DCM, indicating that the solvent was used for separation. As discussed in first paragraph of this section, n-hexane has been shown to be a better alternative than DCM for extracting the fuel phase from bio-oil, especially when considering physiochemical properties such as calorific value, density and viscosity.



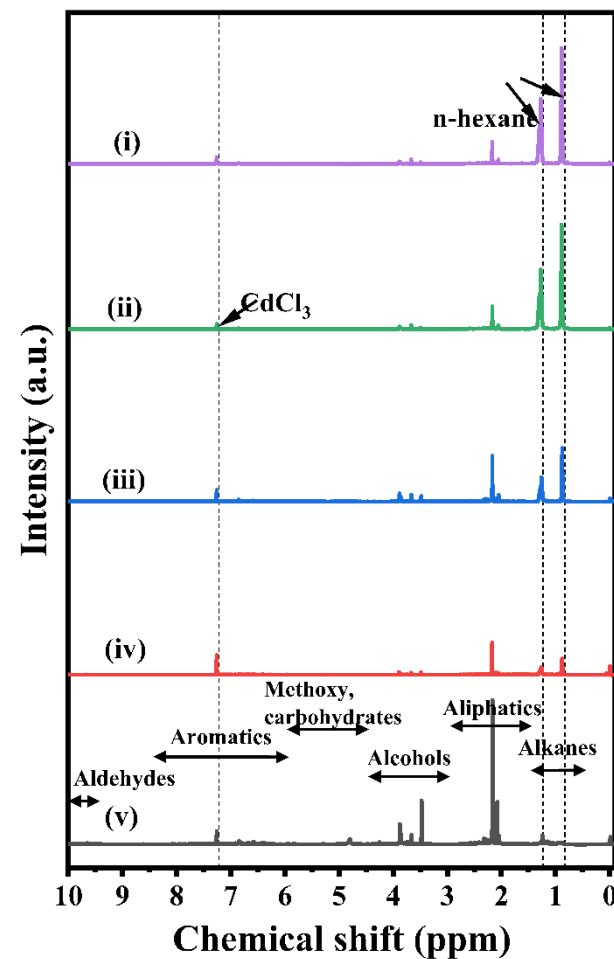


(a): (i) EI-fuel phase with 40 vol.-%-DCM, (ii) EI-fuel phase with 30 vol.-%-DCM, (iii) EI-fuel phase with 20 vol.-%-DCM, (iv) EI-fuel phase with 10 vol.-%-DCM, (v) EI-fuel phase without solvent
 (b): (i) EI-fuel phase with 40 vol.-%-n-hexane, (ii) EI-fuel phase with 30 vol.-%- n-hexane, (iii) EI-fuel phase with 20 vol.-%- n-hexane, (iv) EI-fuel phase with 10 vol.-%- n-hexane, (v) EI-fuel phase without solvent

Figure 6.3.4 Proton nuclear magnetic resonance spectra of fuel phase of bio-oil obtained from single-feed pyrolysis of EI biomass.



(a): (i) AI-fuel phase with 40 vol.-%-DCM, (ii) AI-fuel phase with 30 vol.-%-DCM, (iii) AI-fuel phase with 20 vol.-%-DCM, (iv) AI-fuel phase with 10 vol.-%-DCM, (v) AI-fuel phase without solvent



(b): (i) AI-fuel phase with 40 vol.-%-n-hexane, (ii) AI-fuel phase with 30 vol.-%- n-hexane, (iii) AI-fuel phase with 20 vol.-%- n-hexane, (iv) AI-fuel phase with 10 vol.-%- n-hexane, (v) AI-fuel phase without solvent

Figure 6.3.5 Proton nuclear magnetic resonance spectra of fuel phase of bio-oil obtained from single-feed pyrolysis of AI biomass.

The fuel phases extracted from the bio-oil obtained from single-feed pyrolysis of EI and AI biomass were subjected to GC-MS analysis to gain a comprehensive understanding of the potential compounds present in the fuel phases obtained directly, as well as those extracted using DCM and n-hexane. Analysis of FTIR and ^1H NMR results revealed that increasing the percentage of solvent had minimal impact on functional groups of the extraction of the fuel phase. GC-MS analysis was then performed for the fuel phases obtained directly and those extracted using 10-vol.-%-DCM and 10-vol.-%-n-hexane, providing detailed information on retention duration, area percentage, molecular formula and molecular weight which are detailed in Table 6.3.5 and 6.3.6. The identified compounds in the fuel phases from EI bio-oil ranged from C_5 to C_{25} , primarily falling into categories such as alkanes, alcohols, fatty acids, esters, ethers and ketones. Similarly, the compounds present in the fuel phases from AI bio-oil, spanning the C_5 to C_{27} range, included alkenes, alcohols, ethers, aromatic hydrocarbons, esters, ketones, aldehydes and anisoles. These chemical constituents were consistent with those observed in bio-oils of other lignocellulosic biomass [11,65,93]. Notably, the fuel phases obtained without solvent and with 10-vol.-%-n-hexane exhibited almost similar compound compositions for both EI and AI bio-oil, suggesting minimal alteration in the chemical composition of the fuel phase. Major compounds in the fuel phase from EI bio-oil obtained directly without using any solvent included phenol, 2-methoxy- (8.803 area%), furan, 2-methoxy- (7.205 area%), and ethanol, pentamethyl- (5.643 area%). In contrast, the fuel phase extracted using DCM showed dominant compounds like oleyl alcohol, trifluoroacetate (50.626 area%), methyl 13-methyltetradecanoate (5.239 area%) and phenol, 2-methoxy- (3.516 area%). Using 10-vol.-%-n-hexane, major compounds identified were furan, 2-methoxy- (10.105 area%), ethanol, pentamethyl- (7.3 area%) and phenol, 2-methoxy- (4.322 area%). For the fuel phase extracted from AI bio-oil, the dominant compounds in the fuel phase obtained directly without using any solvent were furan, 2-methoxy- (9.382 area%), ethanol, pentamethyl- (7.241 area%) and phenol, 2-methoxy- (3.197 area%). Extraction using DCM resulted in major compounds such as furan, 2-methoxy- (10.501 area%), ethanol, pentamethyl- (8.336 area%) and phenol, 2,6-dimethoxy- (3.239 area%). On the other hand, n-hexane extraction indicated the presence of furan, 2-methoxy- (21.727 area%), ethanol, pentamethyl- (12.104 area%) and toluene (1.317 area%). The enhanced selectivity of n-hexane over DCM further makes it a more suitable solvent for the extraction of the fuel phase.

Table 6.3.5 Probable compounds identified through gas chromatography-mass spectroscopy analysis of fuel phases of bio-oil obtained from single-feed pyrolysis of EI biomass using DCM, n-hexane and without any solvent.

Name of the compound	Chemical type	Molecular formula	Molecular weight	EI-fuel phase without solvent		EI-fuel phase-with-10%-DCM		EI-fuel phase-with-10%-n-hexane	
				RT	Area %	RT	Area %	RT	Area %
Toluene	Aromatic hydrocarbon	C ₇ H ₈	92	8.178	1.704	-	-	8.178	2.051
1-penten-3-one	Ketone (enone)	C ₅ H ₈ O	84	-	-	-	-	8.759	0.763
Furan, 2-methoxy-	Heterocyclic aromatic compound	C ₅ H ₆ O ₂	98	8.854	7.205	8.779	1.942	8.854	10.105
Ethanol, pentamethyl-	Alcohol (aromatic)	C ₇ H ₁₆ O	116	10.059	5.643	9.979	1.486	10.054	7.300
Phenol	Alcohol (aromatic)	C ₆ H ₆ O	94	14.361	1.209	-	-	14.361	0.687
Phenol, 2-methyl-	Alcohol(phenol), aromatic	C ₇ H ₈ O	108	16.747	1.684	-	-	16.747	0.976
Phenol, 4-methyl-	Alcohol (aromatic)	C ₇ H ₈ O	108	17.427	2.075	-	-	17.412	1.304
Phenol, 3,4-dimethyl-	Alcohol(phenol), aromatic	C ₈ H ₁₀ O	122	19.703	0.775	-	-	-	-
Phenol, 2-methoxy-	Alcohol (phenol), aromatic	C ₇ H ₈ O ₂	124	17.892	8.803	17.817	3.516	17.888	4.322
Phenol, 3,4-dimethyl-	Alcohol(phenol), aromatic	C ₈ H ₁₀ O	122	20.323	0.775	-	-	-	-
Phenol, 2-methoxy-4-methyl-	Alcohol, phenols (aromatic)	C ₈ H ₁₀ O ₂	138	21.044	2.629	-	-	21.039	1.853
Phenol, 4-ethyl-2-methoxy-	Alcohol, aromatic	C ₉ H ₁₂ O ₂	152	23.49	4.032	-	-	23.49	3.129
Phenol, 2,6-dimethoxy-	Alcohol(phenol), aromatic	C ₈ H ₁₀ O ₃	154	25.44	1.592	-	-	-	-
Phenol, 2-methoxy-4-propyl-	Alcohol, aromatic	C ₁₀ H ₁₄ O ₂	166	25.921	1.572	-	-	25.931	1.452

Benzene, 1,2,3-trimethoxy-5-methyl-	Ether, aromatic	C ₁₀ H ₁₄ O ₃	182	29.832	1.103	-	-	-	-
11-bromoundecanoic acid	Fatty acid	C ₁₁ H ₂₁ BrO ₂	278	-	-	41.937	1.278	-	-
Oleic acid	Fatty acid	C ₁₈ H ₃₄ O ₂	282	-	-	42.037	1.799	-	-
Oleic acid	Fatty acid	C ₁₈ H ₃₄ O ₂	282	-	-	42.147	2.445	-	-
Methyl 13-methyltetradecanoate	Fatty acid methyl ester	C ₁₆ H ₃₂ O ₂	256	-	-	42.507	5.239	-	-
Oleyl alcohol, trifluoroacetate	Fatty alcohols	C ₂₀ H ₃₅ F ₃ O ₂	364	-	-	43.283	50.626	-	-
Trans-2-methyl-4-n-butylthiane, s,s-dioxide	Heterocyclic compound (organosulfur)	C ₁₀ H ₂₀ O ₂ S	204	-	-	44.773	2.051	-	-
Oleic acid	Fatty acid	C ₁₈ H ₃₄ O ₂	282	-	-	44.888	1.069	-	-
Hexadecanoic acid, 1-(hydroxymethyl)-1,2-ethanediyl ester	Ester	C ₁₉ H ₃₈ O ₄	568	-	-	45.618	1.526	-	-
Octadecanoic acid, 2,3-dihydroxypropyl ester	Ester	C ₂₅ H ₄₆ O ₆	358	-	-	48.380	1.181	-	-
1-nonylcycloheptane	Cycloalkane	C ₁₆ H ₃₂	224	-	-	48.775	1.149	-	-
6-tridecanol, 3,9-diethyl-	Fatty alcohol	C ₁₇ H ₃₆ O	256	-	-	48.855	0.955	-	-
Hexadecanoic acid, 1-(hydroxymethyl)-1,2-ethanediyl ester	Ester	C ₁₉ H ₃₈ O ₄	568	-	-	49.24	1.493	-	-

Table 6.3.6 Probable compounds identified through gas chromatography-mass spectroscopy analysis of fuel phases of bio-oil obtained from single-feed pyrolysis of AI biomass using DCM, n-hexane and without any solvent.

Name of the compound	Chemical type	Molecular formula	Molecular weight	AI-fuel phase without solvent		AI-fuel phase-with-10 vol.-%-DCM		AI-fuel phase-with-10 vol.-%-n-hexane	
				RT	Area %	RT	Area %	RT	Area %
Toluene	Aromatic hydrocarbon	C ₇ H ₈	92	8.178	1.75	-	-	8.133	1.317
Phenol, 2-(phenylmethoxy)-	Phenol ethers	C ₁₃ H ₁₂ O ₂	200	-	-	8.178	1.244	-	-
Furan, 2-methoxy-	Heterocyclic aromatic compound	C ₅ H ₆ O ₂	98	8.859	9.382	8.854	10.501	8.804	21.727
3-cyclopentene-1-acetaldehyde, 2-oxo-	Aldehyde	C ₇ H ₈ O ₂	124	-	-	9.884	0.701	-	-
Ethanol, pentamethyl-	Alcohol (aromatic)	C ₇ H ₁₆ O	116	10.059	7.241	10.059	8.336	10.009	12.104
Benzyl phenyl sulfone	Benzene sulfonyl compounds	C ₁₃ H ₁₂ O ₂ S	232	-	-	-	-	10.715	-
Pyridine, 3-benzoyl-4-benzylamino-2-trifluoromethyl-	Heterocyclic compound	C ₂₅ H ₂₃ F ₃ N ₂ O	356	10.785	0.334	-	-	-	-
Ethylbenzene	Aromatic hydrocarbon	C ₈ H ₁₀	106	11.05	0.302	-	-	-	-
2-octene, 4-ethyl-, (E)-	Alkene	C ₁₀ H ₂₀	140	11.84	0.164	-	-	-	-
2-cyclopenten-1-one, 2-methyl-	Cyclic ketone	C ₆ H ₈ O	96	-	-	12.085	0.356	-	-
Butanoic acid, 2,2-dimethyl-, methyl ester	Fatty acid esters	C ₇ H ₁₄ O ₂	130	-	-	15.186	0.567	-	-

2-cyclopenten-1-one, 2,3-dimethyl-	Ketones	C ₇ H ₁₀ O	110	16.287	0.301	-	-	-	-
Phenol, 2-methoxy-	Alcohol (phenol), aromatic	C ₇ H ₈ O ₂	124	17.888	3.197	17.892	2.853	17.837	0.872
Benzene, 1,4-dimethoxy-	Ethers	C ₈ H ₁₀ O ₂	138	-	-	-	-	20.994	0.384
Creosol	Alcohol (aromatic)	C ₇ H ₈ O	108	21.039	1.843	21.039	1.308	-	-
Phenol, 4-ethyl-2-methoxy-	Alcohol, aromatic	C ₉ H ₁₂ O ₂	152	23.49	2.511	23.49	1.745	23.45	1.153
Phenol, 2,6-dimethoxy-	Alcohol (phenol), aromatic	C ₈ H ₁₀ O ₃	154	25.436	3.002	25.44	3.239	-	-
Phenol, 2-methoxy-4-propyl-	Alcohol, aromatic	C ₁₀ H ₁₄ O ₂	166	25.921	1.135	25.921		25.891	0.548
1,2,4-trimethoxybenzene	Anisoles	C ₉ H ₁₂ O ₃	168	27.912	1.434	27.906	1.349	-	-
Benzoic acid, 4-nitro-, methyl ester	Nitrobenzoic acids and derivatives	C ₈ H ₇ NO ₄	181	-	-	28.527	1.087	-	-
Benzene, 1,2,3-trimethoxy-5-methyl-	Anisoles	C ₁₀ H ₁₄ O ₃	182	29.832	2.171	29.837	1.562	29.812	0.254
3-hydroxy-4-nitrobenzaldehyde	Aldehyde	C ₇ H ₅ NO ₄	167	-	-	-	-	31.803	-
4-propyl-1,1'-diphenyl	Alkylated aromatic compounds	C ₁₅ H ₁₆	196	-	-	31.828	0.612	-	-
4-pentenoic acid, 2,3-dimethyl-	Methyl-branched fatty acids	C ₇ H ₁₂ O ₂	128	-	-	-	-	38.581	-
2-butenic acid, 2-methoxy-, methyl ester, (z)-	Fatty acid esters	C ₆ H ₁₀ O ₃	130	-	-	-	-	43.688	-
3-methoxy-2,4,5-trifluorobenzoic acid, nonadecyl ester	Ester	C ₂₇ H ₄₃ F ₃ O ₃	472	-	-	-	-	45.419	0.324

6.3.3.2 Characterization of biochar

Commencing with the physiochemical properties, Table 6.3.7 also provides a comprehensive overview of various densities (bulk, tapped, and particle), porosity, flowability and combustion indices associated with the biochar obtained from the single-feed pyrolysis of EI and AI biomass. Similar to the feed material the moisture content of the biochar samples were determined on wet basis whereas the volatile matter, ash and fixed carbon contents were determined on dry basis. Proximate analysis results for the biochar samples reveals a low moisture content of 3.450 wt.% and 3.462 wt.%, respectively for EI and AI biochar. The low volatile matter content (EI: 17.811 wt.% and AI: 19.132 wt.%) of the biochar samples as compared to feed materials supports the proper devolatilization process. Fixed carbon (EI: 70.193 wt.% and AI: 69.854 wt.%) was the primary constituent of the biochar.

The elemental analysis of the biochar samples identified carbon as the predominant constituent, followed by oxygen and minor amounts of hydrogen. Specifically, for EI biochar, the elemental composition was found to be 74.081 wt.% carbon, 2.815 wt.% hydrogen and 23.104 wt.% oxygen, while for AI biochar, it was 66.568 wt.% carbon, 3.681 wt.% hydrogen and 29.751 wt.% oxygen. The low hydrogen content and elevated carbon content resulted in H/C ratios of 0.456 and 0.664 for EI and AI biochar, respectively, indicating proper devolatilization of the feed material. Notably, the complete absence of nitrogen and sulphur in the biochar samples are favourable characteristics that help prevent the formation of nitrogenous and sulphur compounds during combustion. The carbon content of ≈ 74 wt.% is also consistent with TGA final remaining mass ($\approx 25\%$) which is a non-carbonaceous material. The calorific values of EI and AI biochar were found to be 28.030 MJ/kg and 28.500 MJ/kg.

The various density measurements provided in Table 6.3.7 indicate notable improvements in the characteristics of the biochar samples when compared to the original feed material, particularly in terms of enhanced bulk density and particle density. This enhancement ultimately translates to a reduced requirement for storage and transportation space, leading to potential cost savings in handling. Additionally, the biochar samples produced through the single-feed pyrolysis reactions exhibited improved flowability indices. The angle of repose, Hausner ratio and Carr Compressibility Index for EI biochar are 29.421° , 1.216 and 17.592, respectively. Correspondingly, for AI biochar, the values are 27.356° , 1.218 and 17.544, respectively. The comparison of flowability indices of the feed material and biochar samples indicate an improvement in material flowability properties from poor to fair.

The fuel ratio values for both EI and AI biochar were determined to be 3.947 and 3.654, respectively, which is considerably higher than the fuel ratio of coal (0.5-2.0) [176]. Although the combustibility index of EI and AI biochar is relatively low, with values of 6.982 MJ/kg and 7.734 MJ/kg compared to coal, the volatile ignitability for EI and AI biochar is notably higher at 20.212 MJ/kg and 21.633 MJ/kg, respectively, well exceeding the minimum requirement of 14 MJ/kg [132,176,177]. These results suggest that the flowability and combustion indices of EI and AI biochar make it comparable to conventional coal used in coal-based power plants. In other words, the improved flowability indices would facilitate material handling in continuous feed systems, while the enhanced combustion indices are an indication of a good fuel. Thus, the results confirm that biomass processing through pyrolysis has been advantageous in producing a solid fuel with better quality.

Table 6.3.7 Physiochemical properties, different types of densities, porosity, flowability and combustion indices of biochar produced through single-feed pyrolysis of EI and AI biomass.

Properties	Biochar derived from	
	EI biomass	AI biomass
Proximate analysis	Moisture content (wet basis) (wt.%)	3.450
	Volatile matter content (dry basis) (wt.%)	17.811
	Ash content (dry basis) (wt.%)	11.966
	Fixed Carbon content ^a (dry basis) (wt.%)	70.193
	Carbon (wt.%)	74.081
Ultimate analysis	Hydrogen (wt.%)	2.815
	Nitrogen (wt.%)	-
	Sulphur (wt.%)	-
	Oxygen ^b (wt.%)	23.104
H/C ratio	0.456	0.664
O/C ratio	0.234	0.335
Calorific value (MJ/kg)	28.030	28.500
Densities	Bulk density, (ρ_b) (g/mL)	0.202
	Tapped density, (ρ_{tb}) (g/mL)	0.239
	Particle density, (ρ_p) (g/mL)	0.933
Porosity, (ε_o)	0.784	0.649
Flowability indices	Angle of repose (θ)	29.412
	Hausner ratio (HR)	1.216
	Carr compressibility index, (CCI)	17.592
	Fuel ratio, (FR)	3.947
Combustion indices	Combustibility index, (CI) (MJ/kg)	6.982
	Volatile ignitability, (VI) (MJ/kg)	20.212
^a calculated by difference		^b calculated by difference

The TGA-DTG curves for biochar obtained from the single-feed pyrolysis reactions of EI and AI biomass are illustrated in Figures 6.3.6 (a) and (b). The TGA curves demonstrated progressive but minimal mass loss for both EI and AI biochar as the temperature increased, signifying that the primary constituents of the biochar samples are, fixed carbon and inorganic components, stable under inert conditions. The absence of significant mass loss in the TGA curves of the biochar samples between 200 and 390°C supports the complete conversion of cellulose and hemicellulose of biomass through pyrolysis. EI biochar exhibited a mass loss of approximately 15%, whereas AI biochar displayed a mass loss of around 27%. This mass loss in biochar samples are primarily attributed to the removal of residual organic matter, any unconverted lignin or residual water present in the biochar due to physisorption. The slow and gradual mass loss resulted in a slightly different trend of the TGA curves for the biochar samples compared to its original feed (Figure 6.1.1). Additionally, the DTG curve also depicted a different trend as compared to its original feed. There was only one minimum for the DTG curve of biomass, whereas for the biochar there were several local minima. The formation of several local minima in the DTG curve of biochar is a result of the complex composition of biochar and their devolatilization temperatures.

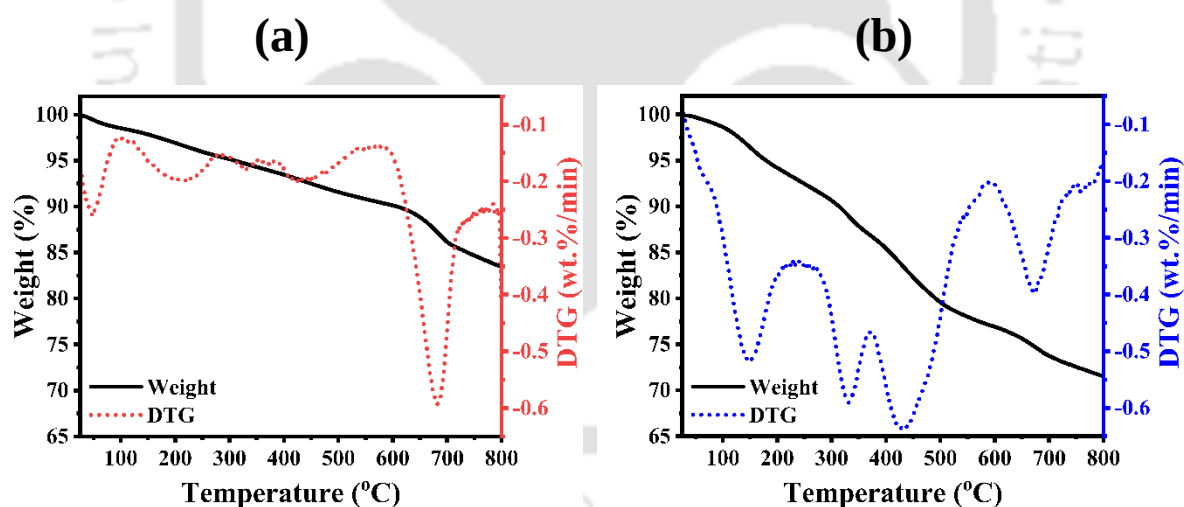


Figure 6.3.6 Thermogravimetric and differential thermogravimetric curves of (a) EI biochar and (b) AI biochar obtained from single-feed pyrolysis of EI and AI biomass.

The crystal structure of the biochar samples obtained from the single-feed pyrolysis of EI and AI biomass was examined using a powder X-ray diffractogram. Figure 6.3.7 (a) and (b) illustrate the graphical representation of the XRD spectra of biomass and biochar samples obtained from the single-feed pyrolysis of EI and AI biomass, respectively. The crystallinity of the lattice spacing of cellulose in biomass was confirmed by the broad peaks at a 2θ value

of 22°. Hemicellulose and lignin are amorphous, so no other broad peaks were observed for the feed materials. Wang et al. [178] obtained a similar diffractogram for raw pine wood. Pyrolytic conversion of the biomass led to the decomposition of cellulose, eliminating the crystallinity of the biomass, as evident from the disappearance of the broad peak at 22° present in the feed material. This absence of broad peaks is a clear indication of the effective devolatilization of the feed material during the pyrolysis reactions. Remarkably, the XRD spectra of the biochar samples exhibited striking similarity and lacked the broad peaks that typically denote crystallinity. The sharp peaks obtained at 28.5°, 29.5°, 36°, 39°, 40°, 43°, 47.5° and 48.5° confirm the amorphous nature of the biochar. The existence of sharp and high-intensity peaks at 29.5° for the biochar sample may be ascribed to the presence of high inorganic material present in the biochar [179]. Hence, the nature of the biochar was observed to be amorphous.

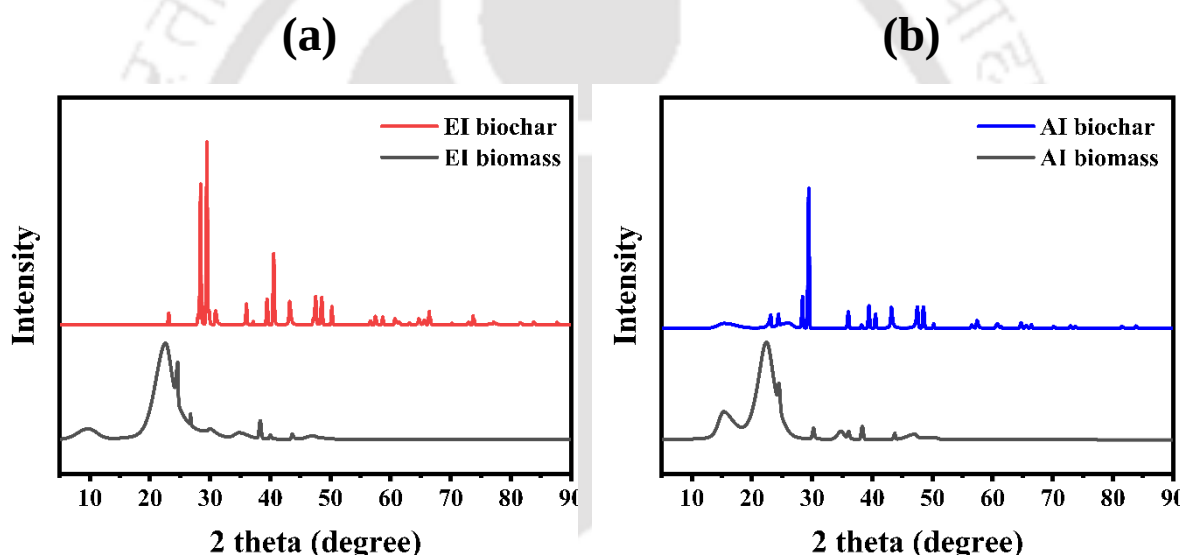


Figure 6.3.7 Powder X-ray diffractogram of (a) EI biomass and biochar and (b) AI biomass and biochar obtained from single-feed pyrolysis of EI and AI biomass.

The Debye-Scherrer technique, as explained by equation (4.1.16), was employed to determine the crystallite size of the biochar samples obtained from the single-feed pyrolysis reactions. Table 6.3.8 provides the full width at half of the maximum (FWHM) and size of crystallite for the EI and AI biomass and biochar samples obtained from the single-feed reactions. The crystallite size of EI and AI biomasses were found to be 23.960 Å and 22.430 Å, respectively, whereas EI and AI biochar samples were found to have crystallite size of 455.270 Å and 379.760 Å, respectively. The size of the crystallites in the particles were observed to grow when the biomass was transformed into biochar. Similar trends were

observed in the biochar particles produced by the pyrolysis and catalytic pyrolysis of *Delonix regia* biomass [40].

Table 6.3.8 FWHM and crystallite size of EI and AI biomass and biochar produced through single-feed pyrolysis of EI and AI biomass.

Co-feed ratios	2 θ (degrees)	FWHM (radians)	Crystallite size ($\text{\AA}$)
EI biomass	22.571	6.162×10^{-02}	23.960
EI biochar	29.444	3.288×10^{-03}	455.270
AI biomass	22.103	6.579×10^{-02}	22.430
AI biochar	29.404	3.943×10^{-03}	379.760

Figure 6.3.8 illustrate the FESEM images of EI and AI biomass, as well as the biochar generated from their single-feed pyrolysis. These images were taken at a magnification of 10kX. Unlike the biomass samples, which exhibited relatively smooth, sturdy and non-porous surfaces, the biochar samples presented a rough, fragile and porous appearance. The honeycomb structure was predominantly formed from EI biomass, while the irregular, fragmented and rough structure was derived from AI biomass. The development of pores on the surface of the biochar samples were mainly attributed to the devolatilization of volatiles present in the biomass during pyrolysis.

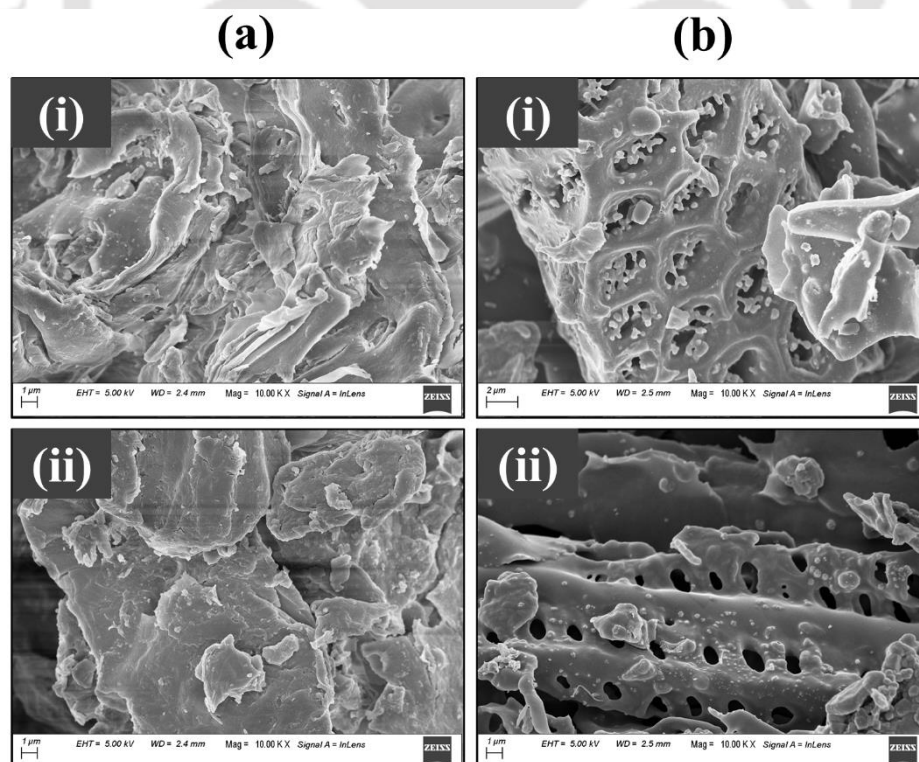
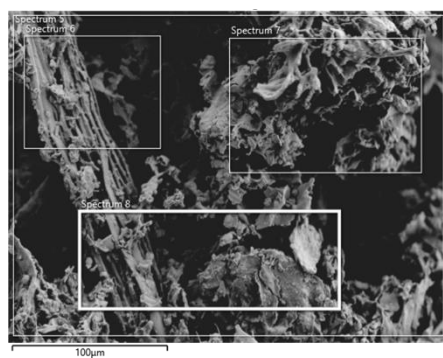
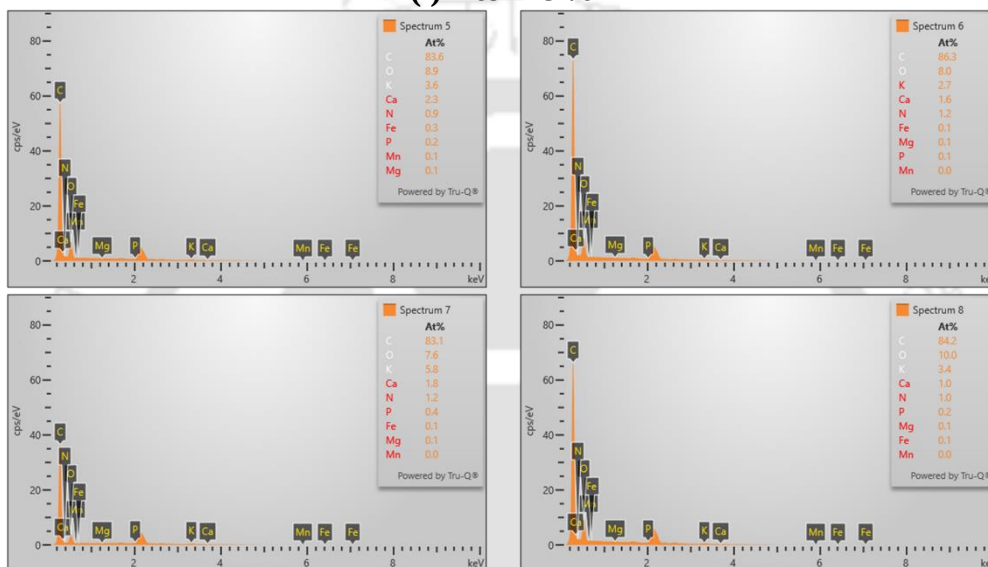


Figure 6.3.8 Field emission scanning electron microscopy images of (a) (i) EI biomass (ii) AI biomass and (b) (i) EI biochar (ii) AI biochar obtained from single-feed pyrolysis of EI and AI biomass.

The compositional analysis of the biochar samples obtained from the single-feed pyrolysis reactions of EI and AI biomass were further examined through EDX analysis to ascertain information on the concentration of primary, secondary and micro-nutrients present in it. The surface scan of the biochar samples depicted the presence of various elements essential for soil conditioning, including carbon, nitrogen, phosphorus, potassium, calcium, magnesium, iron, oxygen and manganese. The results of the EDX analyses of the biochar samples obtained from the single-feed pyrolysis of EI and AI biomass are presented in Figure 6.3.9 and 6.3.10, respectively. Notably, the EDX analyses revealed that the biochar predominantly consisted of carbon as its primary constituent, while the other elements were present in minor concentrations. Studies have reported the application of biochar as a soil conditioner [180–182], suggests a high possibility that the biochar produced from the single-feed pyrolysis of EI and AI biomass can serve as an useful soil conditioner or be utilized in industrial wastewater treatment.



(i) Atomic %



(ii) Weight %

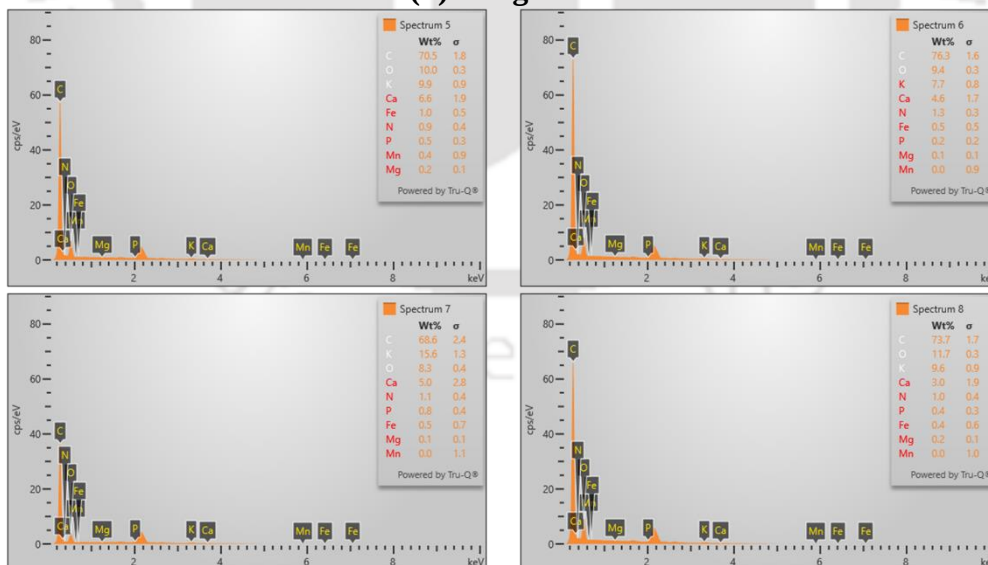
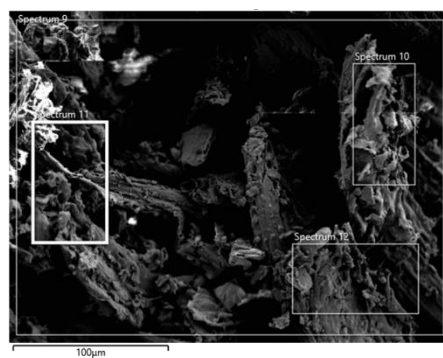
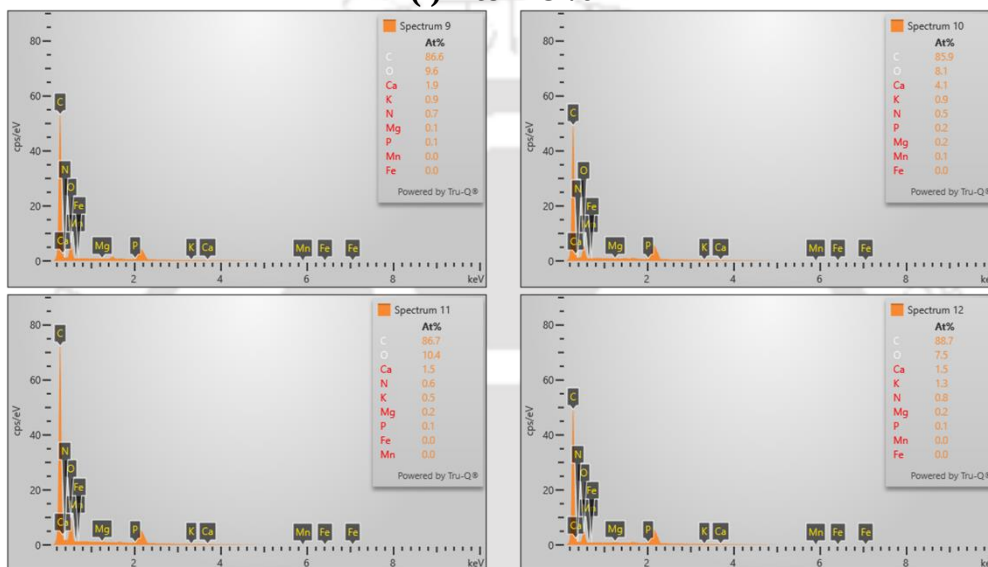


Figure 6.3.9 Energy dispersive X-ray spectroscopic analysis of biochar obtained from single-feed pyrolysis of EI biomass.



(i) Atomic %



(ii) Weight %

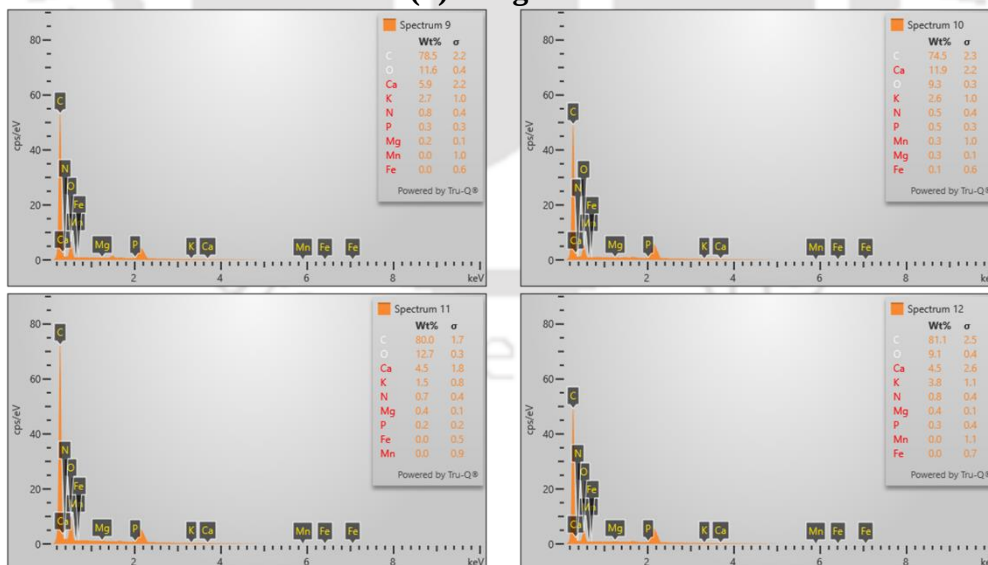


Figure 6.3.10 Energy dispersive X-ray spectroscopic analysis of biochar obtained from single-feed pyrolysis of AI biomass.

6.3.3.3 Characterization of non-condensable gases

The non-condensable gases obtained from the single-feed pyrolysis reactions of EI and AI biomass primarily consisted of four components: carbon dioxide, methane, hydrogen and carbon monoxide. The volumetric compositions of non-condensable gases obtained from EI biomass included 16.822 vol.% hydrogen, 24.664 vol.% carbon monoxide, 23.183 vol.% methane and 35.329 vol.% carbon dioxide, whereas those from AI biomass comprised 15.874 vol.% hydrogen, 26.656 vol.% carbon monoxide, 23.849 vol.% methane and 33.620 vol.% carbon dioxide. It was discovered that among all the components, carbon dioxide was the predominant one for both the biomasses. The presence of oxygen in the feed material (EI: 46.907 wt.% and AI: 35.561 wt.%) contributed significantly to the formation of carbon dioxide. The disintegration of biopolymers and carboxy groups present in protein molecules was linked to carbon dioxide generation, while the reduction of volatile compounds and carbon dioxide led to the synthesis of carbon monoxide [183]. Methane yield was primarily associated with the methoxy groups linked to the phenyl propane units of lignin, while the generation of hydrogen was attributed to the cracking and reformation of aromatic rings present in the biomass [184–186]. These results align with the findings from other studies on various lignocellulosic biomass sources [65,187,188]. The average calorific values of non-condensable gases obtained from the single-feed pyrolysis of EI and AI biomass were found to be 14.486 MJ/Nm³ and 14.882 MJ/Nm³, respectively. Most importantly these gases comprise of ≈47-50% hydrogen and carbon monoxide by volume which can be utilized as it is or as source for synthetic gas or green hydrogen.

6.4 CO-FEED PYROLYSIS OF ERYTHRINA INDICA AND AZADIRACHTA INDICA BIOMASS

6.4.1 Yield analysis of products

The co-feed pyrolysis of *Erythrina indica* (EI) and *Azadirachta indica* (AI) biomass waste was conducted at seven distinct co-feed ratios of 1:4, 1:3, 1:2, 1:1, 2:1, 3:1 and 4:1. Figure 6.4.1 provides a graphical representation of the yields of co-feed pyrolysis products obtained from the reactions, as evaluated using equations (4.4.1), (4.4.2) and (4.4.3) presented in section 4.4 of materials and methods. The bio-oil yield ranged from 29.512 to 32.399 wt.%, while the yields of biochar and non-condensable gases ranged from 38.249 to 42.480 wt.% and 26.901 to 30.730 wt.%, respectively. The maximum bio-oil yield of 32.399 wt.% was observed for the co-feed ratio of EI:AI-1:3, whereas the minimum bio-oil yield of 29.512 wt.% was noted at the co-feed ratio of EI:AI-4:1. For biochar, the maximum yield of 42.480 wt.% was achieved at the co-feed ratio of EI:AI-4:1, while the minimum biochar yield of 38.249 wt.% was recorded at EI:AI-1:3. In the case of non-condensable gases, the maximum yield of 30.730 wt.% was observed at EI:AI-1:2, while the minimum yield of non-condensable gases of 26.901 wt.%, was observed at EI:AI-1:1. Comparing these results with those obtained from single-feed pyrolysis reactions of EI (bio-oil yield: 26.873 wt.% and biochar yield: 42.870 wt.%) and AI (bio-oil yield: 27.286 wt.% and biochar yield: 41.053%) biomass, the co-feed pyrolysis of EI and AI biomass exhibited an enhancement in the bio-oil yield with a reduction in biochar yield. This suggests a positive synergistic effect of the co-feed pyrolysis process on the yield of liquid product.

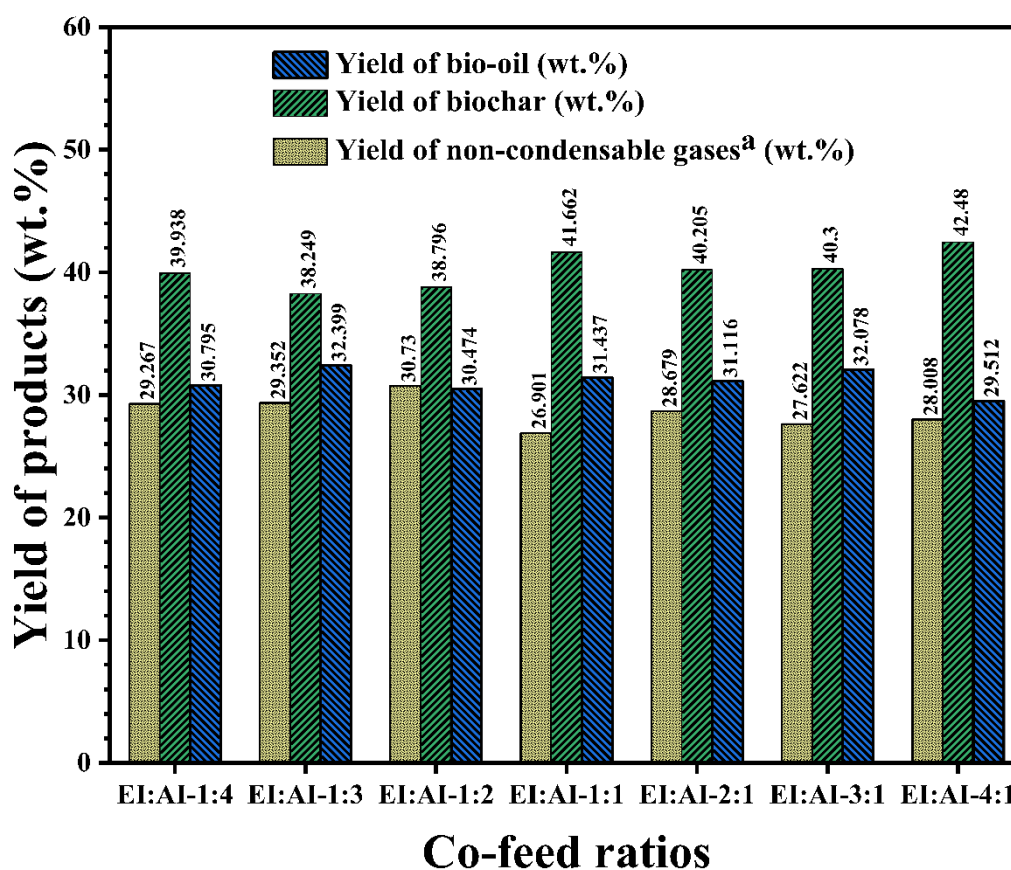


Figure 6.4.1 Pyrolysis product distribution (in wt.%) of co-feed pyrolysis of EI and AI biomass.

The extraction of fuel phase of bio-oil produced from the co-feed pyrolysis reactions of EI and AI biomass was carried out using n-hexane at 10 vol.% of solvent relative to the volume of raw bio-oil. Figure 6.4.2 illustrates the volumetric distribution of the fuel and non-fuel phases extracted from the bio-oil produced through the co-feed pyrolysis reactions. The volumetric % distribution of both the fuel and non-fuel phase depicted a mixed trend. The fuel phase distribution ranged from 16.098 vol.% to 21.818 vol.%, whereas the non-fuel phase distribution ranged from 74.111 vol.% to 83.254 vol.%. Co-feed ratio of EI:AI-3:1 exhibited the maximum distribution of fuel phase of 21.818 vol.%, while the minimum distribution of 16.098 vol.% was recorded for EI:AI-1:4. On the other hand, the non-fuel phase exhibited a maximum distribution of 83.254 vol.% at EI:AI-1:2 ratio, while the minimum distribution of 74.111 vol.% was recorded for the co-feed ratio of EI:AI-4:1. Similar to the single-feed cases, the mixture of the bio-oil and the solvent does not form an ideal mixture. The non-ideal nature of the mixture is the reason why the total makeup of the fuel and non-fuel phases did not sum up to 100% for each individual co-feed pyrolysis case, as illustrated in Figure 6.4.2. In the

following sections, additional characterizations of the co-feed pyrolysis products are covered in order to obtain a deeper knowledge of the synergistic effects of co-feed pyrolysis.

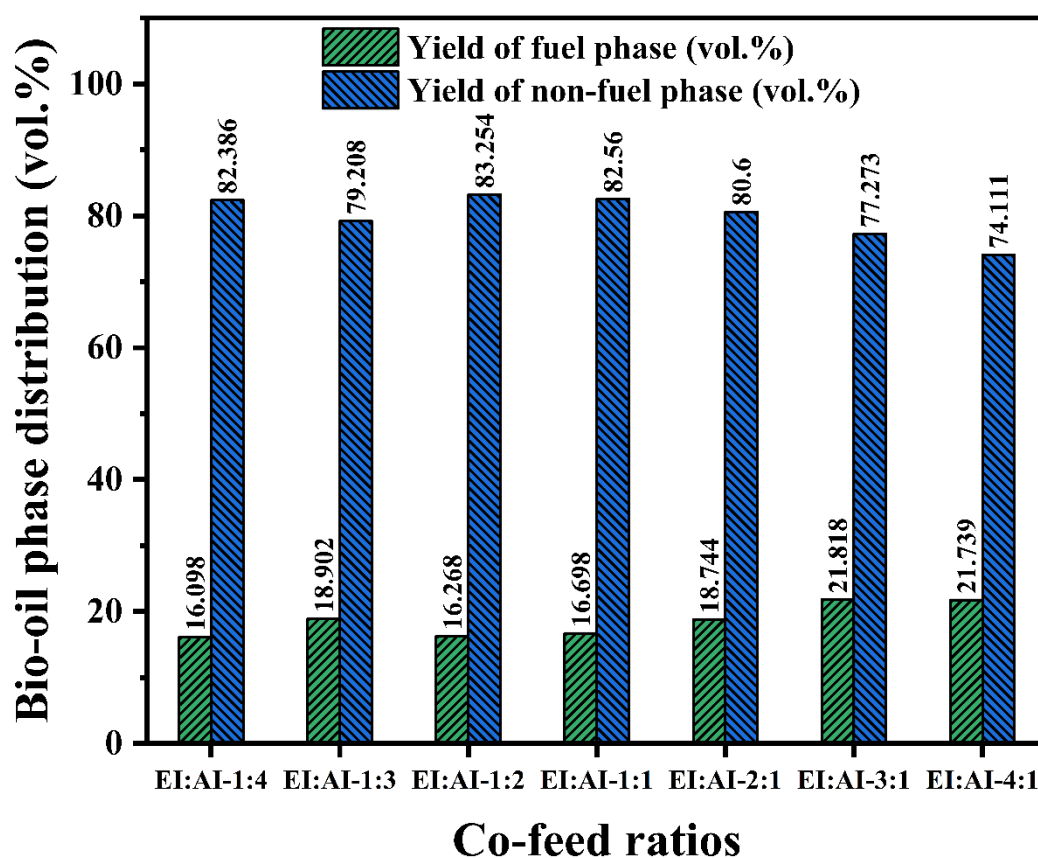


Figure 6.4.2 Fuel and non-fuel phase distribution (in vol.%) of bio-oil produced through co-feed pyrolysis of EI and AI biomass.

6.4.2 Pyrolysis product characterization

6.4.2.1 Characterization of bio-oil

The physiochemical properties including the density, pH and calorific value of the fuel and non-fuel phases of bio-oil produced by co-feed pyrolysis of EI and AI biomass are presented in Table 6.4.1. The fuel phases of bio-oil formed as a result of the co-feed pyrolysis reactions between EI and AI biomass exhibited densities ranging from 0.820 g/mL to 1.013 g/mL, while the non-fuel phase displayed densities between 1.005 g/mL and 1.013 g/mL. Remarkably, the fuel phase extracted from the co-feed ratio of EI:AI-1:1 exhibited the lowest density at 0.820 g/mL, whereas the highest density, reaching 1.013 g/mL, was observed for the co-feed ratio of EI:AI-2:1. However, it was interesting to see that the density of the non-fuel phase remained relatively almost constant across all co-feed ratios. The pH values for the fuel phases varied between 3.080 to 3.640, whereas the pH of the non-fuel phases ranged from 2.670 to 3.140.

The fuel phase obtained at the co-feed ratio of EI:AI-4:1 showed the highest pH value of 3.640, while the lowest pH value of 3.080 was recorded for the fuel phase at the co-feed ratio of EI:AI-1:2. For the non-fuel phase, the highest pH value of 3.140 was noted at the co-feed ratio of EI:AI-3:1, while the lowest pH value of 2.670 was observed at the co-feed ratio of EI:AI-1:4. Calorific values of the fuel phases ranged from 31.351 to 36.798 MJ/kg, with the co-feed ratio of EI:AI-1:1 showing the highest calorific value at 36.798 MJ/kg, and the co-feed ratio of EI:AI-1:4 exhibiting the lowest at 31.351 MJ/kg. Notably, a remarkable enhancement in the physiochemical properties of the fuel phases produced through co-feed pyrolysis processes was observed in comparison to their individual counterparts as discussed in Section 6.3.3.1.

Table 6.4.1 Density, pH and calorific value of fuel and non-fuel phases of bio-oil obtained from co-feed pyrolysis of EI and AI biomass.

Co-feed ratios	Fuel phase			Non-fuel phase	
	Density (g/mL)	pH	Calorific value (MJ/kg)	Density (g/mL)	pH
EI:AI-1:4	0.880	3.370	31.351	1.011	2.670
EI:AI-1:3	0.939	3.280	32.334	1.007	2.920
EI:AI-1:2	0.946	3.080	32.208	1.011	2.720
EI:AI-1:1	0.820	3.580	36.798	1.005	2.830
EI:AI-2:1	1.013	3.190	32.259	1.010	2.860
EI:AI-3:1	0.988	3.460	32.437	1.008	3.140
EI:AI-4:1	1.006	3.640	32.655	1.013	3.130

The stacked FTIR spectra of the fuel phases of bio-oil obtained from the co-feed pyrolysis of EI and AI biomass is illustrated in Figure 6.4.3. Remarkably, these fuel phases exhibited a consistent trend across all samples, suggesting the presence of similar functional groups. These fuel phases exhibited intensities of % transmittance at various wavenumbers, including 3400, 2967, 2933, 2858, 1707, 1609, 1509, 1458, 1370, 1220, 1110, 1027, 745, 596 and 444 cm^{-1} . The co-feed fuel phases displayed a similar kind of spectrum when contrasted with their individual counterparts. Moreover, these spectra were found to be comparable to the fuel phase obtained from other lignocellulosic biomass, and hence they were verified by comparing those results [11,65,161,189,190]. Table 6.4.2 list out the identified functional groups and their corresponding categories present in the fuel phase samples obtained from the co-feed pyrolysis reactions. Notably, the broad peaks observed at a wavenumber of 3400 cm^{-1} suggest the presence of polymeric-OH compounds and water impurities in the fuel phase of the bio-oil. Peaks exhibiting transmittance at 2967, 2933 and 2858 cm^{-1} indicate the presence of aliphatic molecules, including methyl and methylene groups. Furthermore, peaks at 1707 cm^{-1}

suggest the existence of ketones with C=O functional groups. Peaks showing transmittance at 1609 and 1509 cm^{-1} signify the presence of benzene rings, characteristic of aromatic compounds, while the peaks showing transmittance at 1370 cm^{-1} indicate the presence of isopropyl group of isopropyl compounds. Conversely, peaks with intensities at 1458 cm^{-1} also provide evidence of the methylene group found in aliphatic compounds. A comparison of spectral features at 1220 and 1110 cm^{-1} reveals evidence of the C-H group in aromatic compounds and aliphatic ethers, respectively. Furthermore, the appearance of transmittance at 745 cm^{-1} indicates evidence of o-benzenes within the aromatic compounds, while the peak occurring at 1027 cm^{-1} suggests the existence C-OH group of cyclic alcohols. Peaks formed at 596 and 444 cm^{-1} indicate the evidence of O=C=O functional group of carboxylic acids and $\text{C}_n\text{H}_{2n+1}$ of the alkyl group, respectively.

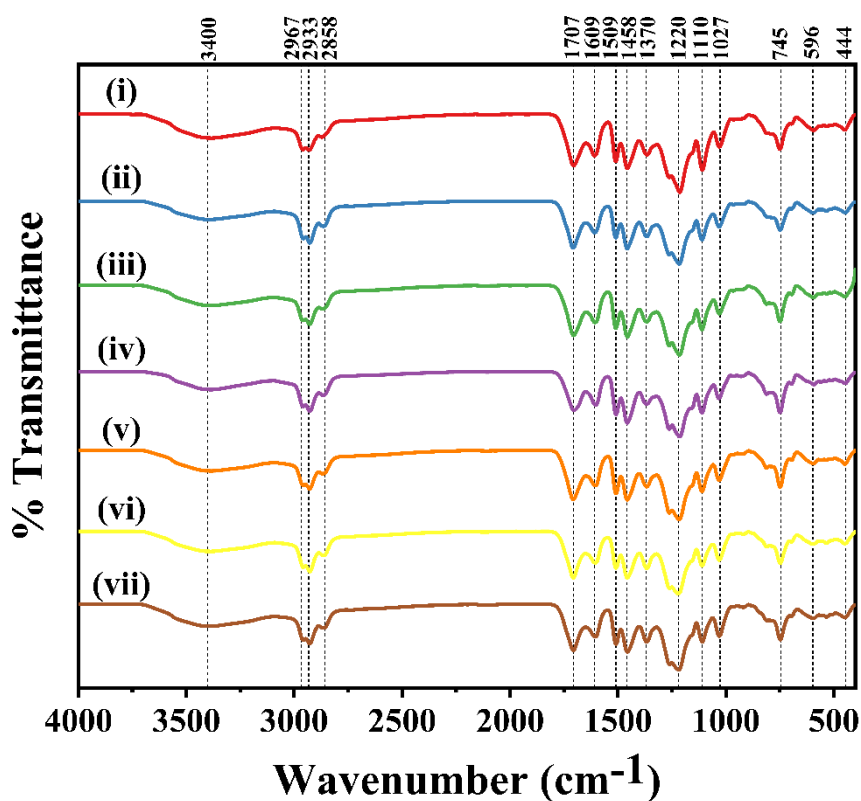


Figure 6.4.3 Fourier transform infrared spectra of fuel phases obtained from co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (i) EI:AI-1:4, (ii) EI:AI-1:3, (iii) EI:AI-1:2, (iv) EI:AI-1:1 (v) EI:AI-2:1, (vi) EI:AI-3:1 and (vii) EI:AI-4:1.

Table 6.4.2 Functional groups present in the fuel phases of bio-oil obtained from co-feed pyrolysis of EI and AI biomass.

Wavenumber (cm ⁻¹)	Wavenumber range (cm ⁻¹)	Class of compound
3400	3420-3250	Polymeric OH and water impurities
2967, 2933, 2858	2990-2850	Methyl and methylene groups of aliphatic compounds
1707	1720-1700	C=O group of ketones
1609	1615-1590	Benzene ring in aromatic compounds
1509	1515-1485	Benzene ring in aromatic compounds
1458	1475-1450	Methylene group of aliphatic compounds
1370	1400-1370	isopropyl group of isopropyl compounds
1220	1280-1180	C-H group in aromatic compounds
1110	1150-1085	Aliphatic ethers
1027	1065-1015	C-OH group of cyclic alcohols
745	760-740	o-benzenes of aromatics
596	700-590	O-C=O group of carboxylic acids
444	565-440	C _n H _{2n+1} group in alkyl groups

The stacked ¹H NMR spectra of the fuel phases obtained from the co-feed pyrolysis of EI and AI biomass is illustrated in Figure 6.4.4. The chemical makeups of the fuel phases were determined by comparing it to known pyrolysis data and other relevant studies [65,171–174]. The investigation revealed that the solvent used, chloroform-D, contributed to the appearance of the peak at 7.26 ppm. Additionally, the peak at 0 ppm indicated water impurities from the solvent tetramethylsilane. Alkanes and aliphatic compounds were identified by peaks ranging from 0.5 to 1.5 ppm and 1.5 to 3.0 ppm, respectively, while alcohols and methylene-dibenzene were indicated by peaks falling between 3.0 and 4.5 ppm. Peak values between 4.5 and 6.0 ppm confirmed the presence of alkenes and methoxy polysaccharides. Aromatic (hetero-) and aldehyde-containing compounds were identified by peaks falling between 6.0–8.5 ppm and 9.5–10.0 ppm ranges, respectively. The fuel phase derived from various lignocellulosic biomass sources exhibited very similar peak patterns and are also comparable to their individual counterparts, confirming the presence of similar chemical elements within it [11,93,161]. The ¹H NMR spectrum of the fuel phases within the bio-oil resulting from co-feed pyrolysis demonstrated consistent chemical compound types. However, noticeable variations in the intensities of these compounds were apparent in the ¹H NMR spectra. For instance, the fuel phases obtained at co-feed ratios of EI:AI-1:4, 1:3, 3:1 and 4:1 displayed higher proportions of alcohols, whereas the co-feed ratio of EI:AI-1:1 exhibited a more pronounced presence of alkanes. The prevalence of alkanes indicates an improved quality of the fuel phase

for the co-feed ratio of EI:AI-1:1, a characteristic supported by the physiochemical properties of the bio-oil, particularly in terms of calorific content and density, as discussed at the beginning of this section.

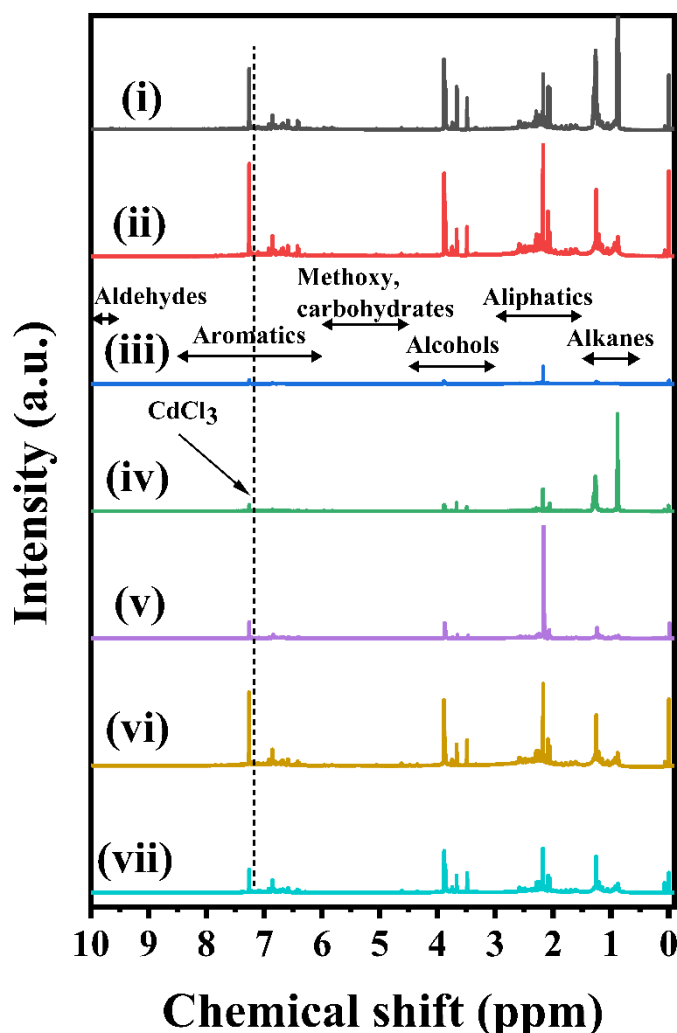


Figure 6.4.4 ^1H NMR spectra of fuel phases obtained from co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (i) EI:AI-1:4, (ii) EI:AI-1:3, (iii) EI:AI-1:2, (iv) EI:AI-1:1 (v) EI:AI-2:1, (vi) EI:AI-3:1 and (vii) EI:AI-4:1.

Figure 6.4.5 illustrate the GC-MS spectra of the fuel phases obtained from the co-feed pyrolysis reactions of EI and AI biomass. Table 6.4.3 provides a comprehensive data on various compounds identified through the analysis, including details on their chemical type, molecular formula, molecular weight, retention time and area percentage. The detected compounds in the analysis range from C_5 to C_{24} , encompassing various chemical categories such as alkanes, alkenes, alcohols, aromatics, esters, nitro compounds and organosilicons. These findings align with the results from our previous research on co-feed pyrolysis of *Delonix regia* and pine

wood conducted by Kawale and Kishore [65]. Among the most notable compounds present in the fuel phase samples obtained from the co-feed pyrolysis reactions include cyclopentane, methyl- (4.965% area) for EI:AI-1:4, cyclopentane, methyl- (4.783% area) for EI:AI-1:3, 1-cyclohexyl-2-propen-1-ol (7.405% area) for EI:AI-1:2, cyclopentane, methyl- (6.165% area) for EI:AI-1:1, 1-cyclohexyl-2-propen-1-ol (6.294% area) for EI:AI-2:1, 1-pentene, 3-methyl- (4.025% area) for EI:AI-3:1, and cyclopentane, methyl- (4.783% area) EI:AI-4:1.

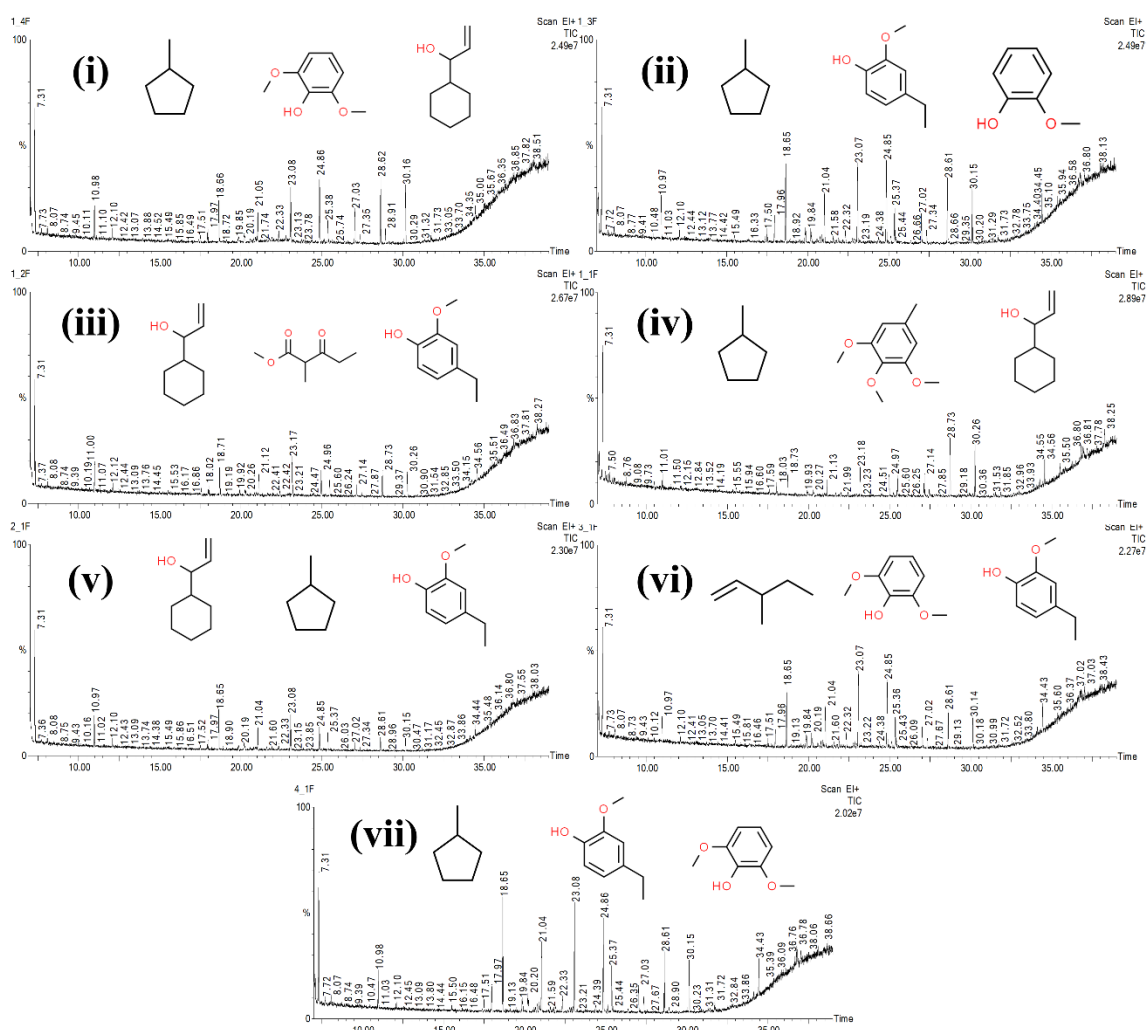


Figure 6.4.5 GC-MS spectra of fuel phases obtained from co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (i) EI:AI-1:4, (ii) EI:AI-1:3, (iii) EI:AI-1:2, (iv) EI:AI-1:1 (v) EI:AI-2:1, (vi) EI:AI-3:1 and (vii) EI:AI-4:1.

Table 6.4.3 Probable chemical compounds identified through GC-MS analysis of fuel phases of bio-oil obtained from co-feed pyrolysis of EI and AI biomass.

Name of the compound	Chemical type	Molecular formula	Molecular weight	EI:AI-1:4 fuel phase		EI:AI-1:3 fuel phase		EI:AI-1:2 fuel phase		EI:AI-1:1 fuel phase		EI:AI-2:1 fuel phase		EI:AI-3:1 fuel phase		EI:AI-4:1 fuel phase	
				RT	Area %	RT	Area %	RT	Area %	RT	Area %	RT	Area %	RT	Area %	RT	Area %
1-cyclohexyl-2-propen-1-ol	Alcohol	C ₉ H ₁₆ O	140	7.018	3.560	7.018	2.775	7.018	7.405	7.01	2.598	7.018	6.294	-	-	7.018	2.704
Cyclopentane, butyl-	Cycloalkanes	C ₉ H ₁₈	126	-	-	-	-	-	-	-	-	-	-	7.018	3.012	-	-
Pentanoic acid, 2-methyl-3-oxo-, methyl ester	Ester	C ₇ H ₁₂ O ₃	144	7.098	2.476	7.098	3.240	7.314	5.359	7.108	0.979	-	-	7.093	2.141	7.093	2.140
Cyclopentane, methyl-	Cycloalkane	C ₆ H ₁₂	84	7.314	4.965	7.309	4.783	-	-	7.314	6.165	7.309	6.002	-	-	7.309	4.783
1-pentene, 3-methyl-	Alkene	C ₆ H ₁₂	84	-	-	-	-	-	-	-	-	-	-	7.314	4.025	-	-
Cyclohexane	Cycloalkane	C ₆ H ₁₂	84	-	-	-	-	-	-	-	-	8.079	0.550	-	-	-	-
Furan, 2-methoxy-	Heterocyclic aromatic compound	C ₅ H ₆ O ₂	98	10.980	1.692	10.975	1.636	11.000	1.793	-	-	10.975	1.930	10.975	1.012	10.973	1.143
Ethanol, pentamethyl-	Alcohol (aromatic)	C ₇ H ₁₆ O	116	-	-	-	-	12.120	0.613	-	-	12.100	0.697	-	-	-	-
Phenol, 3-methyl-	Phenol	C ₁₃ H ₁₄ O ₂	108	17.968	0.678	17.963	1.217	18.023	0.770	-	-	17.978	0.672	17.968	0.880	17.973	-
Phenol, 2-methoxy-	Alcohol (phenol), aromatic	C ₇ H ₈ O ₂	124	18.658	1.927	18.648	3.622	18.713	1.831	18.733	1.106	18.653	2.360	18.648	2.441	18.653	4.319
Creosol	Alcohol (aromatic)	C ₈ H ₁₀ O ₂	138	21.049	1.414	21.039	2.010	21.124	1.261	-	-	21.044	1.384	21.044	1.754	21.044	2.402
Phenol, 2,3-dimethyl-	Phenol	C ₈ H ₁₀ O	122	22.335	0.632	-	-	-	-	-	-	-	-	-	-	-	-

Phenol, 4-ethyl-2-methoxy-	Alcohol, aromatic	C ₉ H ₁₂ O ₂	152	23.080	2.882	23.075	3.751	23.175	2.300	23.185	1.495	23.085	2.502	23.075	3.431	23.080	4.524
Phenol, 2,6-dimethoxy-	Alcohol (phenol), aromatic	C ₈ H ₁₀ O ₃	154	24.856	3.735	-	-	24.956	1.715	24.966	1.314	24.861	1.764	24.845	3.465	24.856	4.406
Phenol, 2-methoxy-4-propyl-	Alcohol, aromatic	C ₁₀ H ₁₄ O ₂	166	25.376	1.213	-	-	25.481	1.091	25.476	1.225	25.371	1.181	25.361	1.697	25.371	1.906
1,2,4-trimethoxybenzene	Anisoles	C ₉ H ₁₂ O ₃	168	27.027	1.616	27.021	1.368	27.136	0.716	27.142	1.267	-	-	27.016	0.882	27.027	1.119
Benzene, 1-methoxy-2-methyl-	Anisoles	C ₈ H ₁₀ O	122	28.617	2.792	-	-	-	-	-	-	-	-	-	-	-	-
Benzene, 1,2,3-trimethoxy-5-methyl-	Anisoles	C ₁₀ H ₁₃ O ₃	182	-	-	28.612	2.531	28.727	1.471	28.727	2.892	28.612	0.852	28.607	1.530	28.613	2.111
Benzene, 1,2,3-trimethoxy-5-(2-propenyl)-	Phenylpropene	C ₁₂ H ₁₆ O ₃	208	28.912	0.617	-	-	-	-	-	-	-	-	-	-	-	-
Benzene, 1-methoxy-3-methyl-	Aromatic compounds	C ₈ H ₁₀ O	122	-	-	30.148	1.980	-	-	-	-	-	-	30.138	1.234	30.148	1.749
Furan, 2-nitro-5-(3-phenyliminoprop-2-enyl)-	Nitro compound	C ₁₅ H ₁₁ NO ₃	242	30.158	2.244	-	-	30.263	1.190	30.263	2.266	30.153	0.736	-	-	-	-
Hexadecanoic acid, methyl ester	Ester	C ₁₇ H ₃₄ O ₂	270	-	-	-	-	-	-	34.559	1.146	-	-	34.429	0.900	34.430	1.444
1,1,1,3,5,5,5-heptamethyltrisiloxane	Organosilicon	C ₇ H ₂₁ O ₂ Si ₃	222	-	-	34.449	1.079	34.559	0.716	-	-	34.439	0.739	-	-	-	-
Cyclotrisiloxane, hexamethyl-	Organosilicon	C ₆ H ₁₈ O ₃ Si ₃	222	-	-	36.795	0.757	-	-	36.810	0.936	-	-	36.660	0.973	-	-
4-tert-octylphenol, tms derivative	Alkylbenzene	C ₁₄ H ₂₂ O	278	-	-	-	-	-	-	36.920	1.518	36.795	0.628	-	-	36.776	1.236
Hexestrol, 2tms derivative	Stilbenes	C ₂₄ H ₃₈ O ₂ Si ₂	414	-	-	-	-	-	-	37.186	0.844	-	-	-	-	-	-
Tris(tert-butyl)dimethylsilyloxyarsane	Organoarsenic	C ₁₈ H ₄₅ AsO ₃ Si ₃	468	-	-	-	-	38.266	0.578	38.251	1.152	-	-	-	-	-	-

6.4.2.2 Characterization of biochar

Table 6.4.4 provides a comprehensive overview of the physiochemical properties, along with different types of densities (bulk, tapped and particle), porosity, as well as flowability and combustion indices, associated with the biochar obtained from the co-feed pyrolysis of EI and AI biomass. Proximate analysis results for the biochar samples consistently reveal a low moisture content as measured on wet basis, ranging from 4.923 wt.% to 6.099 wt.%. Similarly, the volatile matter and ash content in the biochar samples are notably low, spanning from 17.560 wt.% to 23.202 wt.% and 8.016 wt.% to 10.488 wt.%, respectively. Predominantly, the biochar samples are composed of fixed carbon, with percentages falling within the range of 68.026 wt.% to 73.152 wt.%. The combination of low volatile matter and high fixed carbon content indicates effective devolatilization of the feed material during the pyrolysis process. Consequently, the biochar stands out as a promising and reliable source of solid fuel and other applications such as fertilizer production and wastewater treatment.

The elemental analysis of the biochar samples identified carbon as the predominant constituent, followed by oxygen and minor amounts of hydrogen. Nitrogen was present in trace amounts, while sulphur was notably absent. Carbon, oxygen, and hydrogen content in the biochar samples ranged from 65.725 to 79.231 wt.%, 18.489 to 25.158 wt.%, and 2.280 to 6.625 wt.%, respectively. Notably, the elemental analysis revealed that the biochar produced at the co-feed ratio of EI:AI-1:1 exhibited the highest carbon content at 79.231 wt.%, accompanied by the lowest oxygen and hydrogen values of 18.489 wt.% and 2.280 wt.%, respectively. The low hydrogen content and elevated carbon content resulted in a lower H/C ratio of 0.345 for the co-feed ratio of EI:AI-1:1, indicating substantial devolatilization of the co-feed sample. Furthermore, the biochar produced at co-feed ratio EI:AI-1:1 displayed a low O/C ratio of 0.175, a favourable characteristic for use as a fuel. Notably, the minimal nitrogen content and the complete absence of sulphur in the biochar samples are favourable characteristics that help prevent the formation of nitrogenous and sulphur compounds during combustion. Specifically, the biochar produced at the co-feed ratio of EI:AI-1:1 completely lacked both nitrogen and sulphur contents, underscoring its environmentally friendly profile. The analysis of calorific values for the biochar samples demonstrated a range from 26.687 to 29.233 MJ/kg. The biochar produced at the co-feed ratio of EI:AI-1:1 exhibited the highest calorific value, while the lowest calorific value was observed for the co-feed ratio of EI:AI-3:1.

The various density measurements provided in Table 6.4.4 indicate notable improvements in the characteristics of the biochar samples, particularly in terms of enhanced bulk density and particle density. This enhancement ultimately translates to a reduced requirement for storage and transportation space, leading to potential cost savings in handling. Additionally, the biochar samples produced through co-feed pyrolysis reactions exhibited improved flowability indices. These indices, encompassing the angle of repose, ranged from 28.799° to 36.279°, indicating that the biochar samples possess good to excellent flowability properties. The Hausner ratio and Carr Compressibility index varied within the range of 1.264 to 1.399 and 20.806 to 28.500, respectively, categorizing the biochar samples as having acceptable flowability. Overall, the flowability indices suggest that the biochar resulting from co-feed pyrolysis displays fair flowability properties, and are better than those of individual biomass feed samples.

The combustibility indices of the biochar resulting from co-feed pyrolysis reactions indicate an enhanced capacity for combustion. The fuel ratio values for the biochar samples ranged from 2.964 to 4.166, surpassing the fuel ratio of coal (typically ranging from 0.5 to 2.0) [176]. While the combustibility index of the biochar samples was generally lower compared to coal [132,176,177], it is notable that the majority of the biochar samples met or exceeded the minimum requirement for volatile ignitability (14 MJ/kg), except for those at the co-feed ratios of EI:AI-2:1 and 3:1. Overall, the biochar samples can be considered to possess favourable combustion properties, making them suitable for safe utilization as solid fuels in various applications, including boilers, etc. in chemical process industries.

Table 6.4.4 Physiochemical properties, different types of densities, porosity, flowability and combustion indices of biochar produced through co-feed pyrolysis of EI and AI biomass.

Properties		Co-feed ratios						
		EI:AI-1:4	EI:AI-1:3	EI:AI-1:2	EI:AI-1:1	EI:AI-2:1	EI:AI-3:1	EI:AI-4:1
Proximate analysis	Moisture content (wet basis) (wt.%)	4.923	5.830	5.648	6.049	5.864	6.099	5.470
	Volatile matter content (dry basis) (wt.%)	17.560	22.153	23.202	19.861	18.306	18.978	21.553
	Ash content (dry basis) (wt.%)	9.287	9.474	8.016	10.488	10.290	10.188	10.421
	Fixed Carbon content ^a (dry basis) (wt.%)	73.152	68.374	68.782	69.651	71.404	70.835	68.026
Ultimate analysis	Carbon (wt.%)	75.881	71.397	65.725	79.231	73.169	73.801	74.224
	Hydrogen (wt.%)	3.401	5.397	6.625	2.280	4.032	3.537	3.265
	Nitrogen (wt.%)	1.690	2.449	2.492	-	2.006	2.162	2.397
	Sulphur (wt.%)	-	-	-	-	-	-	-
	Oxygen ^b (wt.%)	19.028	20.757	25.158	18.489	20.793	20.500	20.114
H/C ratio		0.538	0.907	1.210	0.345	0.661	0.575	0.528
O/C ratio		0.188	0.218	0.287	0.175	0.213	0.208	0.203
Calorific value (MJ/kg)		28.465	28.375	28.701	29.233	27.318	26.687	27.979
Densities	Bulk density, (ρ_b) (g/mL)	0.275	0.290	0.280	0.265	0.239	0.227	0.223
	Tapped density, (ρ_{tb}) (g/mL)	0.350	0.391	0.364	0.371	0.334	0.289	0.281
	Particle density, (ρ_p) (g/mL)	1.235	1.802	1.517	1.499	1.197	1.479	1.539
Porosity, (ε_o)		0.773	0.834	0.810	0.818	0.797	0.845	0.850
Flowability indices	Angle of repose (θ)	31.709	35.391	29.536	28.799	36.279	31.815	35.407
	Hausner ratio (HR)	1.272	1.352	1.299	1.399	1.399	1.272	1.264
	Carr compressibility index, (CCI)	21.284	26.026	23.007	28.385	28.500	21.324	20.806
Combustion indices	Fuel ratio, (FR)	4.166	3.086	2.964	3.507	3.901	3.733	3.156
	Combustibility index, (CI) (MJ/kg)	6.879	9.239	9.865	8.297	6.984	7.137	8.829
	Volatile ignitability, (VI) (MJ/kg)	16.632	18.814	18.900	21.964	13.172	10.946	18.451
^{a, b} calculated by difference								

The TGA-DTG curves for biochar obtained from the co-feed pyrolysis reactions of EI and AI biomass are illustrated in Figures 6.4.6 (a) and (b). The TGA curves revealed progressive mass loss for all biochar samples as the temperature increased, indicating that the primary constituents of biochar are fixed carbon and inorganic components stable at inert conditions. Similar trends were observed for the biochar obtained from single-feed reactions of EI and AI biomass. However, the extent of mass loss in the biochar samples varied with different co-feed ratios. For instance, the maximum mass loss of 24.097 wt.% was observed in the biochar sample at the co-feed ratio of EI:AI-2:1, while the minimum mass loss of 16.210 wt.% was recorded for the co-feed ratio of EI:AI-1:1. The reduced mass loss in the biochar obtained from the EI:AI-1:1 co-feed ratio indicates efficient devolatilization of the feed material. Moreover, the absence of a significant mass loss between 200 and 390°C suggests complete conversion of the feed material's cellulose and hemicellulose throughout the pyrolysis process. The elimination of any unconverted lignin, absorbed volatiles, residual organic matter and any water that remains due to physisorption are the major causes of the mass loss in the biochar. This slow and gradual mass loss pattern resulted in differences in the trends of the TGA curve for biochar samples compared to their biomass counterparts illustrated in Figure 6.1.1 (a) and (b). Additionally, the DTG curve exhibited a unique pattern in contrast to that of its biomass counterparts. While biomass samples displayed only one minimum on their DTG curves, the biochar samples exhibited multiple local minima. The existence of multiple local minima in the DTG curves of the biochar may be explained by the intricate composition of the biochar and the varying temperatures at which its constituents devolatilize.

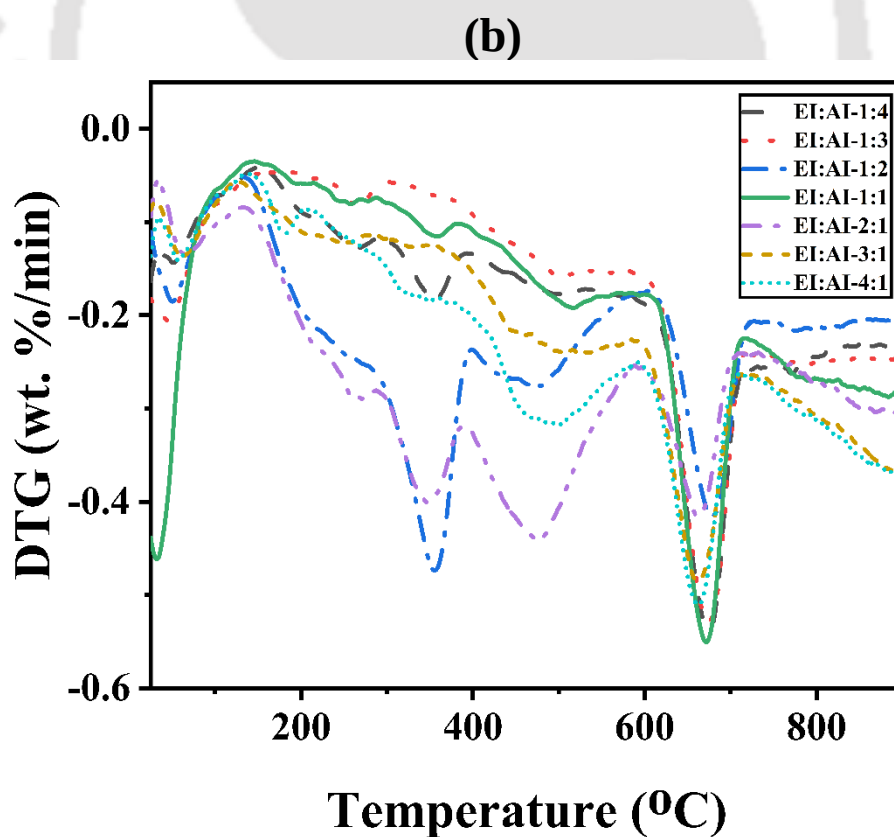
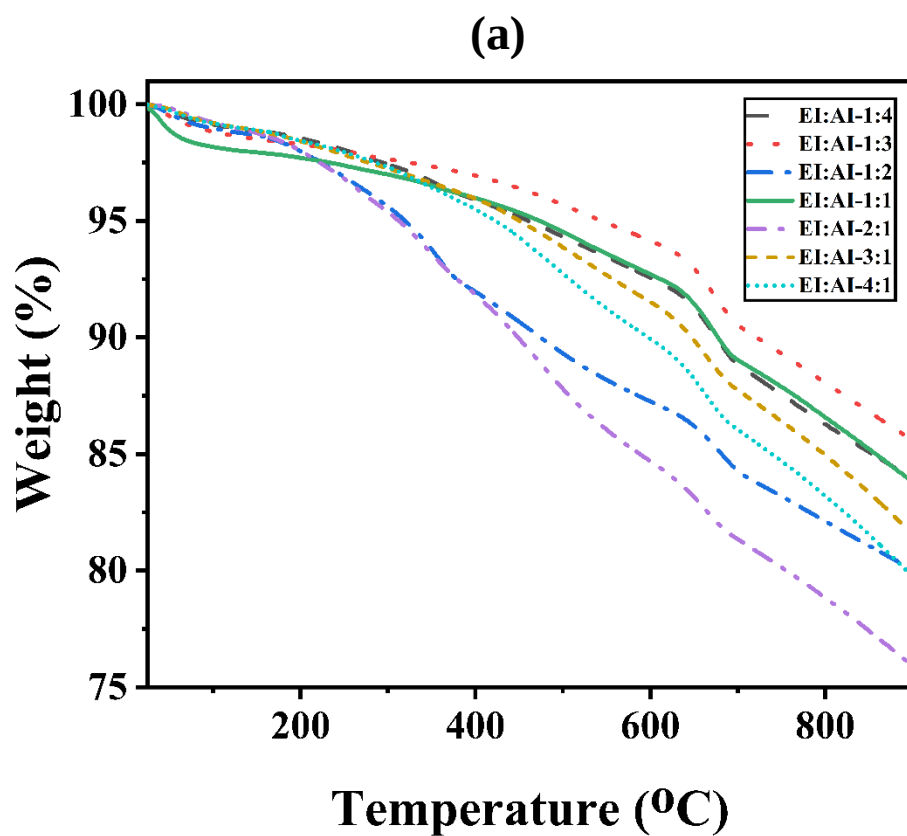


Figure 6.4.6 (a) Thermogravimetric and (b) differential thermogravimetric curves of biochar produced through co-feed pyrolysis of EI and AI biomass.

The crystal structure of the biochar samples obtained from the co-feed pyrolysis of EI and AI biomass was examined using a powder X-ray diffractogram. Figure 6.4.7 illustrates the graphical representation of the XRD spectra of the biochar samples. Remarkably, the XRD spectra of the biochar samples exhibited striking similarity and lacked the broad peaks that typically denote crystallinity. This absence of broad peaks is a clear indication of the effective devolatilization of the feed material which was also observed in the biochar obtained from the single-feed pyrolysis reactions. The breakdown of cellulose during the pyrolytic conversion feed material also eliminates the crystalline nature of the original biomass. The amorphous character of the biochar is reaffirmed in this work by the appearance of sharp peaks at 28° , 29° , 36° , 39° , 40° , 43° , 47.5° and 48° . Furthermore, the enhanced inorganic material concentration in the biochar sample may be the cause of the abrupt, high-intensity peaks seen at 29.5° [179].

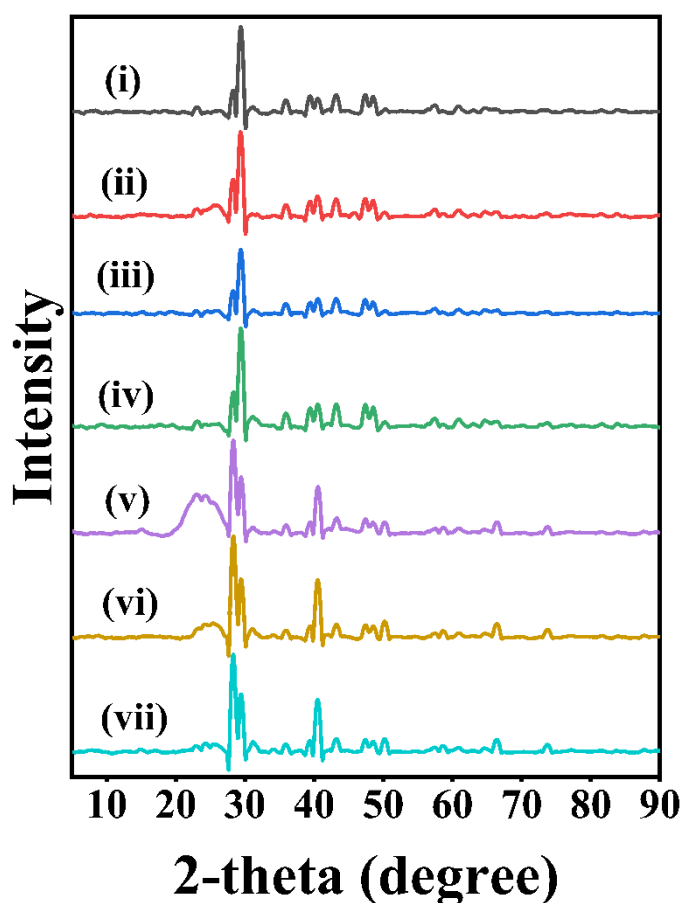


Figure 6.4.7 Powder X-ray diffractogram of biochar obtained from co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (i) EI:AI-1:4, (ii) EI:AI-1:3, (iii) EI:AI-1:2, (iv) EI:AI-1:1 (v) EI:AI-2:1, (vi) EI:AI-3:1 and (vii) EI:AI-4:1.

The Debye-Scherrer technique explained by equation (4.1.16) was employed to determine the crystallite size of the biochar samples obtained from the co-feed pyrolysis

reactions. Table 6.4.5 provides the full width at half of the maximum (FWHM) and size of crystallite for the various biochar samples. The crystallite sizes within the biochar produced through the co-feed pyrolysis process ranged from 371.820 to 886.300. Notably, the crystallite sizes in the particles exhibited growth during the transformation of biomass into biochar. These biochar particles generated through co-feed pyrolysis demonstrated similar crystallite sizes when compared to their individual counterparts, with the exception of the biochar produced at the co-feed ratio of EI:AI-3:1.

Table 6.4.5 FWHM and crystallite size of biochar produced through co-feed pyrolysis of EI and AI biomass.

Co-feed ratios	2 θ (degrees)	FWHM (radians)	Crystallite size (Å)
EI:AI-1:4	29.400	3.424×10^{-03}	437.190
EI:AI-1:3	29.398	3.484×10^{-03}	429.730
EI:AI-1:2	29.386	3.695×10^{-03}	405.220
EI:AI-1:1	29.439	3.986×10^{-03}	375.630
EI:AI-2:1	28.411	4.018×10^{-03}	371.820
EI:AI-3:1	28.395	1.686×10^{-03}	886.300
EI:AI-4:1	28.369	3.468×10^{-03}	430.610

Figure 6.4.8 illustrate the FESEM images of EI and AI biomass, as well as the biochar obtained from their co-feed pyrolysis processes. These images were taken at a magnification of 5kX. Unlike the biomass samples, which exhibited relatively smooth, sturdy and non-porous surfaces, the biochar samples presented a rough, fragile and porous appearance. The honeycomb structure was predominantly formed from EI biomass, while the irregular, fragmented and rough structure was derived from AI biomass. The surface morphology of the biochar obtained from the co-feed pyrolysis reactions are similar to those obtained from the single-feed reactions. However, the pores formed in the biochar from the co-feed pyrolysis process were observed to be more prominent and more compact honeycomb structures than their individual counterparts. The development of distinct pores on the surface of the biochar was mainly attributed to the substantial devolatilization of volatile materials present in the biomass during pyrolysis. The FESEM images provided evidence of synergistic effect and the release of larger quantities of volatiles from the biomass material during pyrolysis, leading to a reduced presence of the original cell structure within the biochar.

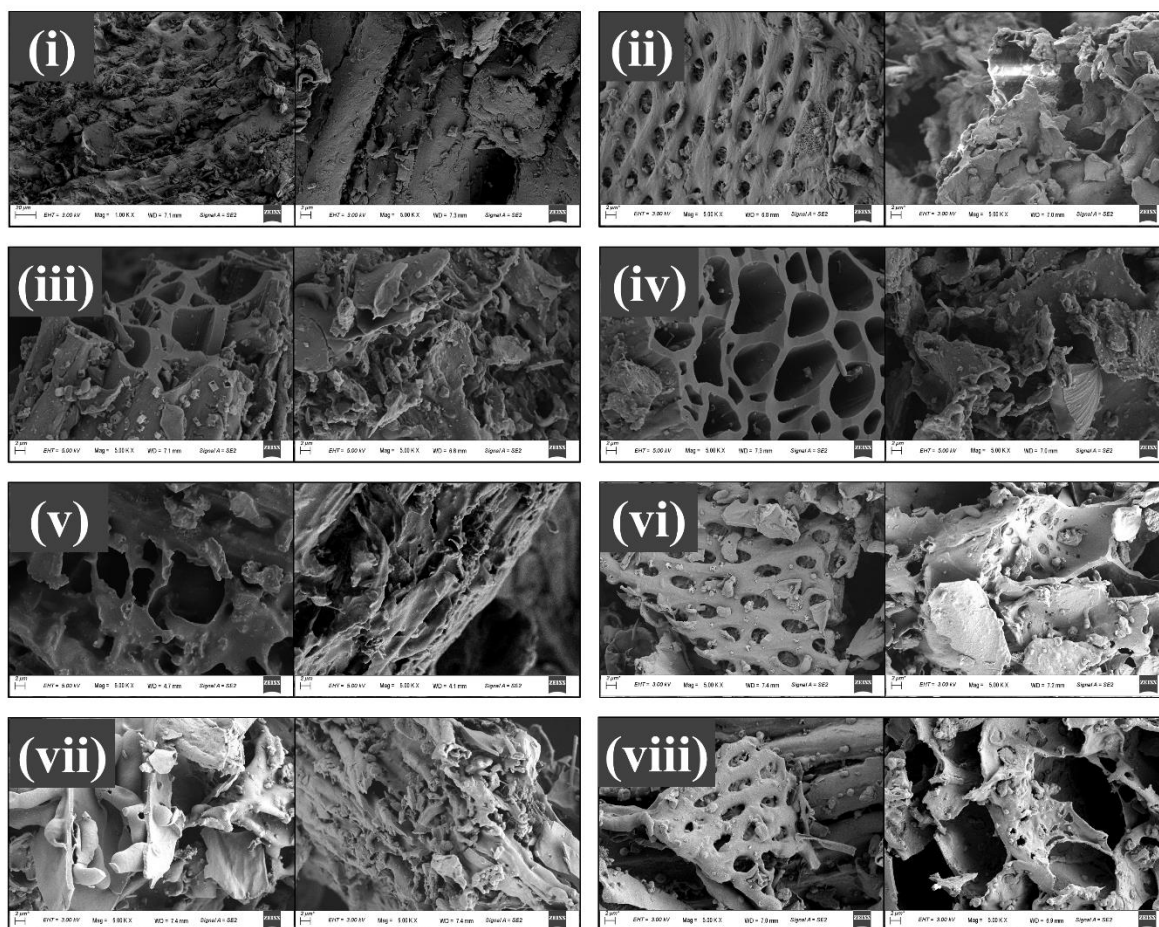
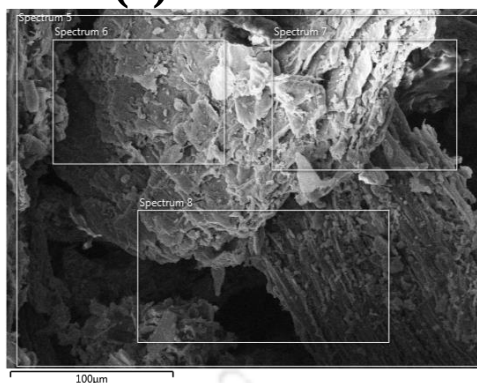


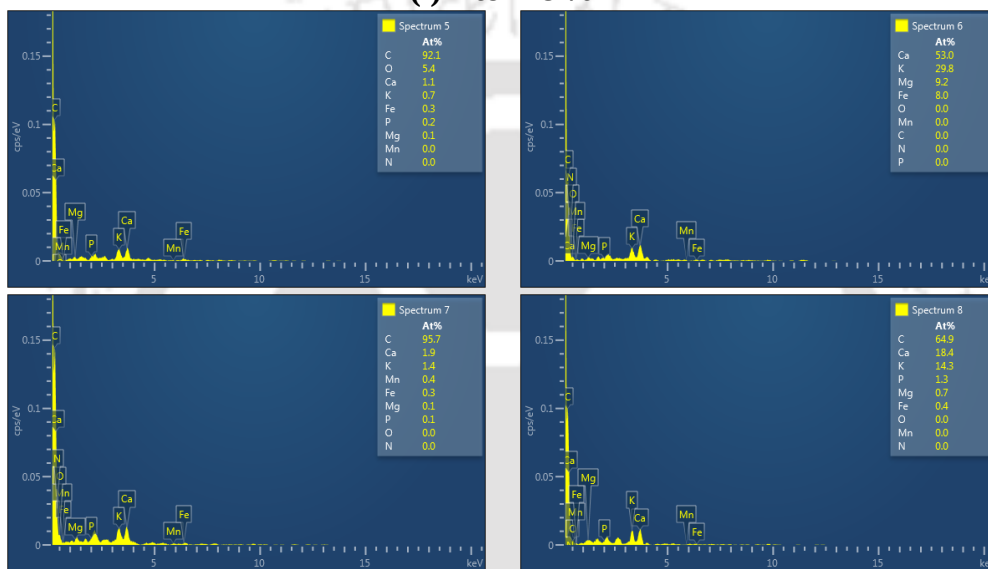
Figure 6.4.8 FESEM images of (i) EI and AI biomass and biochar produced through co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (ii) EI:AI-1:4, (iii) EI:AI-1:3, (iv) EI:AI-1:2, (v) EI:AI-1:1 (vi) EI:AI-2:1, (vii) EI:AI-3:1 and (viii) EI:AI-4:1.

The compositional analysis of the biochar samples obtained from the co-feed pyrolysis reactions of EI and AI biomass were also examined through EDX analysis to ascertain information on the concentration of primary, secondary and micro-nutrients present in it. The surface scan of the biochar samples depicted the presence of various elements essential for soil conditioning, including carbon, nitrogen, phosphorus, potassium, calcium, magnesium, iron, oxygen and manganese which were also observe for the biochar obtained from the single-feed reactions. The results of the EDX analyses of the biochar samples are presented in Figure 6.4.9.

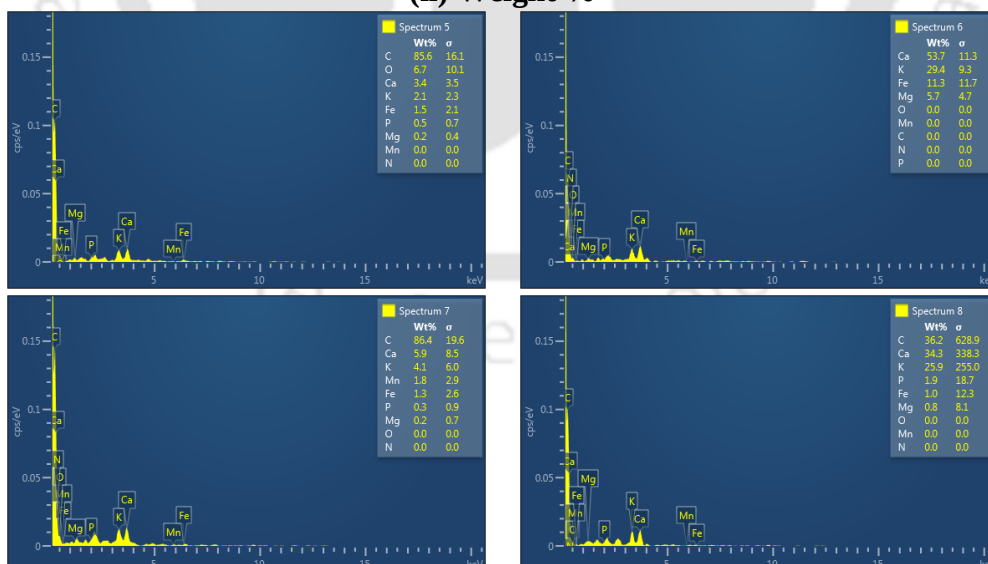
(a) EI:AI-1:4



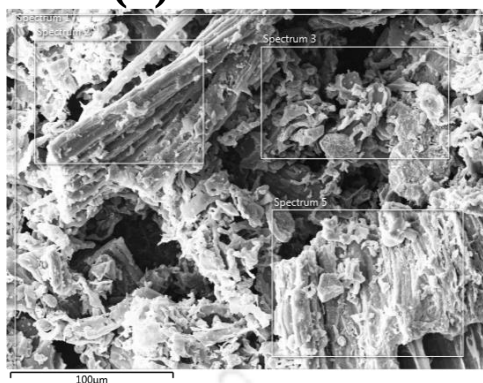
(i) Atomic %



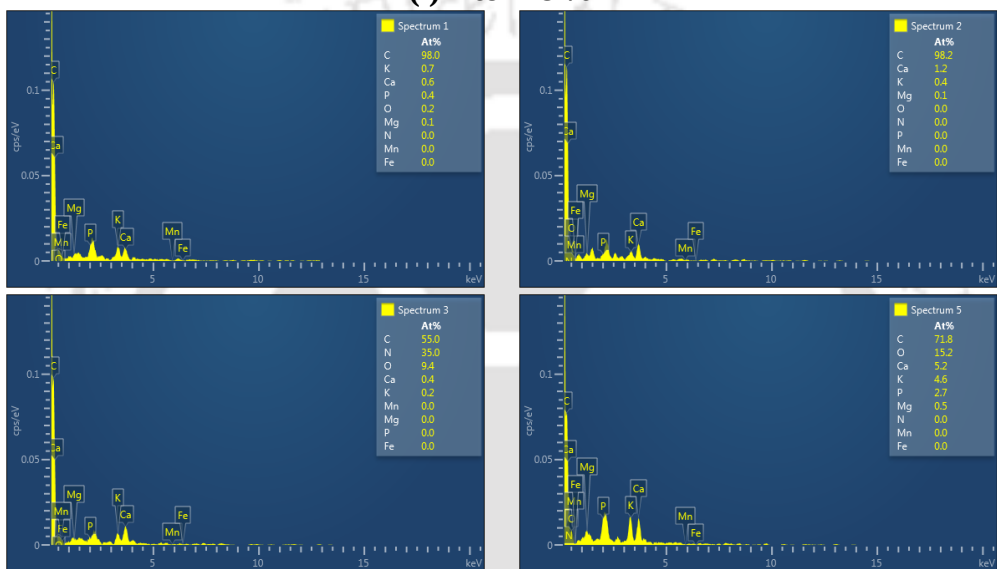
(ii) Weight %



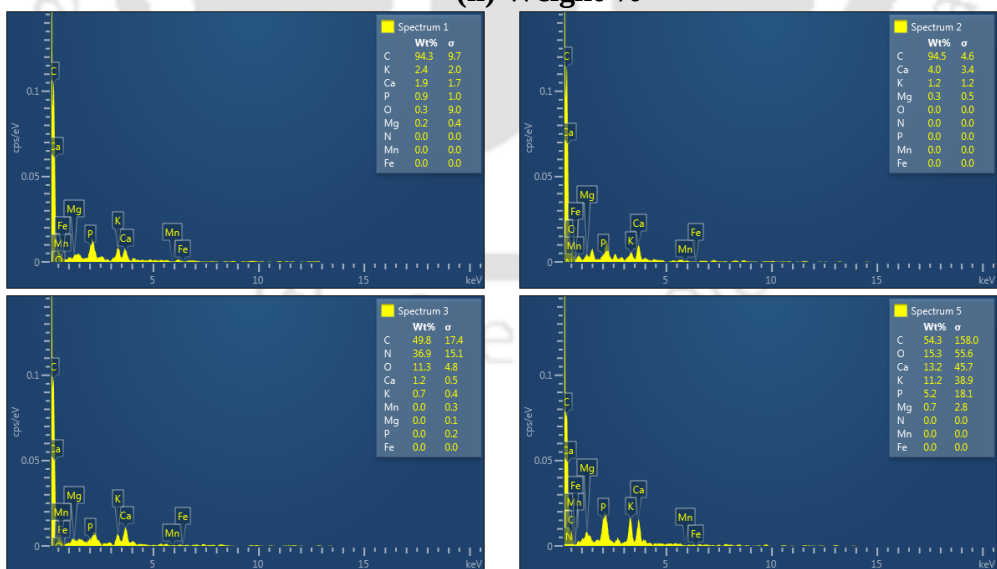
(b) EI:Al-1:3



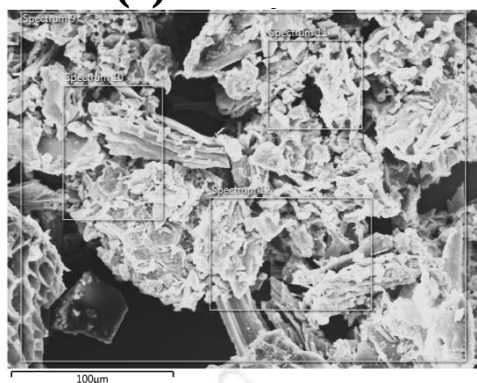
(i) Atomic %



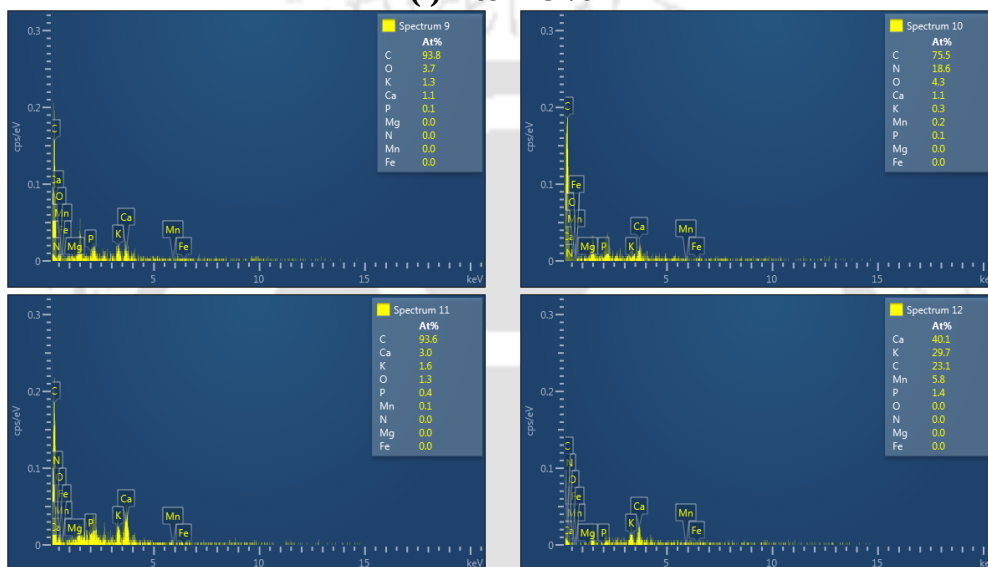
(ii) Weight %



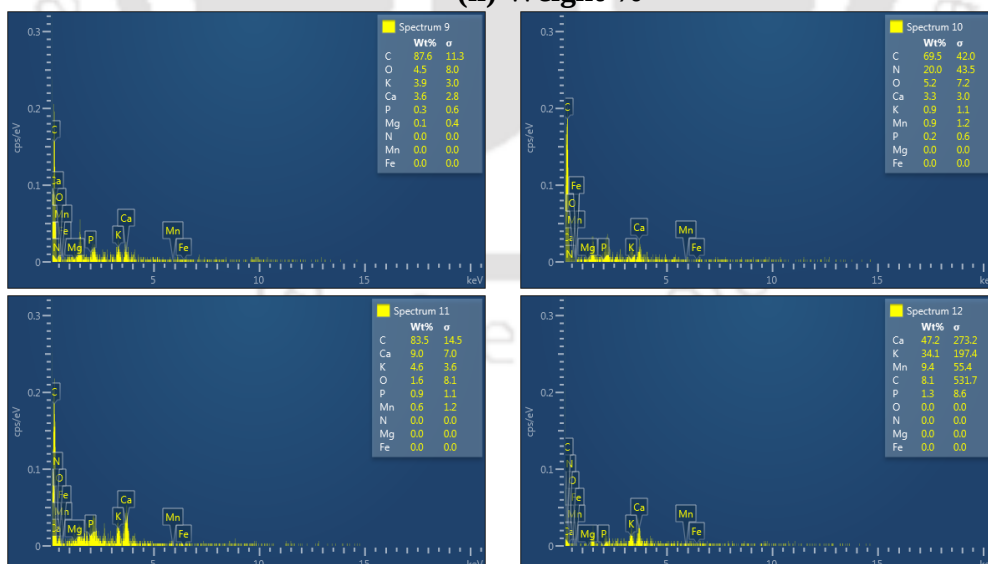
(c) EI:AI-1:2



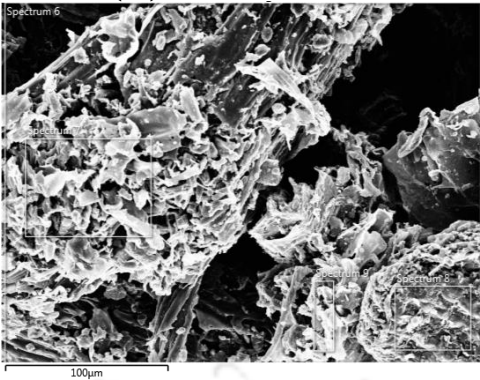
(i) Atomic %



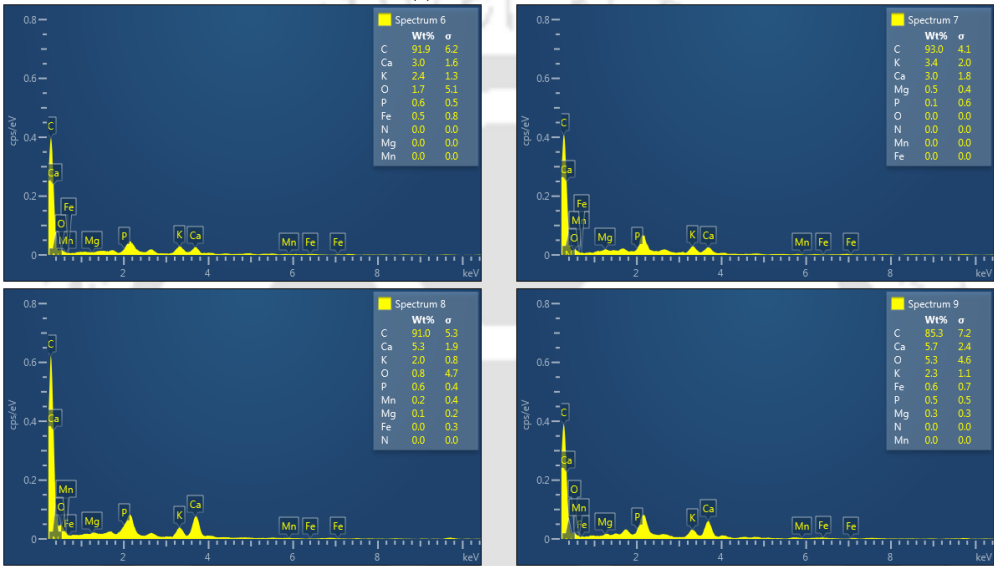
(ii) Weight %



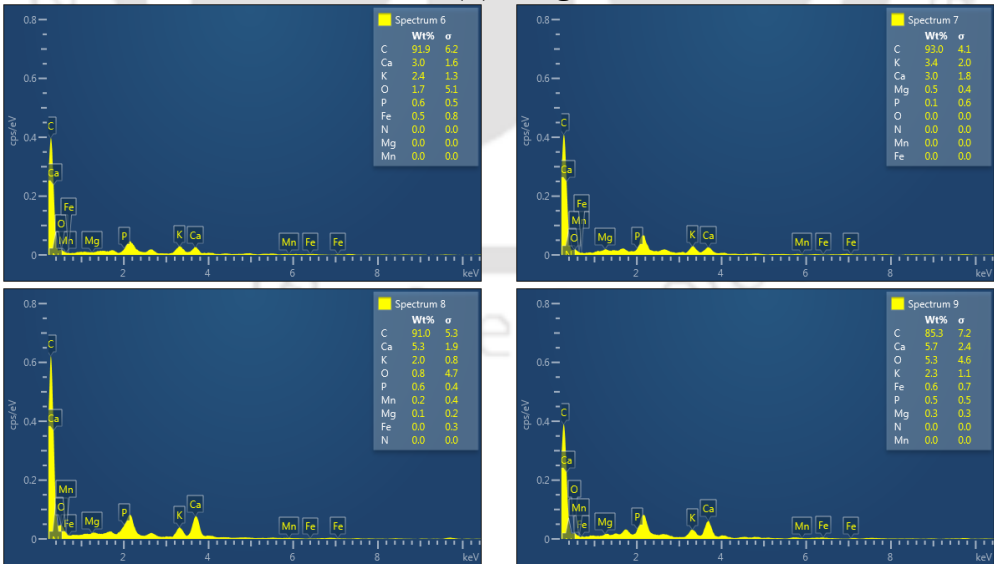
(d) EI:Al-1:1



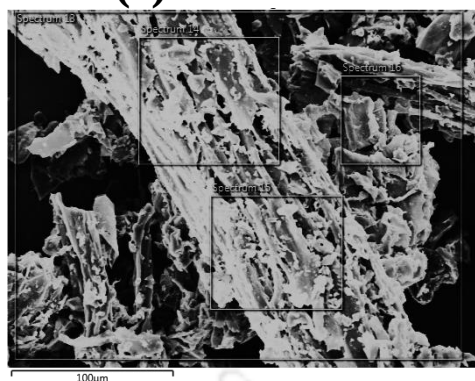
(i) Atomic %



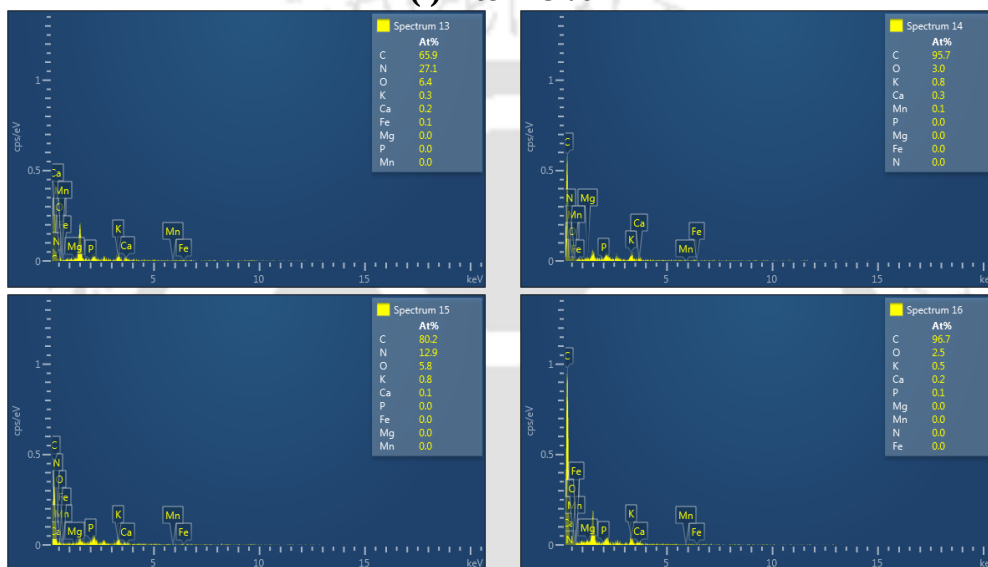
(ii) Weight %



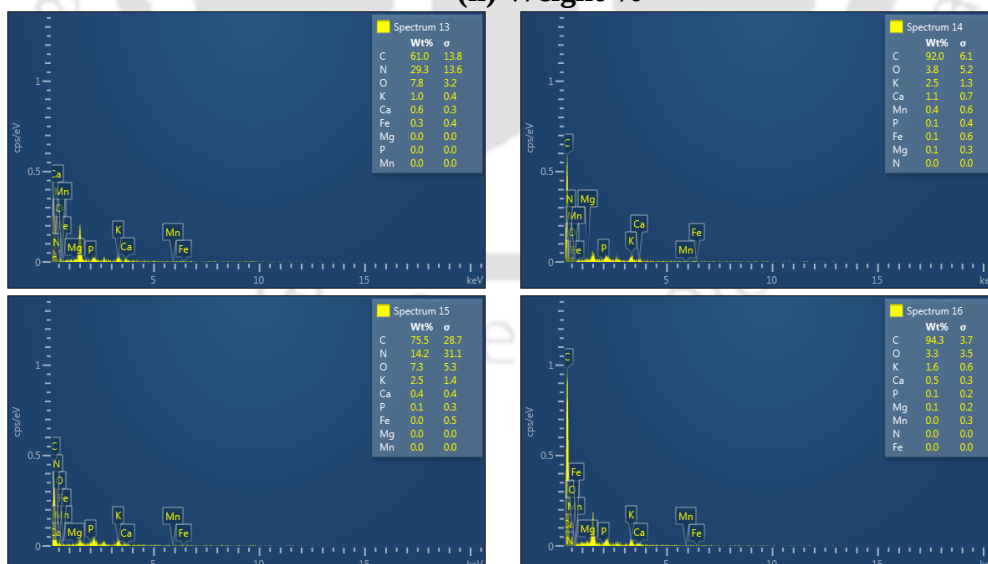
(e) EI:AI-2:1



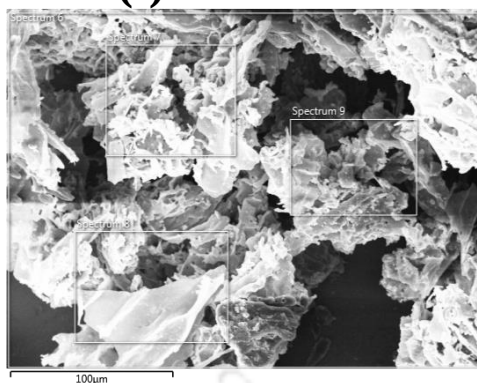
(i) Atomic %



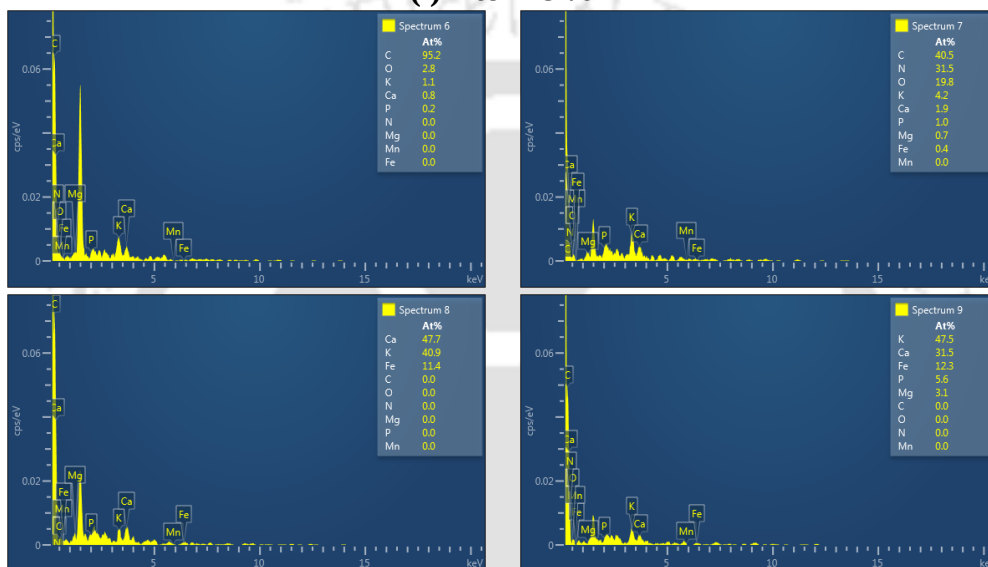
(ii) Weight %



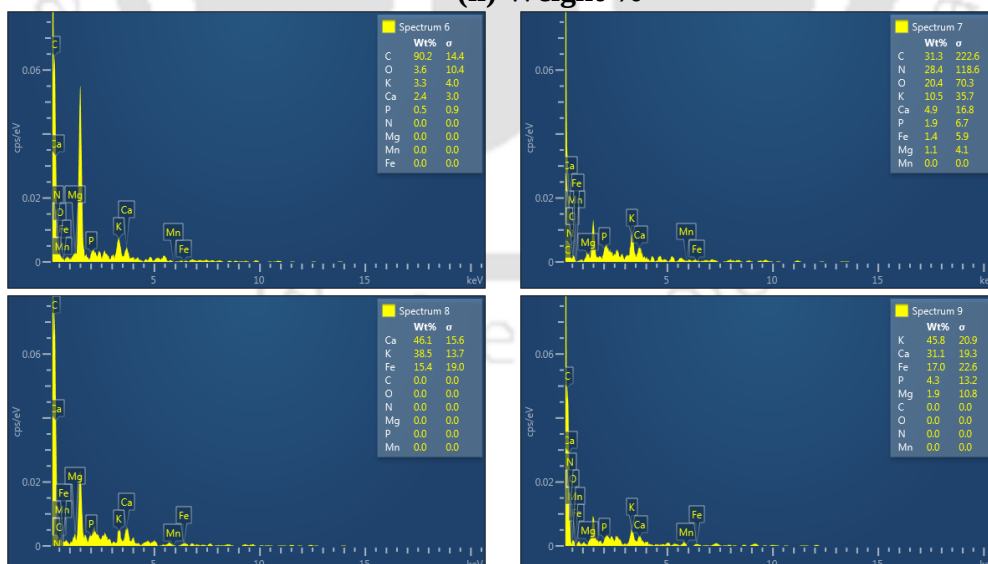
(f) EI:AI-3:1



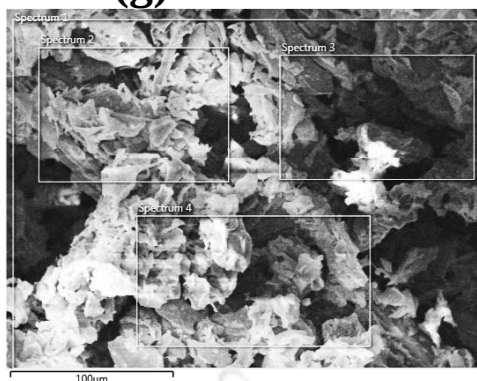
(i) Atomic %



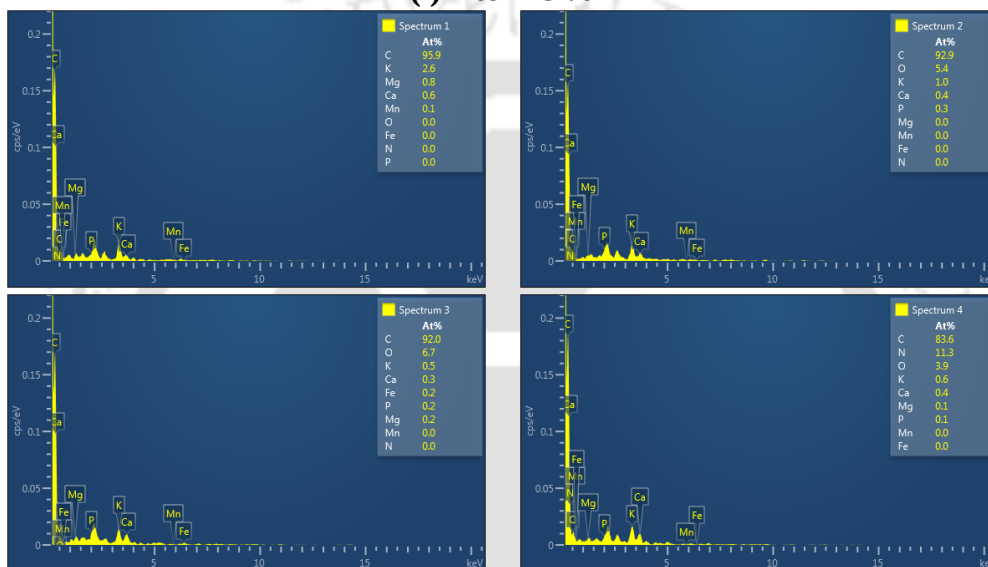
(ii) Weight %



(g) EI:AI-4:1



(i) Atomic %



(ii) Weight %

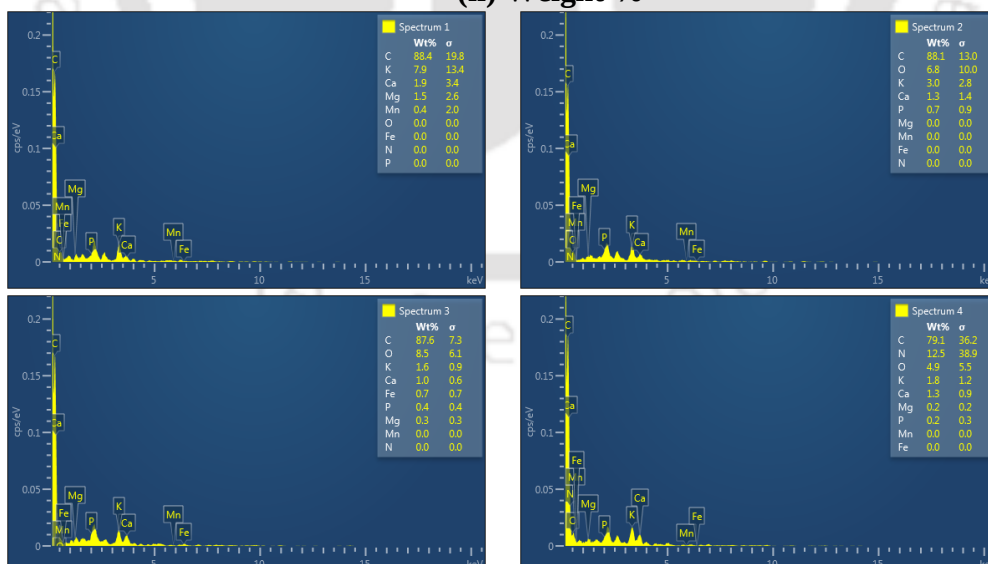


Figure 6.4.9 Energy dispersive X-ray spectroscopic analysis of biochar obtained from co-feed pyrolysis of EI and AI biomass at co-feed ratios of: (a) EI:AI-1:4, (b) EI:AI-1:3, (c) EI:AI-1:2, (d) EI:AI-1:1 (e) EI:AI-2:1, (f) EI:AI-3:1 and (g) EI:AI-4:1.

6.4.2.3 Characterization of non-condensable gases

Similar to the non-condensable gases obtained from the single-feed pyrolysis reactions of EI and AI biomass, the non-condensable gases from co-feed pyrolysis reactions also contained hydrogen, methane, carbon monoxide and carbon dioxide. The compositional analysis of non-condensable gases obtained from the co-feed pyrolysis of EI and AI biomass at co-feed ratio of EI:AI-1:1 was analyzed through GC analysis. The results showed 7.452 vol.% hydrogen, 34.257 vol.% carbon monoxide, 21.322 vol.% methane and 36.969 vol.% carbon dioxide in the gas mixture. The non-condensable gases at 1:1 co-feed ratio was found to possess a calorific value of 13.761 MJ/Nm³. Unfortunately, the hydrogen % in non-condensable gases by co-feed pyrolysis is reduced but carbon monoxide vol.% increased together making up to ≈40-41% which is less than the case of non-condensable gases from individual single-feed pyrolysis process. Thus, if aimed at higher syngas or green hydrogen from their feedstocks, it is more appropriate to use the individual feedstock as feed. It was also notable that the gross calorific value of non-condensable gases produced through the co-feed pyrolysis process is also less than those obtained from the single-feed pyrolysis processes.

6.5 POTENTIAL APPLICATIONS OF THE PYROLYSIS PRODUCTS

The potential applications of the products obtained from the pyrolysis of *Erythrina indica* and *Azadirachta indica* biomass span various industrial sectors, including energy, chemicals, transportation, agriculture, environmental remediation, construction and many more. Specifically, raw bio-oil produced from these biomasses can be used as a fuel for boilers in power plants, chemical industries like distillation, petroleum refining, furnaces in metallurgic industries, power generation and chemical industries, turbines in power plants, aerospace and aviation and in water management [191], as well as industrial burners for heating, drying and other manufacturing processes. The bio-oil produced also contains valuable chemicals such as phenols, aldehydes and organic acids, which can be extracted and utilized to produce adhesives, resins, polymers and other industrial chemicals. Upon upgrading the bio-oil, it can serve as a sustainable aviation fuel or be blended with conventional fuels for use in internal combustion engines, which could offer a lower-carbon alternative to traditional transportation fuels.

The carbon-rich biochar produced from the pyrolysis process can be used as co-feed fuel in coal-based industries and power plants. Further, the biochar indicated the presence of essential soil conditioning elements. Utilizing it as a soil conditioner can improve soil fertility and water retention which could enhance the crop yields. The use of biochar as a soil

conditioner reduces the need for chemical fertilizers and could serve as an efficient method for promoting sustainable agricultural practice, energy production and water filtration. Additionally, the biochar's adsorption capacity can make it useful for removing contaminants, heavy metals and organic pollutants from water as well as soil, which could aid in environmental remediation efforts. The biochar can also be incorporated into building materials to improve thermal properties.

The non-condensable gases produced during pyrolysis can be used in steam turbines and internal combustion engines to generate power. These gases can also serve as feedstock for producing hydrogen, which is essential for various industrial processes such as ammonia synthesis, petroleum refining and electronics industries. Besides, non-condensable gases can be converted into methanol and natural gas, which are used as fuels and chemical feedstocks.

6.6 ECONOMIC ANALYSIS

The economic analysis of the single-feed and co-feed pyrolysis of *Erythrina indica* and *Azadirachta indica* biomass for the co-feed ratio of 1:1 was carried out using the annual cost method. Equation (4.7.1) from section 4.7 was applied to compute the equipment purchase cost for a 10-ton capacity pyrolysis unit of batch type. Table 6.6.1 outlines the initial expenditures for the pyrolysis unit itself and the essential operational equipment listed for the pyrolysis plant.

Cost of pyrolysis unit batch type (5 tons/day capacity) = INR 76,70,000

Cost of pyrolysis unit batch type (10 tons/day capacity) = INR 1,16,25,546

Total cost of pyrolysis unit = Cost of pyrolysis unit batch type (10 tons/day capacity) + Freight charges (@5% of cost of the plant+5% tax on freight charges) = INR 1,22,35,887

Table 6.6.1 Initial cost of setting up the pyrolysis plant.

Item description	Quantity	Price (INR)	Reference
Pyrolysis unit (10 tons/day capacity)	1	1,22,35,887	Shree Balaji Engineering Works, Jaipur, India
Shredder	1	12,00,000	Ragaanvaya India Pvt. Ltd., Guwahati, India
Biomass dryer	1	3,00,000	Rank One Industries, Rajkot, India
Additional storage tank	1	3,50,000	Ragaanvaya India Pvt. Ltd., Guwahati, India
Backhoe loader	1	25,00,000	Ragaanvaya India Pvt. Ltd., Guwahati, India
DG set (62.5 kV)	1	6,26,000	Ragaanvaya India Pvt. Ltd., Guwahati, India
Transformer (100 kV) and wiring	1	13,50,000	Ragaanvaya India Pvt. Ltd., Guwahati, India
Installation		3,00,000	Ragaanvaya India Pvt. Ltd., Guwahati, India
Shed and civil work		25,00,000	Ragaanvaya India Pvt. Ltd., Guwahati, India
Miscellaneous equipment (office supplies)		3,00,000	
Total cost		2,16,61,887	

Based on the sources outlined in Tables 4.7.1 and 4.7.2, the annual fixed and variable costs for operating the pyrolysis plant were computed, as detailed in Table 6.6.2 below. Detailed calculations for plant economics are included in Appendix B of the thesis.

Table 6.6.2 Cost analysis of biomass pyrolysis unit having capacity of 10 tons per day.

	Item	Cost INR/annum			Reference
Fixed cost	Depreciation cost	24,36,962			[148]
	Interest on investment	21,66,189			[149]
	Land rent	1,00,000			Agreement
	Insurance	4,33,238			[148]
	Sum of fixed cost	51,36,389			
	Item	Cost INR/annum			Quantity
Variable cost	Repair and maintenance cost	4,33,238			1
	Labor cost	17,73,648			1
	Biomass waste purchasing and transportation cost	1,56,00,000			1
	Cost of electricity for biomass pre-processing and fuelwood for initial heating of reactor	1,70,000			1
	Packaging and marketing	40,000			1
	Acetone for cleaning	2,80,800			20 litres per day
	n-hexane for extraction of fuel phase of bio-oil	EI	AI	EI:AI-1:1	10 vol.% of the yield of bio-oil
		48,62,938	49,37,675	56,88,840	
	Sum of variable cost	2,31,60,624	2,32,35,361	2,39,86,526	
	Total cost (Fixed + Variable)	2,82,97,013	2,83,71,750	2,91,22,915	

The annual yields of pyrolysis products obtained from both single-feed and co-feed pyrolysis of EI and AI biomass, with a co-feed ratio of 1:1, are detailed in Table 6.6.3.

Table 6.6.3 Yield of pyrolysis products per annum.

Feedstock	Quantity of fuel phase produced (l)	Quantity of biochar produced (kg)	Quantity of non-condensable gases produced (m ³)
EI	142056	1337544	808928
AI	122209	1280854	850865
EI:AI-1:1	169433	1299854	648117

The selling price of biochar varies depending on the feedstock. According to verbal communications with ArSta Eco Pvt. Ltd. in Tumkur, India and Greenfield Eco Solutions Pvt. Ltd. in Jodhpur, India, the selling price of biochar ranges from INR 20 to as high as INR 360. However, for the calculations in this work, the revenue generated from biochar was considered

to be INR 20 as the minimum value. The savings from utilizing non-condensable gases were calculated in terms of the money saved by not using fuelwood to heat the reactor. The minimum fuel selling price of the fuel phase of the bio-oil was calculated using equation (4.7.2) presented in section 4.7. For the fuel phase obtained from the single-feed pyrolysis of EI and AI, the minimum fuel selling price were found to be INR 10.88 and 22.54 while for the fuel phase obtained at co-feed ratio of 1:1 the value was found to be INR 18.45. However, the revenue generated from the fuel phase of bio-oil was calculated by considering the selling price of bio-oil at INR 50 per litre which is close to the commercial furnace oil [192]. Table 6.6.4 below provides the total revenue generated by selling the fuel phase of bio-oil and biochar along with the revenue saved by using non-condensable gases for heating reactor.



Table 6.6.4 Revenue generated from the pyrolysis plant per annum.

Feedstock		Fuel phase (l)	Biochar (kg)	Non-condensable gases (m ³)	Total revenue generated by selling fuel phase of bio-oil and biochar (INR)	Total revenue saved by using non- condensable gases for heating reactor (INR)
EI	Rate	INR 50/l	INR 20/kg	INR 4.02/Nm ³		
	Quantity	142056	1337544	808928	3,38,53,680	32,55,034
	Amount (INR)	71,02,800	2,67,50,880	32,55,034		
AI	Rate	INR 50/l	INR 20/kg	INR 4.13/Nm ³		
	Quantity	122209	1280854	850865	3,17,27,530	35,17,382
	Amount (INR)	61,10,450	2,56,17,080	35,17,382		
EI:AI-1:1	Rate	INR 50/l	INR 20/kg	INR 3.82/Nm ³		
	Quantity	169433	1299854	648117	3,44,68,730	24,77,426
	Amount (INR)	84,71,650	2,59,97,080	24,77,426		

6.6.1 Break-even analysis

The break-even analysis was conducted using equation (4.7.3) presented in section 4.7.1. The analysis revealed that the payback period for single-feed pyrolysis of EI and AI biomass was 3.90 years and 6.46 years, respectively. When using a co-feed ratio of 1:1, the payback period was determined to be 4.05 years.

6.6.2 Net present value

Considering the initial investment of INR 2,16,61,887 at the start of the first year, the annual cash flows for the single-feed pyrolysis processes of EI and AI were INR 55,56,667 and 33,55,780, respectively. For the co-feed ratio of 1:1, the annual cash flow was INR 53,45,815. The salvage value of the project, considered to be 10% of the initial investment, was calculated to be INR 21,66,189. The net present value of the project using EI biomass was INR +2,11,21,132, while for AI biomass it was INR +43,81,010. For the co-feed ratio of 1:1, the net present value was INR +1,95,17,375. The higher positive net present value from the single-feed pyrolysis of EI biomass and the co-feed pyrolysis of EI and AI biomass implies a stronger probability of project success. Conversely, AI biomass indicates a slightly lower net present value. Despite the lower net present value for AI biomass, all scenarios indicate economically viable projects, with returns exceeding the initial investment of INR 2,16,61,887 within the life of the project.

6.6.3 Internal rate of return

The project using EI biomass as a single-feed demonstrates a robust internal rate of return of 24.82%, indicating strong potential for generating returns. Conversely, the internal rate of return for AI biomass, though slightly lower at 13.32%, still signifies profitability. The co-feed ratio of 1:1 yields an IRR of 23.77%, aligning closely with the EI biomass project. These figures collectively highlight the favorable economic prospects of all scenarios, with each offering attractive rates of return on investment.

The economic analysis of the pyrolysis plant was based on several sources necessary to structure the feasibility study, though these sources may introduce uncertainties. However, they are grounded in current industry standards and market conditions [148–150]. The data utilized in this analysis were obtained from recent and reliable studies, industry reports and verified suppliers (Shree Balaji Engineering Works, Jaipur, India, Ragaanvaya India Pvt. Ltd., Guwahati, India, Rank One Industries, Rajkot, India, Jay Bio Fuel, Nadiad, India, Valia

Industries, Bharuch, India and Siddhi Vinayak Industries, Ahmedabad, India). While the pyrolysis process is continuously evolving, our analysis incorporates the latest commercially viable technologies to reflect current industry standards. Although the primary focus was on economic feasibility, we acknowledge the importance of technical, environmental and social impacts and plan to include comprehensive assessments of these aspects in our future work.



6.7 KINETICS AND THERMODYNAMICS OF SINGLE-FEED PYROLYSIS OF ERYTHRINA INDICA AND AZADIRACHTA INDICA BIOMASS

6.7.1 Thermogravimetric and differential thermogravimetric analysis

To investigate the kinetics and thermodynamics associated with the single-feed pyrolysis processes of *Erythrina indica* (EI) and *Azadirachta indica* (AI) biomass, thermal degradation studies were conducted individually at four distinct heating rates of 10, 20, 30 and 40°C/min spanning over a temperature range of 25 to 900°C. Figures 6.7.1 (a) and (b) illustrate the TGA curves for EI and AI biomass, respectively, revealing three discernible stages of degradation for both biomasses. The first stage of degradation for EI biomass took place within the temperature range of 70°C to 190°C, while for AI biomass, it occurred between 70°C to 200°C. The second stage of degradation spanned from 190°C to 545°C for EI biomass and 200°C to 600°C for AI biomass. The third and final stage of degradation initiated at 545°C for EI biomass and 600°C for AI biomass, persisting until the end of the analysis. Stage I, corresponds to the dehydration zone, involves moisture removal and the release of minor amounts of volatile compounds with lower molecular weight. Stage II, the active pyrolysis zone, involved the disintegration of cellulose, hemicellulose and a portion of lignin. Cellulose and hemicellulose disintegrated between 190°C and 380°C for EI biomass and 200°C and 380°C for AI biomass, while lignin fraction degradation occurred at temperatures above 380°C. This stage resulted in the conversion of higher molecular weight components into lower molecular weight compounds such as phenols, acids, aldehydes and ketones due to the absence of oxygen and the application of heat, leading to the significant production of volatiles. Stage III, the passive pyrolysis phase, primarily involved the gradual degradation of the remaining portion of lignin, occurring gradually over a broad temperature range due to the complex structure of lignin, indicating its relatively high thermal stability. The presence of inorganic material in the biomass contributed to the low reactivity and high thermal stability of the sample towards the end of the analysis. The DTG curves of two biomasses Figures 6.7.2 (a) and (b) also display same degradation stages with corresponding ranges of temperatures. However, same additional observations from DTG are as below.

Notably, an increase in heating rate correlated with a rise in the peak degradation temperature. Precisely, peak temperatures of 316°C, 327°C, 328°C and 338°C were recorded for EI biomass, while for AI biomass, peak temperatures were 329°C, 341°C, 342°C and 352°C for the heating rates of 10, 20, 30 and 40°C/min, respectively. Concurrently, the maximum weight loss remained relatively constant at approximately 75.3 wt.%, 74.2 wt.%, 74.3 wt.%

and 75 wt.% for EI biomass and 77.6 wt.%, 77.2 wt.%, 76.2 wt.% and 77.1 wt.% for AI biomass at the respective heating rates.

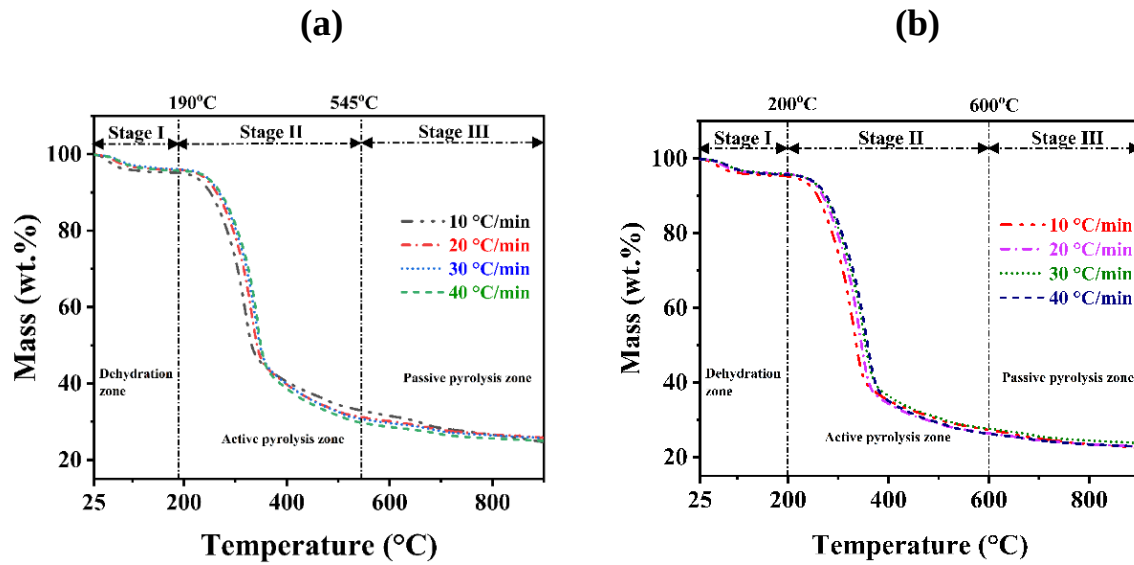


Figure 6.7.1 TGA curves for (a) EI and (b) AI biomass at four heating rates of 10, 20, 30 and 40°C/min.

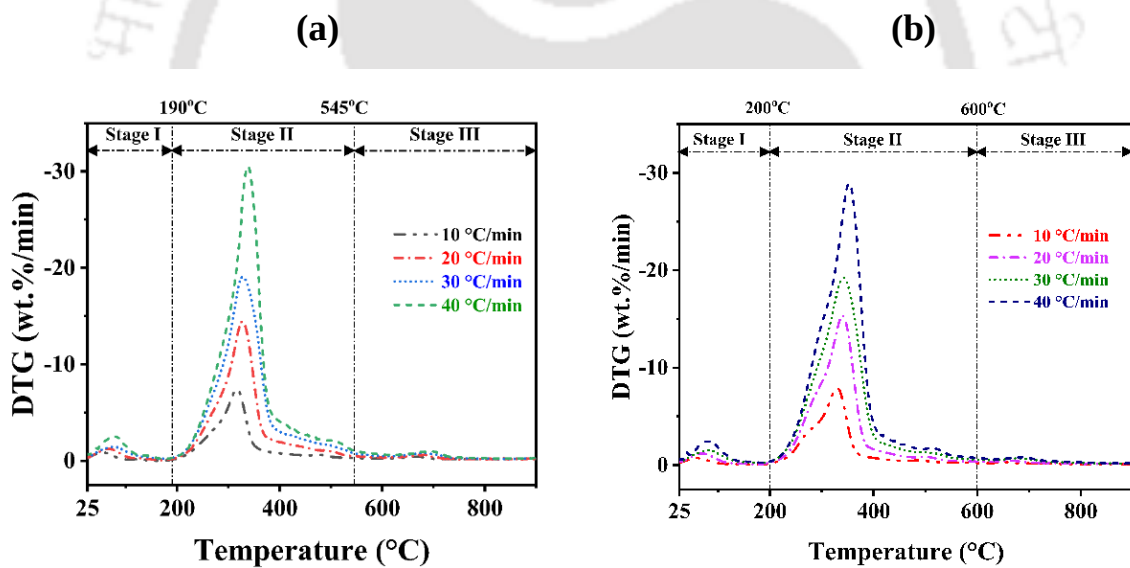


Figure 6.7.2 DTG curves for (a) EI and (b) AI biomass at four heating rates of 10, 20, 30 and 40°C/min.

6.7.2 Evaluation of the kinetic triplets

Kinetic studies are highly beneficial in designing thermochemical conversion systems. Understanding the reaction rate, reactor design, process optimization, reactor scaling up and catalyst development, all rely on the kinetic triplets. The focus of the kinetic analysis was directed toward the active pyrolysis zone, spanning temperatures from 190°C to 545°C for EI biomass and 200°C to 600°C for AI biomass, utilizing DTG data obtained for each biomass individually. The kinetics investigation involved the application of five distinct iso-

conversional models explained in sections 5.2.1.1-5.2.1.5 for determining the apparent activation energy and pre-exponential factor, considering conversions within the range of 0.1 to 0.8, whereas the reaction mechanism for the pyrolysis process was studied based on the results obtained from the differential Friedman method. The approach aimed to provide a comprehensive understanding of the thermal degradation behavior of EI and AI biomass through single-feed pyrolysis, contributing valuable insights for the efficient utilization of biomass resources in thermochemical processes.

6.7.2.1 Calculation of activation energy

The apparent activation energy is referred to the minimum energy required for a chemical reaction or chemical process to occur. A lower activation energy is advantageous for an ideal situation as it implies a faster reaction, indicating the ease of a reaction with lower energy requirements. Activation energy of biomass serves as an indicator of solid biomass fuel reactivity [193,194]. However, the physical interpretation of activation energy obtained from iso-conversional methods may appear limited. To better comprehend this concept, insights can be drawn from molecular collision theory. According to this theory, in the random pyrolysis process, specific molecules experience impacts that increase their kinetic energy, allowing them to break the existing chemical bonds and initiate reactions.

The determination of the apparent activation energy involved the analysis of slopes from kinetic plots generated through iso-conversional methods. The kinetic data obtained for EI and AI biomass using iso-conversional methods at various conversion levels and heating rates are presented in Tables C1 and C2, respectively of Appendix C, while the corresponding kinetic plots obtained using the same data are illustrated in Figures 6.7.3 (a-e) and 6.7.4 (a-e), respectively. A comprehensive summary of computed activation energy values for various iso-conversional methods at distinct conversion levels for EI and AI biomass is presented in Tables C3 and C4, respectively of Appendix C, while a summary of the average values for EI and AI biomass are presented in Table 6.7.1. Figures 6.7.3 (f) and 6.7.4 (f) further illustrates the plot between the activation energy and conversion for EI and AI biomass, respectively. Subtle fluctuation in activation energy values were seen, possibly stemming from variations in estimation techniques and mathematical formulations across different iso-conversional approaches.

The activation energy values of pyrolysis of EI and AI biomass, determined through various iso-conversional methods, exhibited general similarity, except for DFM, which

displayed a slight deviation, likely stemming from noise introduced during the differential formulation. Nevertheless, the activation energy trends from the other iso-conversional methods showed consistency with each other. However, a comparative analysis of Figures 6.7.3 (f) and 6.7.4 (f) for EI and AI biomass, respectively revealed differences and variations in the activation energy at various conversion levels and its trends. In the case of EI biomass, the activation energy requirement decreased as the reaction progressed from 0.1 to 0.2 conversion, indicating reduction in endothermic nature of the reaction in the pyrolysis process. However, from 0.2 to 0.8 conversion, there was an increase in activation energy requirement as the reaction progressed, indicating an increased endothermic nature of the reaction. For AI pyrolysis, unlike the case of EI pyrolysis, the activation energy requirement increased as the reaction progressed from 0.1 to 0.3 conversion, whereas, from 0.3 to 0.7 conversion, a decline in activation energy requirement was observed as the reaction progressed. An abrupt rise in activation energy requirement was noted towards the end of the reaction, from 0.7 to 0.8 conversion, for both EI and AI biomass pyrolysis, possibly due to the high activation energy required for lignin degradation at higher conversion and both biomasses are of similar type. The fluctuations in activation energy values at various conversion levels can be attributed to the diverse energy requirements for the degradation of varying fractions of cellulose, hemicellulose and lignin in two biomass feedstocks. Generally, this complexity suggests a multi-step reaction mechanism for biomass pyrolysis. The average activation energy (kJ/mol) values obtained for EI biomass were as follows: DFM: 184.787, KAS: 176.861, OFW: 177.493, STK: 177.111 and DAEM: 176.861. Meanwhile, for AI biomass the average activation energy (kJ/mol) values were as follows: DFM: 196.635, KAS: 187.613, OFW: 187.841, STK: 187.859 and DAEM: 187.613. Notably for both the biomasses, KAS and DAEM exhibited the minimum activation energy values, whereas DFM yielded the maximum value of activation energy despite its advantages, such as avoiding assumptions during activation energy calculation, which may introduce noise into the results due to the numerical differentiation of thermogravimetric data. Table C3 and C4 of Appendix C also summarizes the R^2 values using iso-conversional methods across various conversions, which were found to be generally exceeding 0.98 for both EI and AI biomass, indicating a good fit of TGA data across all methods.

6.7.2.2 Calculation of pre-exponential factor

The pre-exponential (k_o) factor was elucidated employing the intercepts of all the models and they were found to be ranging between 10^{11} to 10^{22} min^{-1} for EI biomass pyrolysis and 10^{12} to

10^{22} min^{-1} for AI biomass which are also summarized in Tables C3 and C4 of Appendix C, respectively. The average values of k_o (min^{-1}) for EI biomass were found to be 1.038×10^{22} for DFM, 7.991×10^{19} for KAS, 2.680×10^{17} for OFW, 6.366×10^{19} for STK and 4.965×10^{19} for DAEM. Meanwhile, for AI biomass the average values of k_o (min^{-1}) were found to be 1.178×10^{22} for DFM, 1.213×10^{17} for KAS, 5.068×10^{14} for OFW, 9.749×10^{16} for STK and 9.961×10^{17} for DAEM. Value of k_o , below 10^{10} are indicative of surface reactions. When the reaction is not dependent on surface area, a low k_o value indicates a closed complex, whereas a larger value indicates a simple complex. For first-order pre-exponential factors, the empirical range can vary from 10^5 to 10^{19} [195]. The complex structure of the biomass sample and the complex pyrolysis process are primarily responsible for the variations in k_o with regard to conversion.



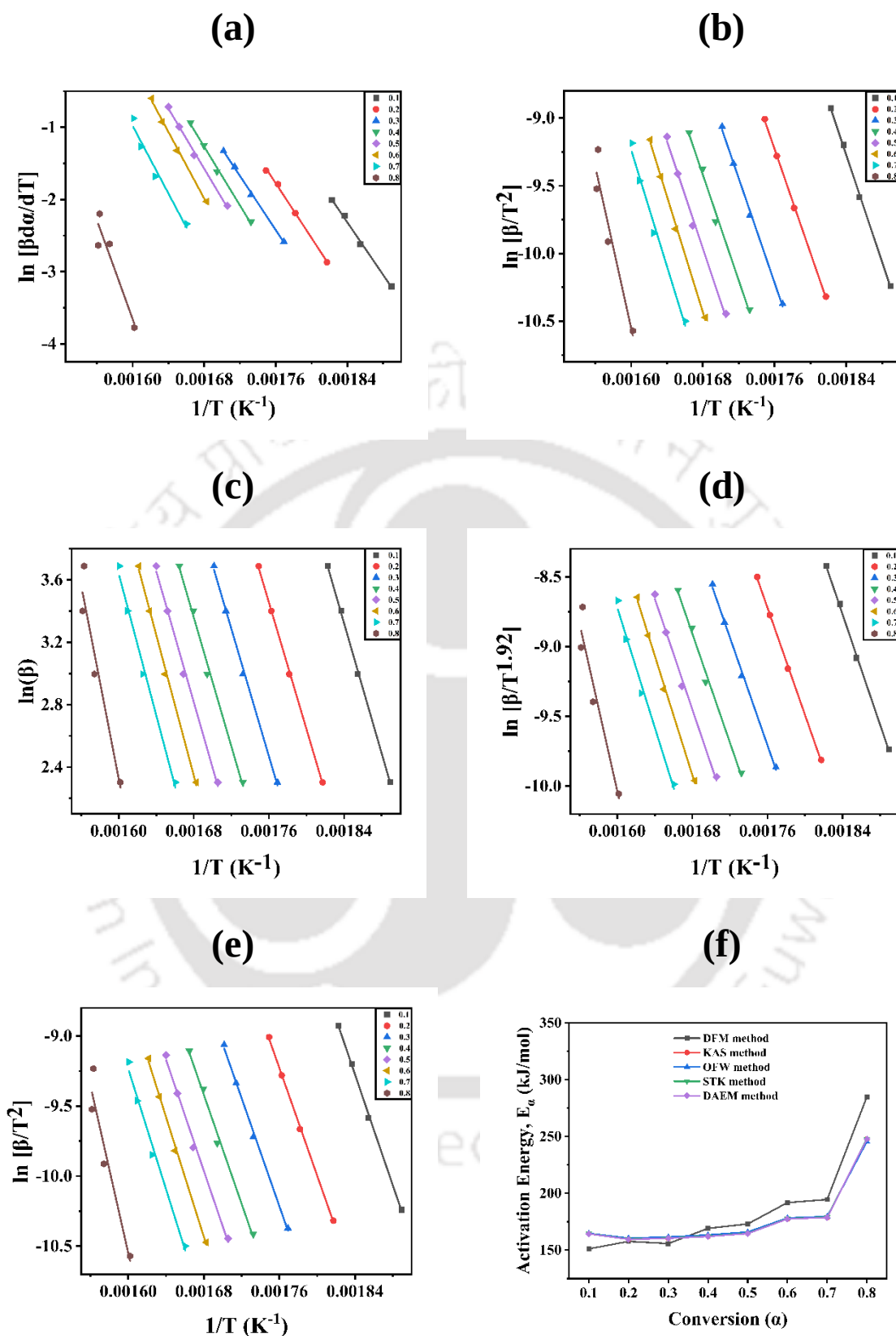


Figure 6.7.3 (a-e) Iso-convensional plots of EI biomass pyrolysis: (a) DFM, (b) KAS, (c) OFW, (d) STK, (e) DAEM and (f) apparent activation energy vs. conversion.

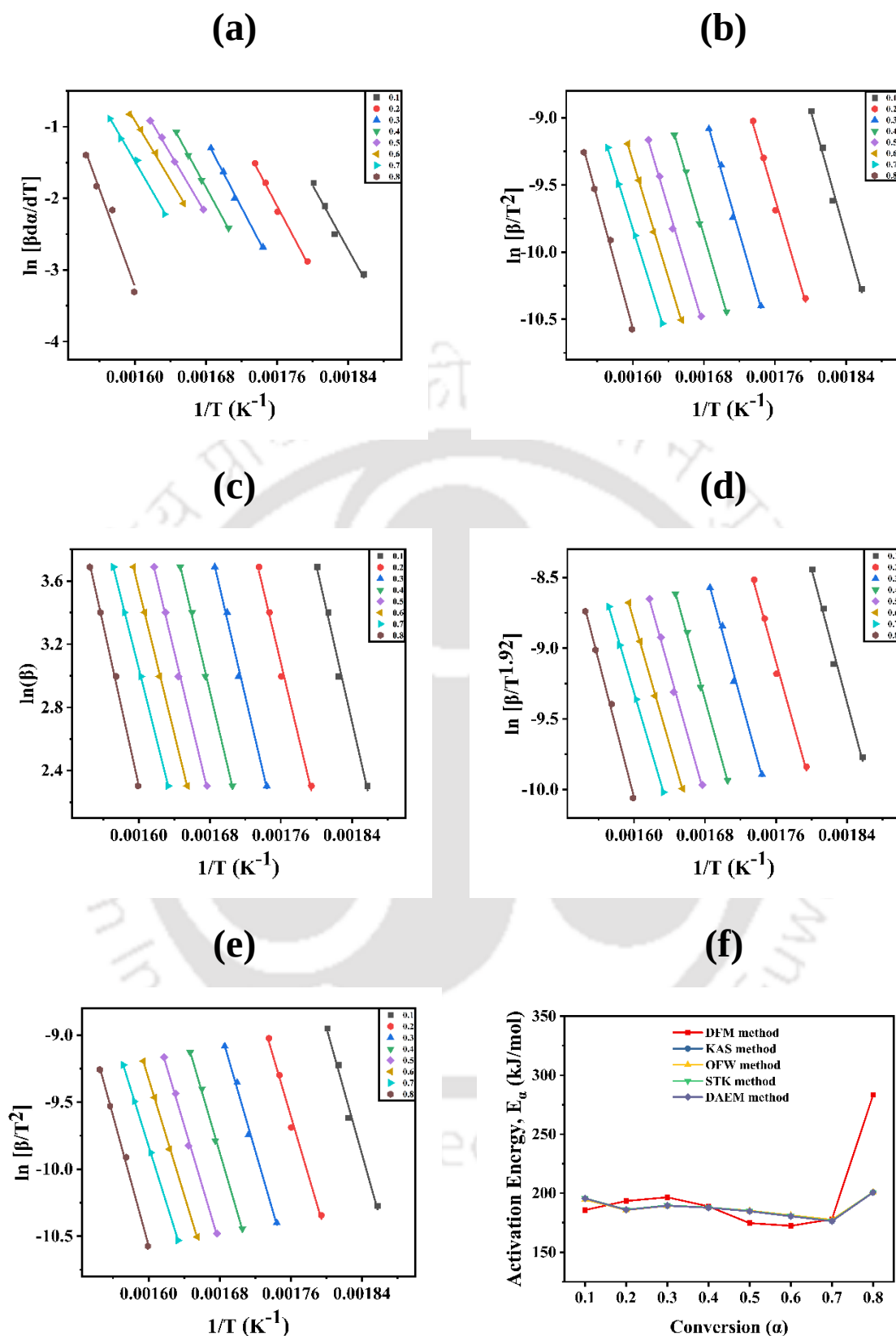


Figure 6.7.4 (a-e) Iso-conversional plots of AI biomass pyrolysis: (a) DFM, (b) KAS, (c) OFW, (d) STK, (e) DAEM and (f) apparent activation energy vs. conversion.

Table 6.7.1 Average activation energy (kJ/mol), pre-exponential factor (min⁻¹) and R² for EI and AI biomass pyrolysis.

Method	Feedstock					
	EI			AI		
	E_a	k_o	R ²	E_a	k_o	R ²
DFM	184.787	1.038×10^{22}	0.980	196.635	1.178×10^{22}	0.991
KAS	176.861	7.991×10^{19}	0.986	187.613	1.213×10^{17}	0.996
OFW	177.493	2.680×10^{17}	0.987	187.841	5.068×10^{14}	0.996
STK	177.111	6.366×10^{19}	0.986	187.859	9.749×10^{16}	0.996
DAEM	176.861	4.965×10^{19}	0.986	187.613	9.961×10^{17}	0.996

6.7.2.3 Reaction mechanism

6.7.2.3.1 Criado's master plots method

The reaction mechanism involved in the single-feed pyrolysis of EI and AI biomass, as revealed through Criado's master plot using the results obtained from the differential Friedman method under four distinct heating rates of 10, 20, 30 and 40°C/min, are illustrated in Figures 6.7.5 (a-d) and 6.7.6 (a-d), respectively. It was notable that the degradation of both EI and AI biomass did not adhere to a single reaction model; instead, it involved a combination of various models including power law, Avrami-Erofeev, contracting area, diffusion and various order reaction models. This complexity arises in pyrolysis process due to the diverse influences of biomass components—hemicellulose, cellulose and lignin, especially under varied heating rates.

For instance, Figure 6.7.5 (a-d) revealed that at a heating rate of 10°C/min, the pyrolysis of EI biomass primarily followed the R2 reaction model at 0.1 conversion, transitioning to a mix of P2, P3, P4, D1 and F0 models as the conversion progressed from 0.2 to 0.4. Advancing further, it adopts the R3 model at 0.6 conversion, followed by the F2 model at 0.7 and the F3 model at 0.8 conversion. Under heating rates of 20, 30 and 40°C/min, EI biomass pyrolysis consistently followed a combination of P2, P3, P4, D1 and F0 models from 0.1 to 0.4 conversion. However, as the conversion progressed, the reaction mechanism becomes more intricate. For instance, at a heating rate of 40°C/min, EI biomass pyrolysis adhered to the combination of P2, P3, P4, D1 and F0 models up to 0.6 conversion but changes to D2 and R2 models at 20 and 30°C/min heating rates, respectively. Progressing further the EI biomass pyrolysis shifts to a combination of F1, A2, A3 and A4 models at 0.7 conversion and ultimately concluding with F3 reaction model at 0.8 conversion for the heating rate of 40°C/min. For the 20°C/min heating rate, the EI biomass pyrolysis adopted the D2, F2 and F3 reaction models at

conversions of 0.6, 0.7 and 0.8 whereas for the 30°C/min heating rate, the EI biomass pyrolysis exhibited the R2, F2 and F3 models at 0.6, 0.7 and 0.8.

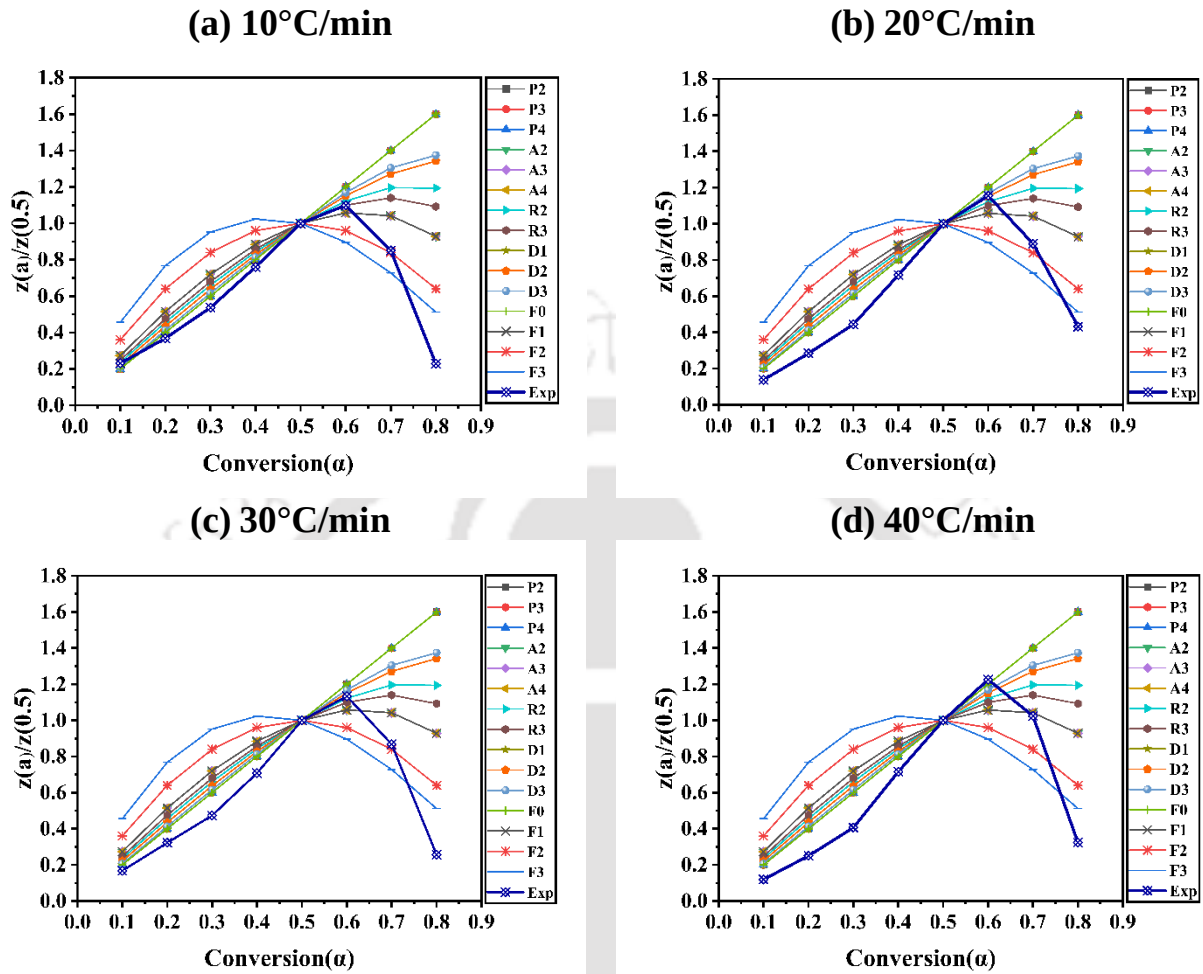


Figure 6.7.5 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI biomass using DFM results.

Similarly, Figure 6.7.6 (a-d) revealed that at heating rate of 10°C/min, AI biomass pyrolysis primarily adhered to the D3 reaction model at 0.1 conversion. Progressing from 0.2 to 0.6 conversion, it exhibited a combination of P2, P3, P4, D1 and F0 models. Advancing further, it adopted the R3 model at 0.7 conversion, followed by the F3 model at 0.8 conversion. At heating rates of 20, 30 and 40°C/min, AI biomass pyrolysis predominantly followed the combination of P2, P3, P4, D1 and F0 models from 0.1 to 0.6 conversion. However, as the conversion progressed, the reaction mechanism becomes more intricate and showed variations. For instance, under a heating rate of 20°C/min, the AI biomass pyrolysis adhered to the D3 model at 0.7 conversion but shifted to the D2 model under the heating rate of 30°C/min. At 0.8 conversion, the AI biomass pyrolysis maintained the F2 model for both heating rates of 20 and 30°C/min. Whereas, at 40°C/min heating rate, the AI biomass pyrolysis followed the D3 model at 0.7 conversion but shifted to a combination of A2, A3, A4 and F1 models at 0.8 conversion.

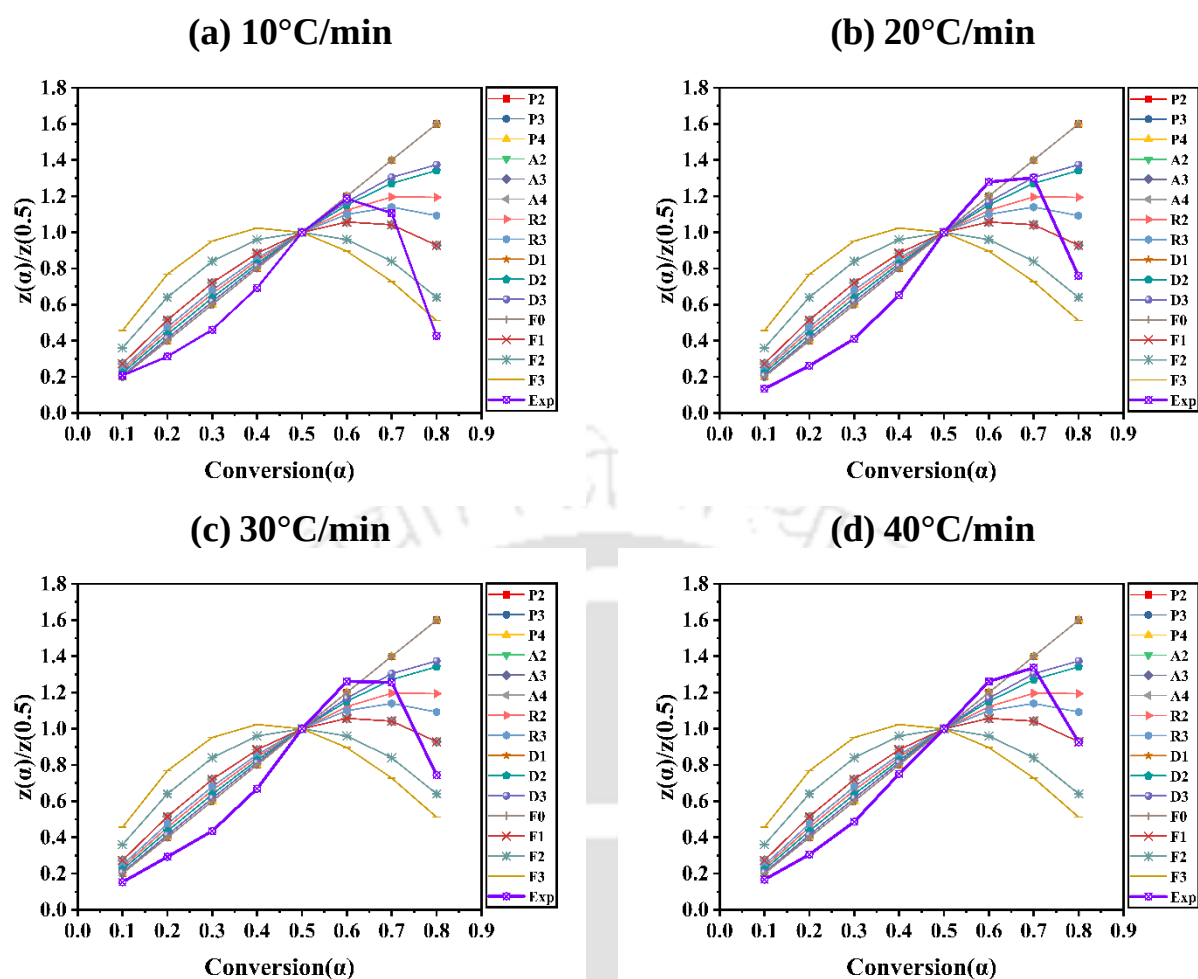


Figure 6.7.6 (a-d) Criado's master plots for reaction mechanism of pyrolysis of AI biomass using DFM results.

6.7.2.3.2 Master plot based on integral form of kinetic data

The reaction mechanism involved in the single-feed pyrolysis of EI and AI biomass carried out at heating rates of 10, 20, 30 and 40°C/min were also unveiled through the integral method using results obtained from the differential Friedman method which are illustrated in Figures 6.7.7 (a-d) and 6.7.8 (a-d), respectively. Notably, irrespective of the heating rate applied, the pyrolysis process consistently adhered to the power law and Avrami-Erofeev models. Compared to the findings from Criado's master plots, EI and AI biomass decomposition revealed a complex reaction mechanism and did not adhere to a single reaction model or a straightforward trend. However, too many variations were not displayed by this approach.

For instance, Figure 6.7.7 revealed that at a heating rate of 10°C/min, EI biomass pyrolysis predominantly followed the P4 model from 0.1 to 0.7 conversion, eventually transitioning to the P3 model at 0.8 conversion. In contrast, at heating rates of 20, 30 and 40°C/min, the biomass displayed a combination of power law and Avrami-Erofeev models. At a heating rate of 20°C/min, the reaction initiated with the A3 model at 0.1 conversion which

continued till 0.3 conversion, shifted to the A4 model at 0.4 conversion, and further changed to the P3 model at 0.6 conversion. Subsequently, it adopted the A4 model at 0.7 conversion and ultimately concluded with the A3 model at 0.8 conversion. At a heating rate of 30°C/min, the EI biomass pyrolysis initiated with the A4 model from 0.1 to 0.3 conversion, followed by the P3 model at 0.4 conversion. It subsequently shifted to the P4 model at 0.6 conversion, which briefly returned to the P3 model at 0.7 conversion, and ultimately culminated with the P2 model at 0.8 conversion. For the 40°C/min heating rate, the EI biomass pyrolysis began with the P2 model from 0.1 conversion and continued till 0.3 conversion, and briefly transitioned to the A3 model at 0.4 conversion. As the reaction progressed, the biomass shifted to the A4 model at 0.6 conversion, followed by a sequence of P2 and A3 models at 0.7 and 0.8 conversions.

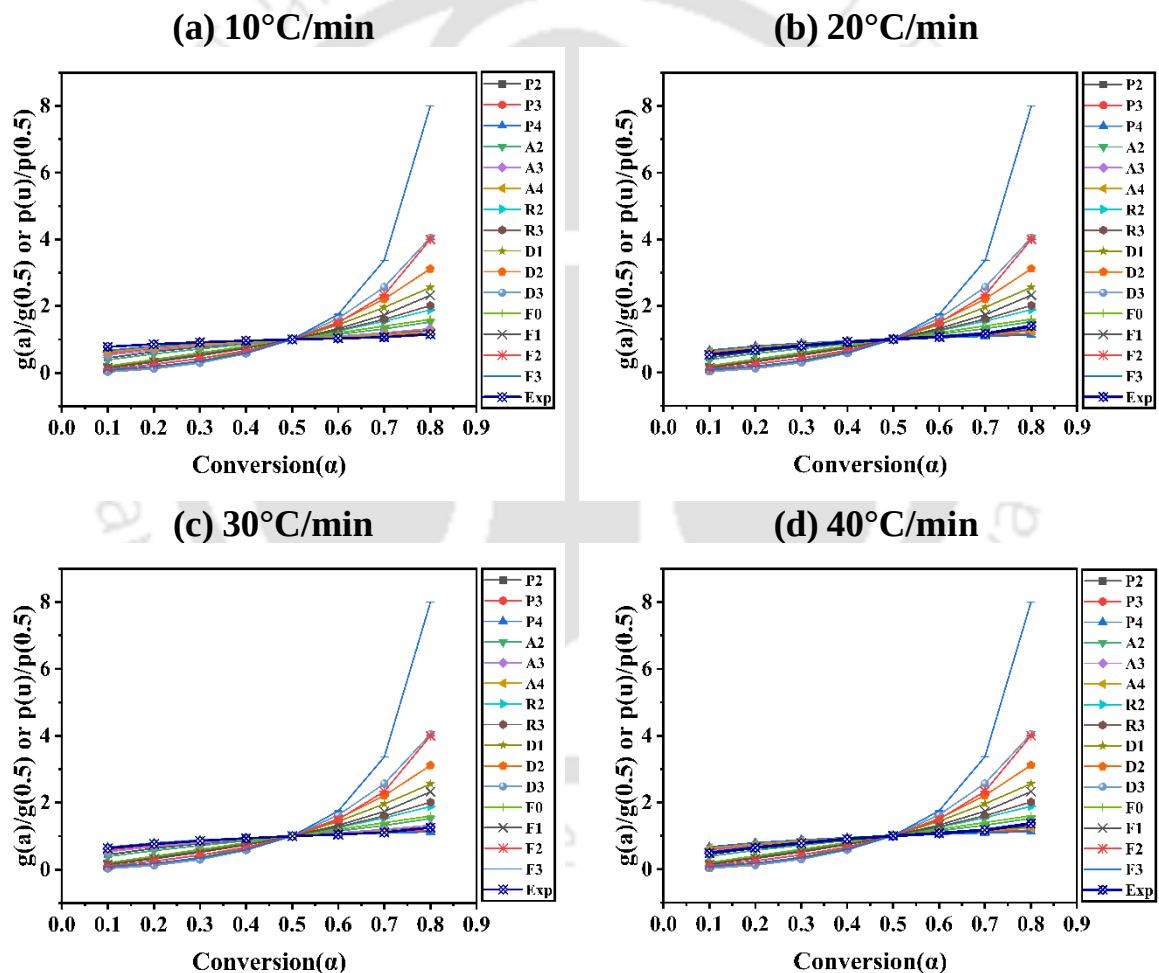


Figure 6.7.7 (a-d): Master plot based on integral method for reaction mechanism of pyrolysis of EI biomass using DFM results.

Similarly, Figure 6.7.8 revealed that under a heating rate of 10°C/min, AI biomass pyrolysis primarily adhered to the P3 model at 0.1 conversion, subsequently transitioning to the A3 model from 0.2 conversion and persisting until 0.4 conversion. As the reaction

progressed, it shifted to the A4 model at 0.6 conversion and continued until 0.7 conversion but shifted to the P2 model at 0.8 conversion. In contrast, at heating rate of 20°C/min, the AI biomass pyrolysis predominantly followed the Avrami-Erofeev model. The reaction adhered to the A2 model from 0.1 to 0.4 conversion but transitioned to the A3 model at 0.6 conversion and continued until 0.7 conversion, then shifted back to the A2 model at 0.8 conversion. At heating rates of 30 and 40°C/min, the reactions exhibited a similar mechanism, initiating with the P2 model at 0.1 conversion. Progressing further, the reaction shifted to the A2 model at 0.2 conversion, persisting until 0.4 conversion. Continuing ahead, the AI biomass pyrolysis transitioned to the A3 model at 0.6 conversion and continued this model until 0.8 conversion.

The results of the master plots underscore the intricate nature of the pyrolysis process of EI and AI biomass, showcasing the dynamic interplay of various reaction models at different conversion levels and heating rates, aligning with the degradation mechanism of the constituting biopolymers.

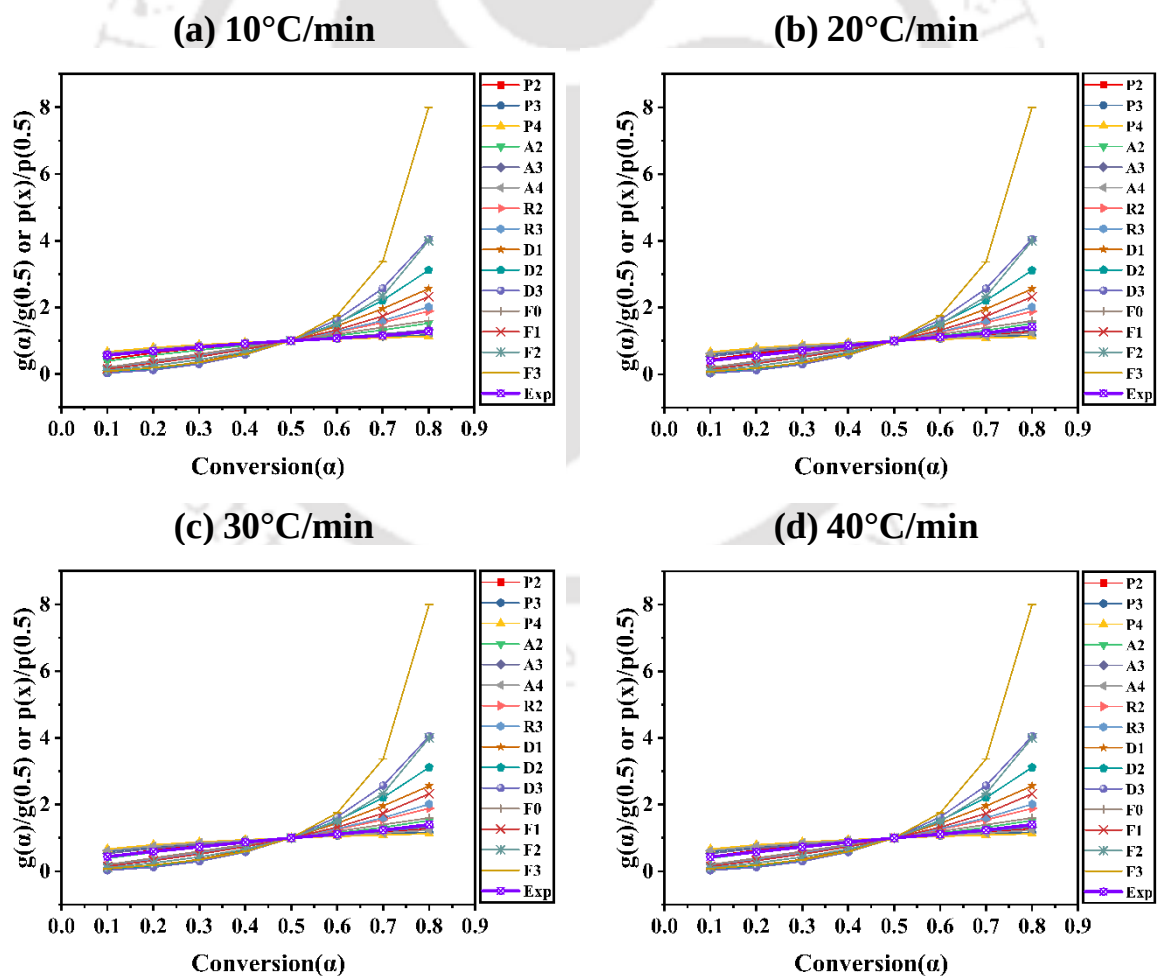


Figure 6.7.8 (a-d): Master plots based on integral method for reaction mechanism of pyrolysis of AI biomass using DFM results.

6.7.3 Thermodynamic properties

Apart from the kinetics, thermodynamic properties such as the change in enthalpy (ΔH), change in Gibbs free energy (ΔG) and change in entropy (ΔS) are pivotal in the design, optimization and scaling up of a pyrolyzer [194,196]. The thermodynamic properties associated to the single-feed pyrolysis of EI and AI biomass were evaluated using equations 5.3.2-5.3.4 explained in section 5.3. The graphical representations of these outcomes have been illustrated in Figures 6.7.9-6.7.14, while their details have been reported in Tables C5 and C6 of Appendix C for pyrolysis of EI and AI biomass, respectively. The average values of the thermodynamic properties were also presented in Table 6.7.2.

ΔH represents a thermodynamic attribute related to the thermal content of a system, indicating the amount of heat absorbed or released during a transformation under specific pressure conditions. This parameter serves as a crucial indicator to discern whether a reaction is either endothermic or exothermic. A positive ΔH signifies an endothermic reaction, while a negative ΔH indicates an exothermic process. In the context of pyrolysis, enthalpy specifically denotes the quantum of heat necessary for the conversion of biomass. The variation in apparent activation energy and enthalpy change reflects the energy disparity between the reactants and the activated complex, with a narrower margin favoring the conversion of activated complexes into the products [197]. Figures 6.7.9 (a-e) and 6.7.10 (a-e), respectively illustrate the change in enthalpy versus conversion plots for EI and AI biomass pyrolysis at four different heating rates using five different iso-conversional models. The average ΔH values (kJ/mol) at four different heating rates ($\beta=10, 20, 30$ and $40^\circ\text{C}/\text{min}$) for pyrolysis of EI biomass were DFM: 179.890, 179.799, 179.790, 179.707; KAS: 171.964, 171.873, 171.864, 171.781; OFW: 172.596, 172.504, 172.496, 172.413; STK: 172.214, 172.014, 172.114, 172.031; and DAEM: 171.964, 171.873, 171.864, 171.781, respectively. Similarly, for pyrolysis of AI biomass the corresponding average ΔH values (kJ/mol) at four heating rates ($\beta=10, 20, 30$ and $40^\circ\text{C}/\text{min}$) were: DFM: 191.638, 191.539, 191.522, 191.447; KAS: 182.616, 182.516, 182.500, 182.425; OFW: 182.844, 182.744, 182.728, 182.653; STK: 182.863, 182.763, 182.746, 182.671; and DAEM: 182.616, 182.516, 182.500, 182.425, respectively. Figure 6.7.9 (a-e) for pyrolysis of EI biomass revealed that the ΔH values slightly decreased from 0.1 to 0.2 conversion, followed by a subtle increase until 0.7 and finally a notable rise from 0.7 to 0.8 conversion. Conversely, in the case of pyrolysis of AI biomass, as illustrated in Figure 6.7.10 (a-e), the ΔH values exhibited a slight decrease from 0.1 to 0.2 conversion, followed by a slight increase until 0.3 conversion, followed by a slight decrease again till 0.7 conversion, and finally, a notable rise

from 0.7 to 0.8 conversion. Furthermore, the results suggested that the heating rate had a minimal impact on the ΔH values. The escalating positive values of ΔH indicated that the pyrolysis process was endothermic, and this endothermic nature intensified as the pyrolysis process advanced. Except for the DFM, all ΔH values were relatively consistent with each other with insignificant variations [197].

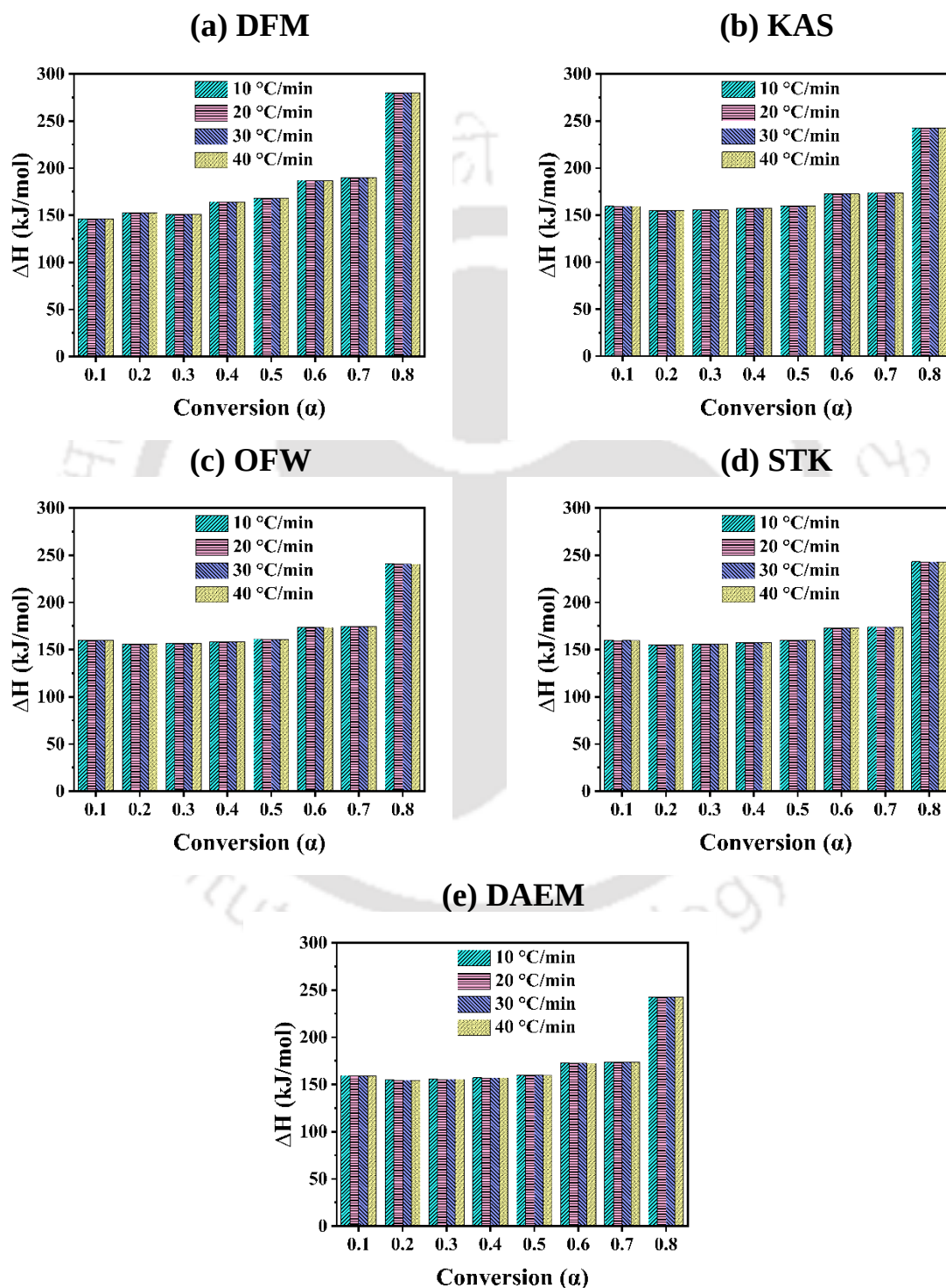


Figure 6.7.9 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots for EI biomass pyrolysis.

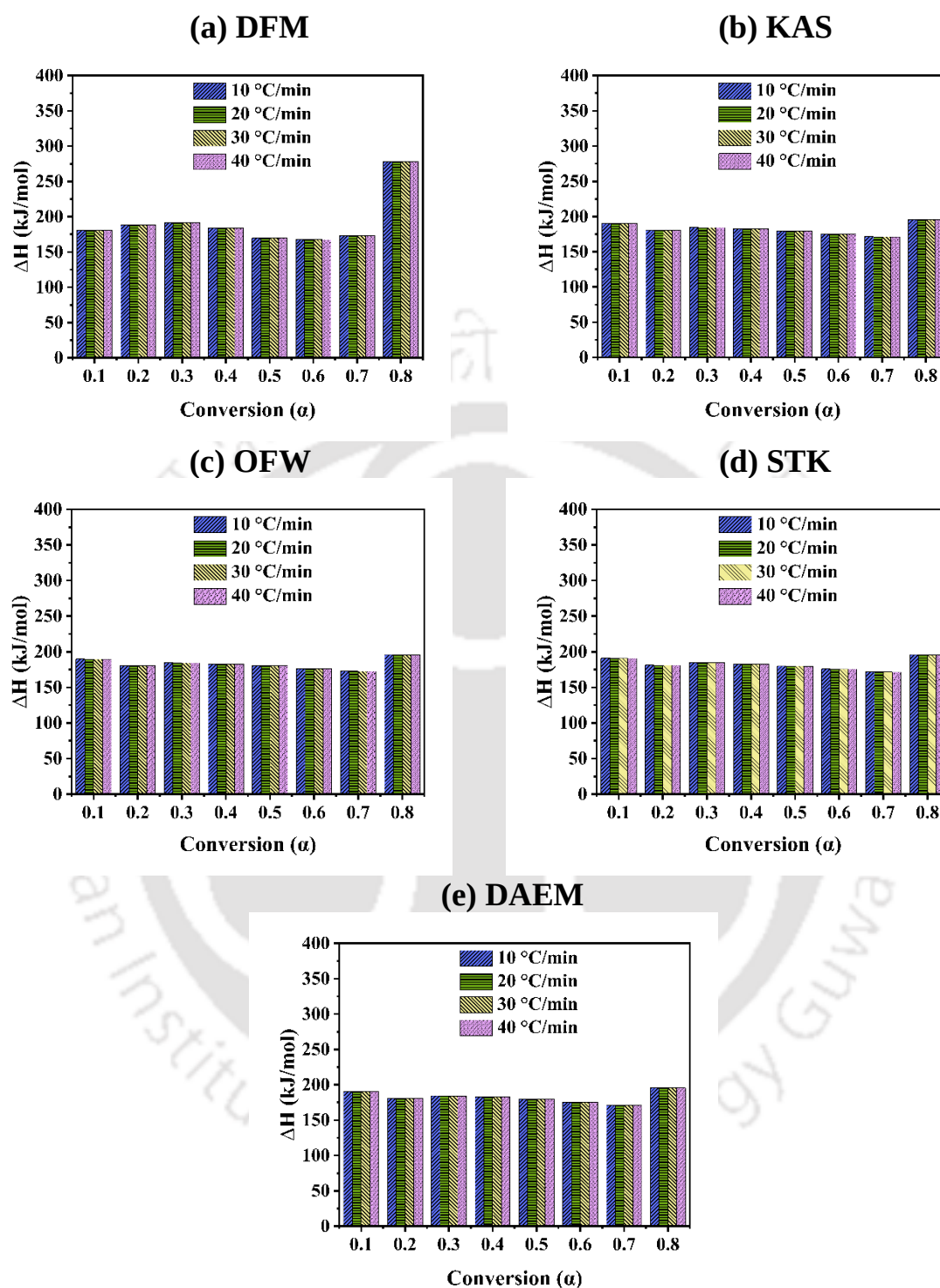


Figure 6.7.10 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots for AI biomass pyrolysis.

Meanwhile, ΔG aids in ascertaining the equilibrium and likelihood of a reaction proceeding in a particular direction. A positive ΔG signifies a non-spontaneous reaction, indicating an energy requirement during the process, which is unfavorable from a thermodynamic standpoint. On the contrary, a negative ΔG signifies a spontaneous reaction.

Figures 6.7.11 (a-e) and 6.7.12 (a-e), respectively illustrate the change in Gibbs free energy versus conversion plots for single-feed pyrolysis of EI and AI biomass at four different heating rates using five different iso-conversional models. The average ΔG values (kJ/mol) at four different heating rates ($\beta=10, 20, 30$ and $40^\circ\text{C}/\text{min}$) for pyrolysis of EI biomass were: DFM: 169.916, 169.909, 168.191, 169.780; KAS: 170.083, 170.078, 168.361, 169.952; OFW: 169.885, 170.057, 168.339, 169.930; STK: 170.076, 170.071, 168.354, 169.945; and DAEM: 170.083, 170.078, 168.361, 169.952, respectively. Similarly, for pyrolysis of AI biomass the corresponding average ΔG values (kJ/mol) at four heating rates ($\beta=10, 20, 30$ and $40^\circ\text{C}/\text{min}$) were: DFM: 173.330, 173.561, 167.288, 173.356; KAS: 173.508, 173.742, 172.285, 173.540; OFW: 173.501, 173.735, 172.279, 173.533; STK: 173.501, 173.735, 172.279, 173.533; and DAEM: 173.508, 173.742, 172.285, 173.540, respectively. Comparing Figures 6.5.11 (a-e) for EI pyrolysis and 6.7.12 (a-e) for AI pyrolysis, both exhibited similar trends in the ΔG values as the conversion progressed. Positive ΔG values for single-feed pyrolysis of EI and AI biomass indicate that the active pyrolysis phase of the pyrolysis process requires an energy input and does not occur spontaneously [198,199]. Elevated ΔG values suggest a less favorable thermodynamic reaction, necessitating a higher energy input for its breakdown. Minor fluctuations in the ΔG values were observed at various heating rates as the conversion progressed. However, as the conversion progressed, there was no significant change on the ΔG values at all conversions, suggesting a relatively similar degree of degradation with respect to conversion.

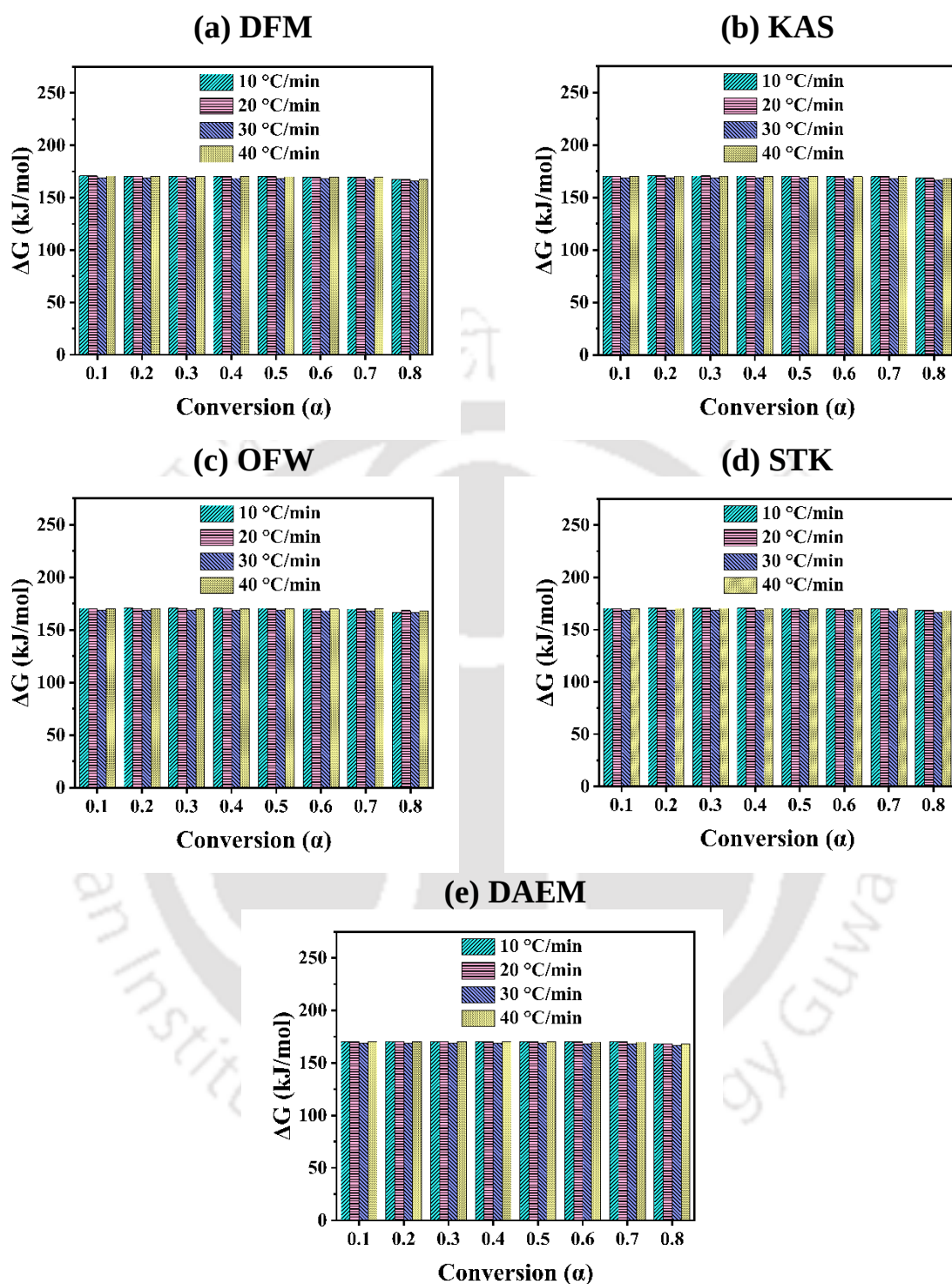


Figure 6.7.11 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) plots for EI biomass pyrolysis.

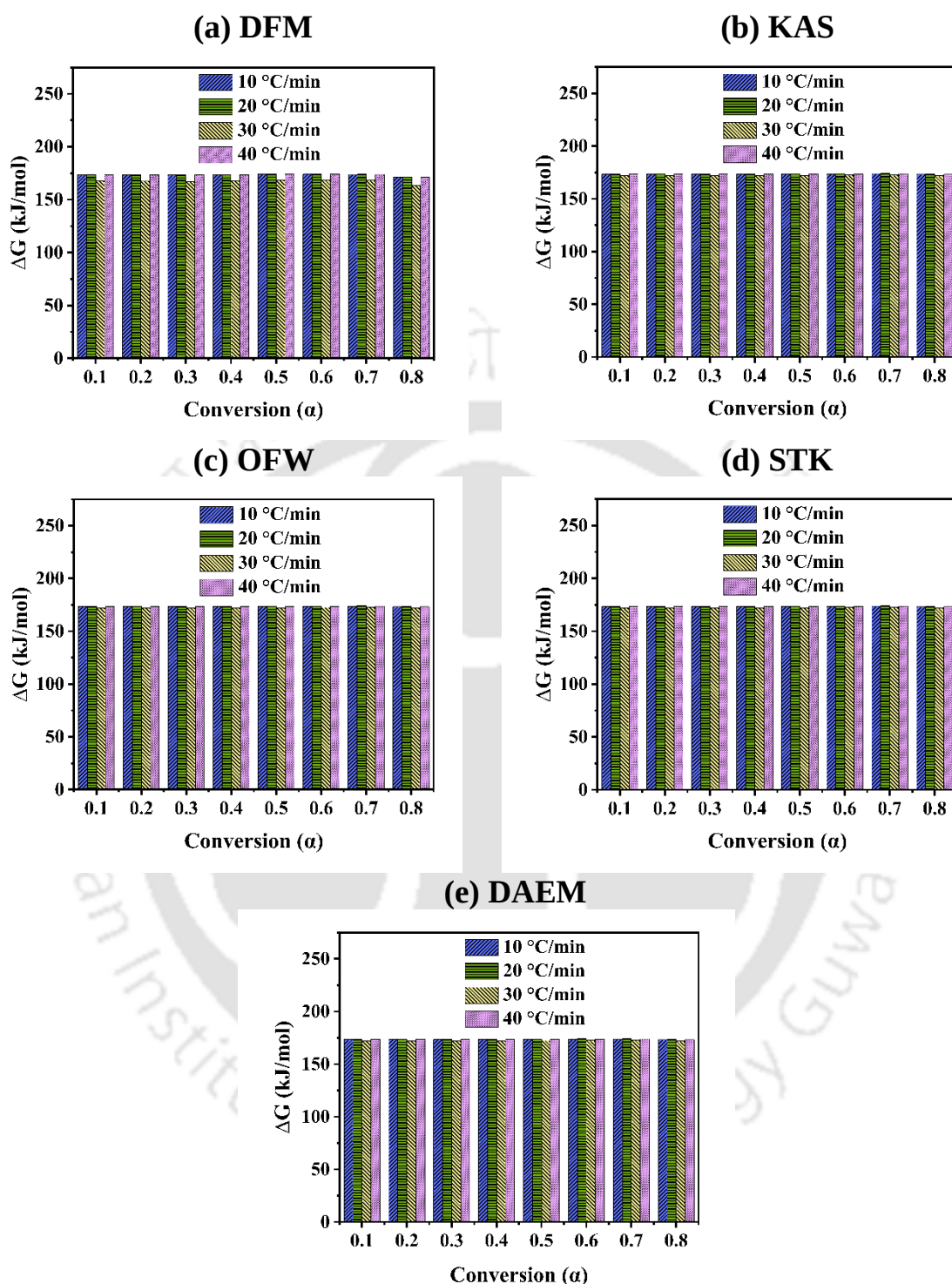


Figure 6.7.12 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) plots for AI biomass pyrolysis.

As for the ΔS is concerned, it aids in predicting the potential count of various permutations of particle positions and energies, often referred to as the thermodynamic characteristic to determine the level of disorder of the system [200]. ΔS plays a crucial role in predicting the stability of the process. A low or negative ΔS value indicates the formation of

thermodynamically more stable products compared to the initial reactants, approaching equilibrium after undergoing physical and chemical changes during the conversion process. In such a state, biomass exhibits minimal tendency to undergo reactions, and requires more time to form activated complex. Conversely, a positive ΔS at higher conversion implies a longer time to reach thermodynamic equilibrium due to a slower rate in achieving thermal stability. Positive ΔS may also result due to the formation of more complex molecules or products. Figures 6.7.13 (a-e) and 6.7.14 (a-e), respectively illustrate the change in entropy versus conversion plots for single-feed pyrolysis of EI and AI biomass at four different heating rates using five different iso-conversional models. The average ΔS values (kJ/mol·K) at four different heating rates ($\beta=10, 20, 30$ and 40°C/min) for pyrolysis of EI biomass were: DFM: 0.017, 0.016, 0.019, 0.016; KAS: 0.003, 0.003, 0.006, 0.003; OFW: 0.004, 0.004, 0.007, 0.004; STK: 0.004, 0.003, 0.006, 0.003; and DAEM: 0.003, 0.003, 0.006, 0.003, respectively. Similarly, for pyrolysis of AI biomass the corresponding average ΔS values (kJ/mol·K) at four heating rates ($\beta=10, 20, 30$ and 40°C/min) were: DFM: 0.030, 0.029, 0.039, 0.029; KAS: 0.015, 0.014, 0.017, 0.014; OFW: 0.016, 0.015, 0.017, 0.015; STK: 0.016, 0.015, 0.017, 0.015; and DAEM: 0.015, 0.014, 0.017, 0.014, respectively. Figures 6.7.13 (a-e) for EI biomass pyrolysis revealed that ΔS values were found to be shifting from negative to positive as the conversion progressed. This suggests that as the conversion advanced, the level of disorder increased. Whereas in the case of AI biomass pyrolysis, as illustrated in Figure 6.7.14 (a-e), ΔS values shift from positive to negative as the conversion progresses, ultimately becoming positive again at the end of the conversion. This suggests that with advancing conversion, the level of disorder decreases, culminating in a highly disordered state towards the end. A positive ΔS at higher conversion implies that it takes more time to reach thermodynamic equilibrium due to a slower rate in achieving thermal stability. This positive ΔS could result from the formation of more complex molecules or products. However, a lower value of ΔS at the end of the conversion indicates lower reactivity of the substances and takes more time to form activated complex [71,197,199,201]. The results of ΔS are also found to be in line with the DTG curves Figures 6.7.2 (a) and (b) which indicated the value of DTG decreased as the reaction progressed towards the end. This may be attributed to the fact that, following the release of volatiles from biomass, the residual material primarily consists of fixed carbon. Subsequently, it can undergo reactions with CO_2 , but these reactions typically require higher temperatures, necessitating an increased input of energy. A positive ΔS suggests weaker binding, as stability decreases, and biomass conversion follows a dissociation pathway.

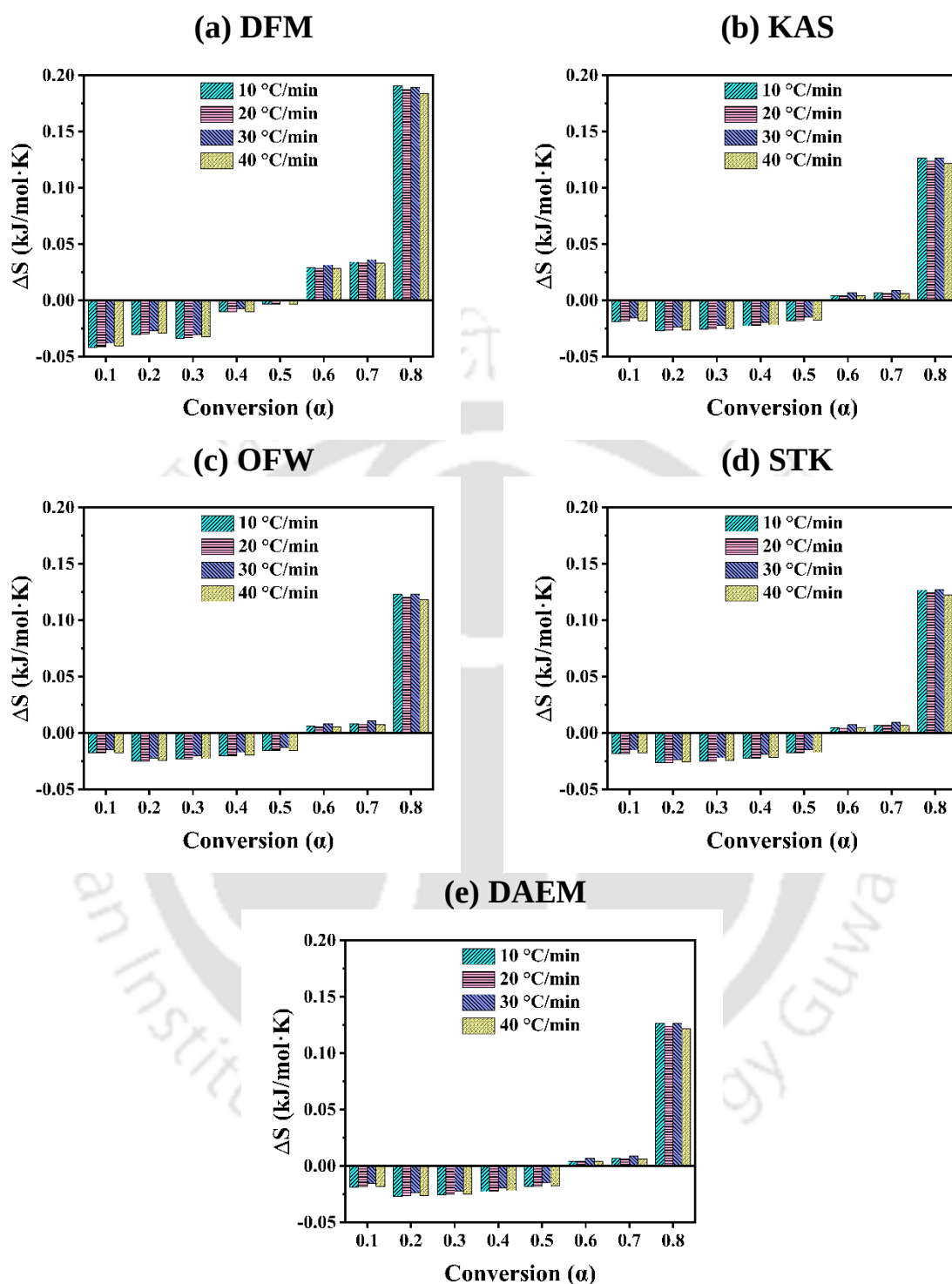


Figure 6.7.13 (a-e) Change in entropy (ΔS) vs. conversion (α) plots for EI biomass pyrolysis.

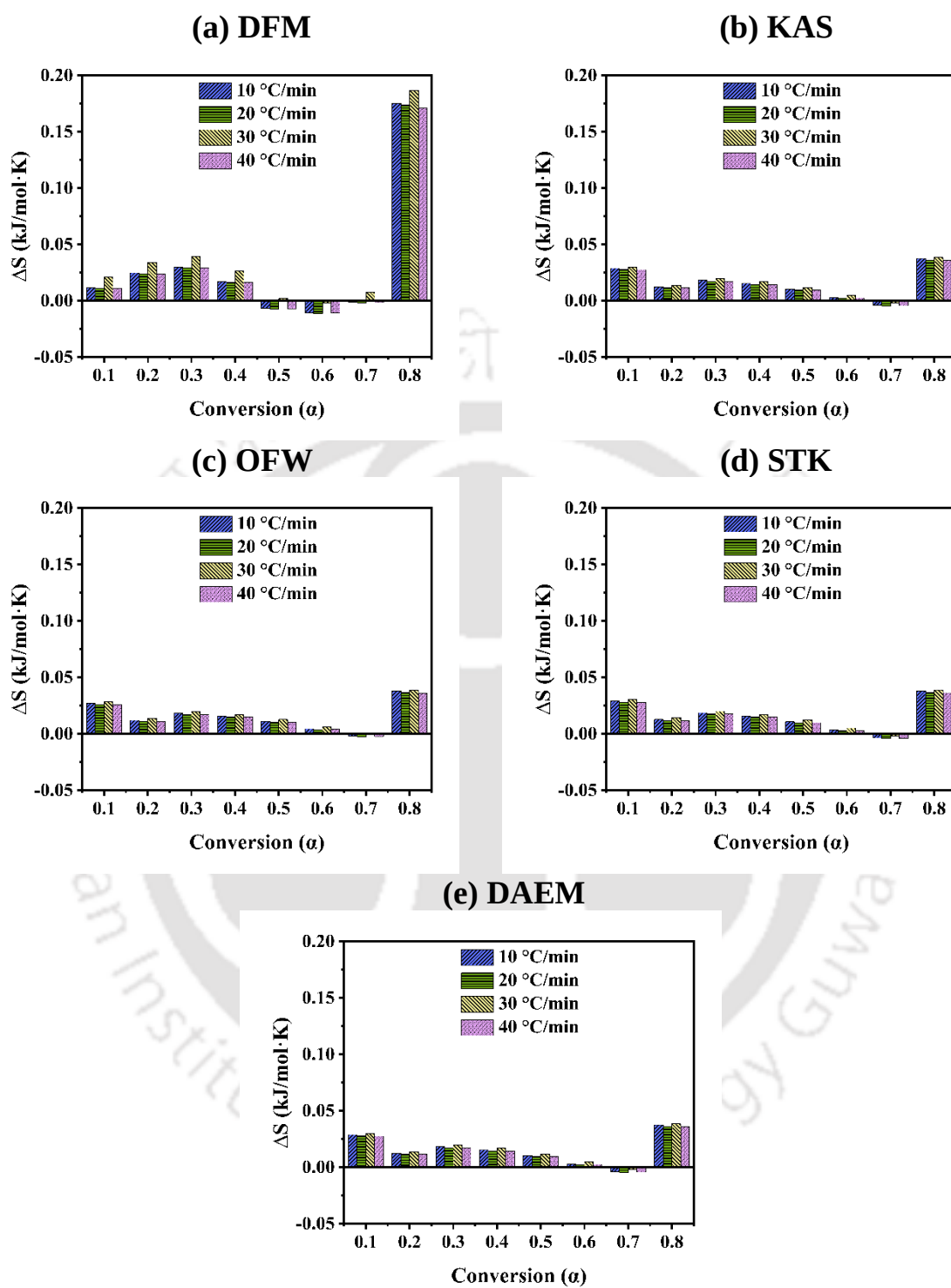


Figure 6.7.14 (a-e) Change in entropy (ΔS) vs. conversion (α) plots for AI biomass pyrolysis.

Table 6.7.2 Average values of enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI and AI biomass pyrolysis.

		DFM											
	Method	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
		ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
EI	DFM	179.890	169.916	0.017	179.799	169.909	0.016	179.790	168.191	0.019	179.707	169.780	0.016
	KAS	171.964	170.083	0.003	171.873	170.078	0.003	171.864	168.361	0.006	171.781	169.952	0.003
	OFW	172.596	169.885	0.004	172.504	170.057	0.004	172.496	168.339	0.007	172.413	169.930	0.004
	STK	172.214	170.076	0.004	172.014	170.071	0.003	172.114	168.354	0.006	172.031	169.945	0.003
	DAEM	171.964	170.083	0.003	171.873	170.078	0.003	171.864	168.361	0.006	171.781	169.952	0.003
AI	DFM	191.638	173.330	0.030	191.539	173.561	0.029	191.522	167.288	0.039	191.447	173.356	0.029
	KAS	182.616	173.508	0.015	182.516	173.742	0.014	182.500	172.285	0.017	182.425	173.540	0.014
	OFW	182.844	173.501	0.016	182.744	173.735	0.015	182.728	172.279	0.017	182.653	173.533	0.015
	STK	182.863	173.501	0.016	182.763	173.735	0.015	182.746	172.279	0.017	182.671	173.533	0.015
	DAEM	182.616	173.508	0.015	182.516	173.742	0.014	182.500	172.285	0.017	182.425	173.540	0.014

6.8 KINETICS AND THERMODYNAMICS OF CO-FEED PYROLYSIS OF ERYTHRINA INDICA AND AZADIRACHTA INDICA BIOMASS

6.8.1 Thermogravimetric and differential thermogravimetric analysis

Similar to the single-feed pyrolysis studies, kinetics and thermodynamics associated with the co-feed pyrolysis processes of *Erythrina indica* (EI) and *Azadirachta indica* (AI) biomass were investigated. Thermal degradation studies were conducted at four distinct heating rates of 10, 20, 30 and 40°C/min across seven distinct co-feed ratios (EI:AI) of 1:4, 1:3, 1:2, 1:1, 2:1, 3:1 and 4:1, spanning over a temperature range of 25 to 900°C. Figures 6.8.1 (a-g) illustrate the TGA curves for EI and AI biomass at the specified co-feed ratios across the four distinct heating rates. It was observed that, across all co-feed ratios of EI and AI biomass, the samples exhibited a similar three stage degradation pattern as observed in their respective single-feed pyrolysis studies. Stage I, recognized as the dehydration zone, involved the moisture removal and release of minor amounts of volatiles with lower molecular weight, which occurred within the temperature range of 70 to 200°C. Stage II representing the active pyrolysis zone, involved the breakdown of cellulose, hemicellulose and a small portion of lignin within the temperature range of 200°C to 450°C. During this phase, cellulose and hemicellulose decomposed between 200°C and 380°C, while the lignin degradation occurred at temperatures beyond 380°C. Moving into Stage III, the passive pyrolysis zone primarily indicated the gradual degradation of the remaining lignin, reflecting its relatively high thermal stability due to its intricate structure, occurred at temperatures >450°C.

The DTG curves derived from the corresponding TGA data, as illustrated in Figures 6.8.2 (a-g), further confirmed the three-stage degradation patterns observed in the TGA curves. The initial peak, observed at around 80°C, marked the removal of moisture and the release of volatile compounds with low molecular weights, persisting up to 200°C. The second peak, spanning from 200 to 450°C, covered the decomposition of cellulose, hemicellulose and a portion of lignin. However, the complete degradation of lignin occurred over a broader temperature range beyond 450°C, and lacked a distinct peak. Through DTG analysis, a noticeable correlation emerged between the increase in peak degradation temperature and the heating rate for all the cases.

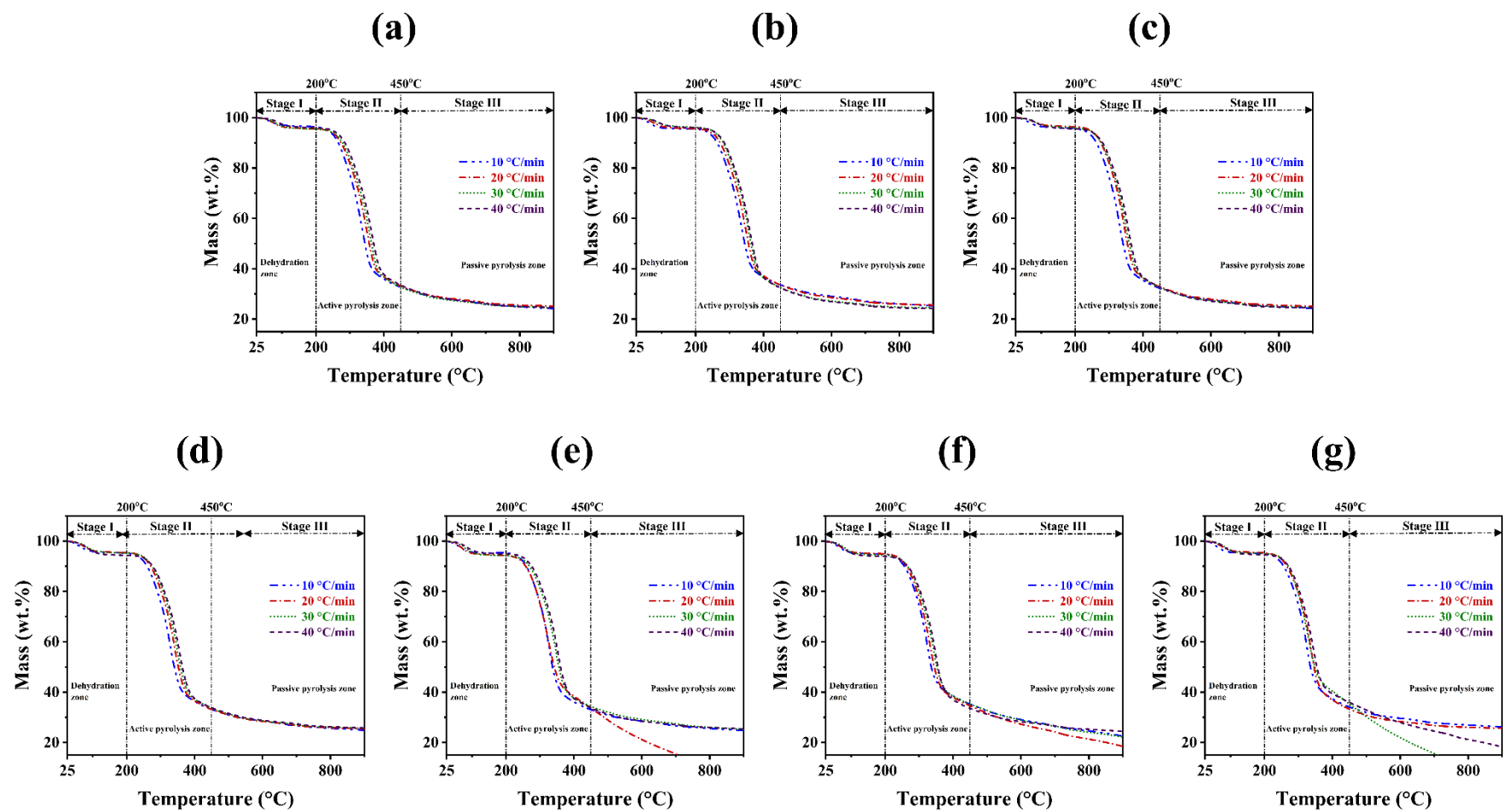


Figure 6.8.1 Thermogravimetric analysis curves of EI and AI biomass at co-feed ratios of (a) 1:4, (b) 1:3, (c) 1:2, (d) 1:1, (e) 2:1, (f) 3:1 and (g) 4:1.

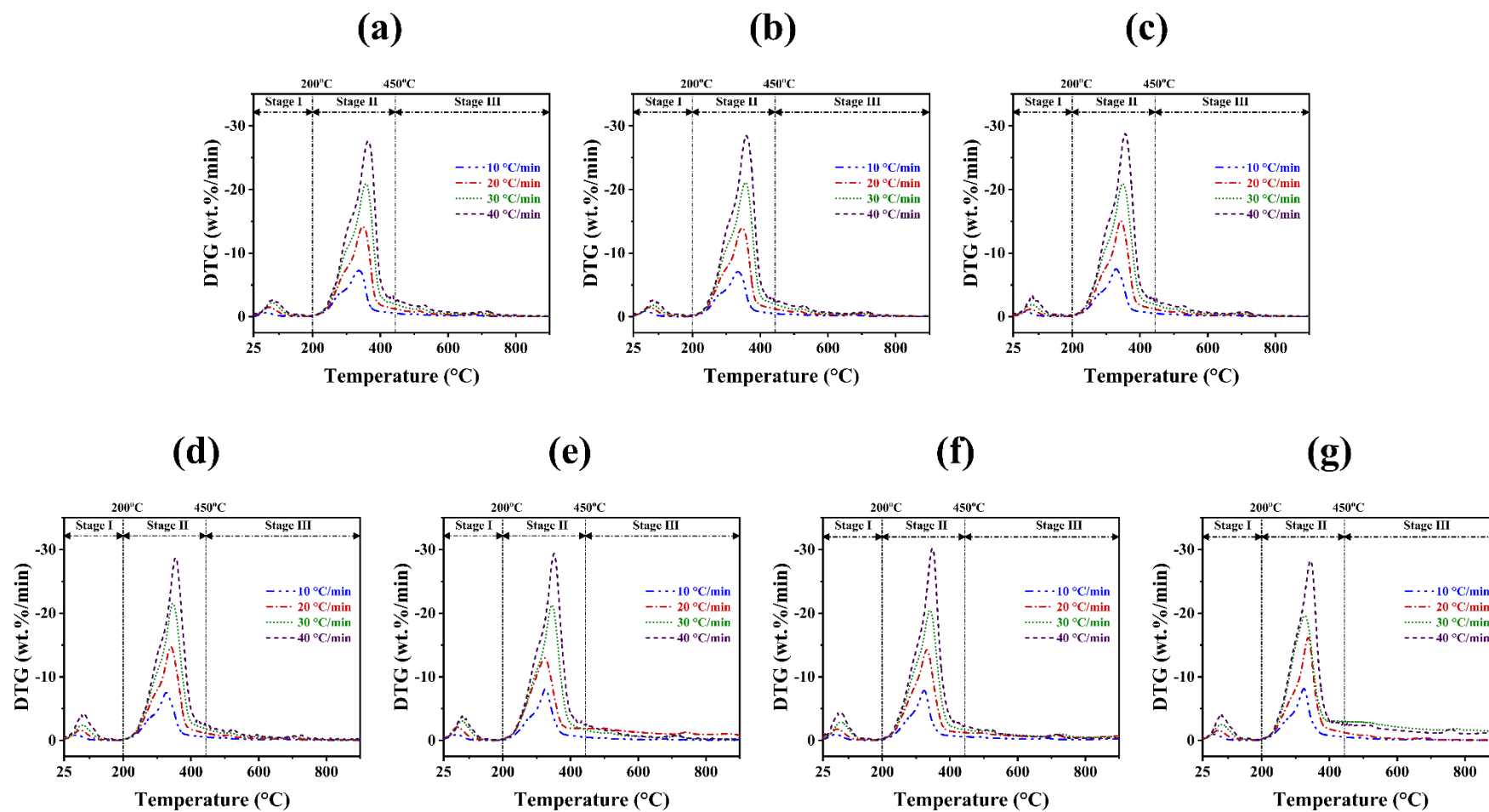


Figure 6.8.2 Differential thermogravimetric analysis curves of EI and AI biomass at co-feed ratios of (a) 1:4, (b) 1:3, (c) 1:2, (d) 1:1, (e) 2:1, (f) 3:1 and (g) 4:1.

6.8.2 Evaluation of the kinetic triplets

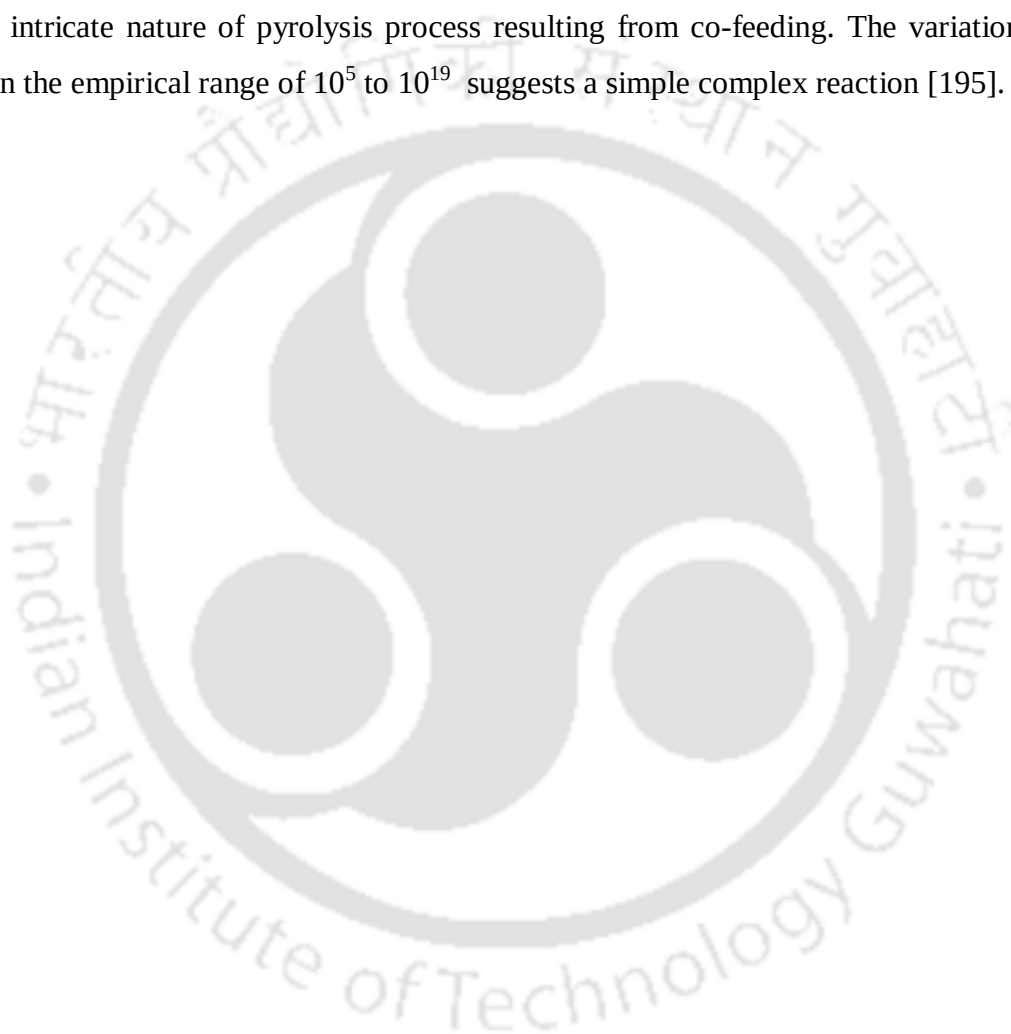
The co-feed pyrolysis of EI and AI biomass was primarily focused on the active pyrolysis zone, covering temperatures ranging from 200°C to 450°C, where maximum decomposition of the samples took place. Similar to the single-feed study, five distinct iso-conversional models were applied to ascertain the apparent activation energy and pre-exponential factor, focusing on conversions within the range of 0.1 to 0.8. Simultaneously, the reaction mechanism involved in the co-feed pyrolysis process was also investigated utilizing the results obtained from the differential Friedman method.

6.8.2.1 Calculation of activation energy

The kinetic data obtained for EI and AI biomass pyrolysis of various co-feed ratios using iso-conversional methods at various conversion levels and heating rates are presented in Tables C7 to C13, respectively of Appendix C, while the corresponding kinetic plots using the same data are illustrated in Figures 6.8.3-6.8.9. The apparent activation energy values were evaluated by analyzing the slopes of kinetic plots. A graphical illustration of the activation energies at various conversions has been shown in Figures 6.8.10 (a-g), while the average activation energies are represented by Figure 6.8.10 (h). The graphical illustrations of activation energy vs. conversion revealed a subtle fluctuation in activation energy at all co-feed ratios, which could have possibly arisen from differences in estimation techniques and mathematical formulations employed by various iso-conversional approaches. However, in Figure 6.8.10 (h), a significant variation in the average activation energy was observed due to the synergistic effect of co-feeding EI with AI. The co-feed ratio of 2:1 depicted the minimum average activation energy (kJ/mol) of 153.359 for DFM, 142.906 for KAS, 145.279 for OFW, 143.186 for STK and 142.906 for DAEM, while the co-feed ratio of 4:1 depicted the maximum average activation energy (kJ/mol) of 238.544 for DFM, 227.534 for KAS, 225.679 for OFW, 227.744 for STK and 227.534 for DAEM. However, considering the R^2 values, the co-feed ratio of 1:1 depicted a better R^2 value and also had a lower average activation energy requirement. The average activation energy (kJ/mol) values for the co-feed ratio of 1:1 were found to be 179.808 for DFM, 169.643 for KAS, 170.738 for OFW, 169.903 for STK and 169.643 for DAEM. For all the cases, KAS and DAEM exhibited the minimum activation energy values, while DFM yielded the maximum value of activation energy. Tables C14-C20 of Appendix C also provide a comprehensive summary of the calculated activation energy values at various co-feed ratios using different iso-conversional methods at various conversion levels, while their average values are being presented in Table 6.8.1.

6.8.2.2 Calculation of pre-exponential factor

The pre-exponential factor k_o (min^{-1}), elucidated by utilizing the intercepts of all the iso-conversional plots were found to be in the empirical range of 10^{11} to 10^{16} for 1:4 ratio, 10^{12} to 10^{17} for 1:3 ratio, 10^{12} to 10^{17} for 1:2 ratio, 10^{11} to 10^{17} for 1:1 ratio, 10^8 to 10^{18} for 2:1 ratio, 10^{13} to 10^{21} for 3:1 ratio and 10^{15} to 10^{25} for 4:1 ratio. A summary of the k_o values has also been presented in Tables C14-C20 of Appendix C. The variations in the rate constant k_o with respect to conversion are primarily attributed to the complex structure of the biomass sample and the intricate nature of pyrolysis process resulting from co-feeding. The variation of k_o values in the empirical range of 10^5 to 10^{19} suggests a simple complex reaction [195].



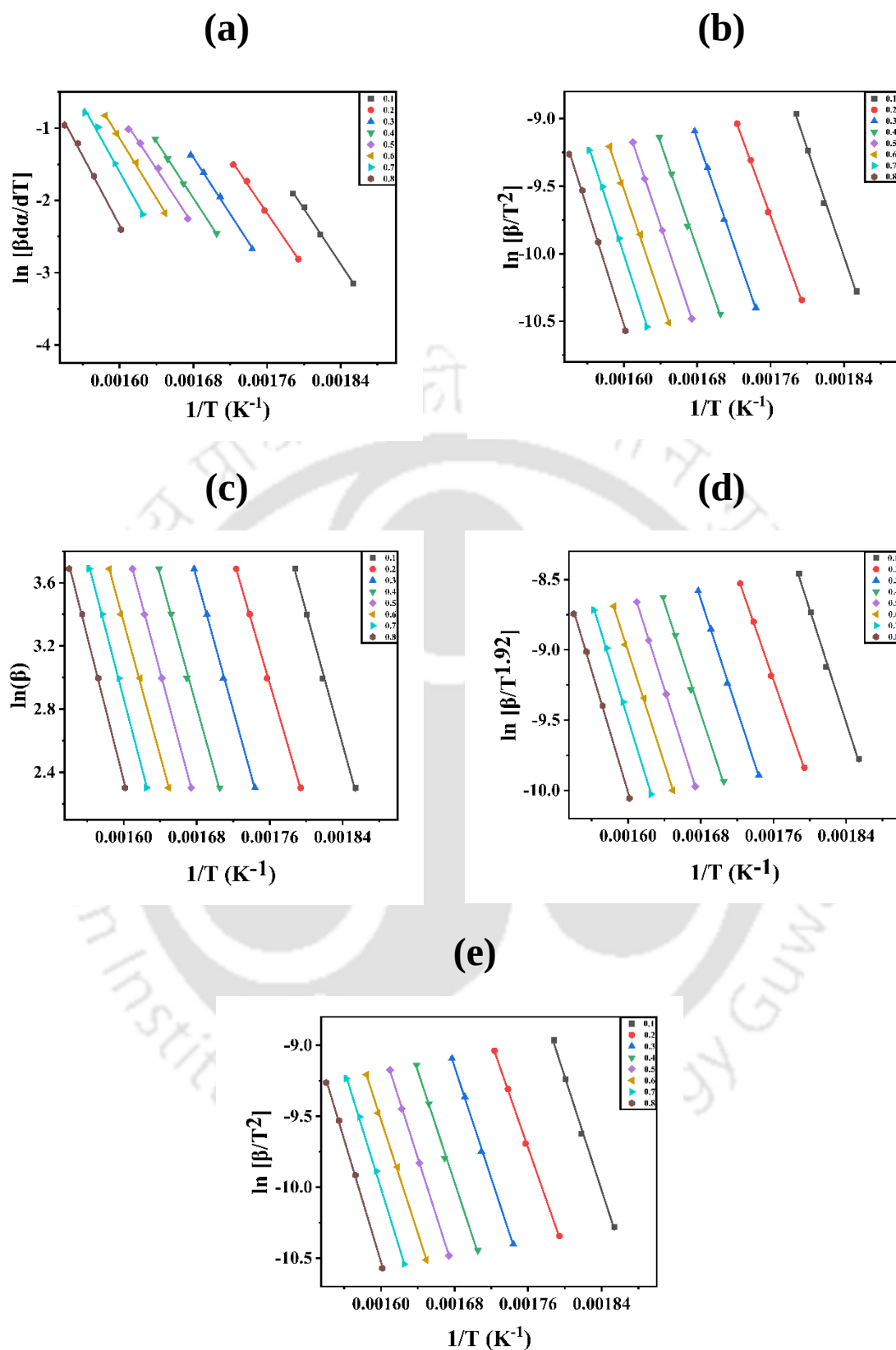


Figure 6.8.3 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:4: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.

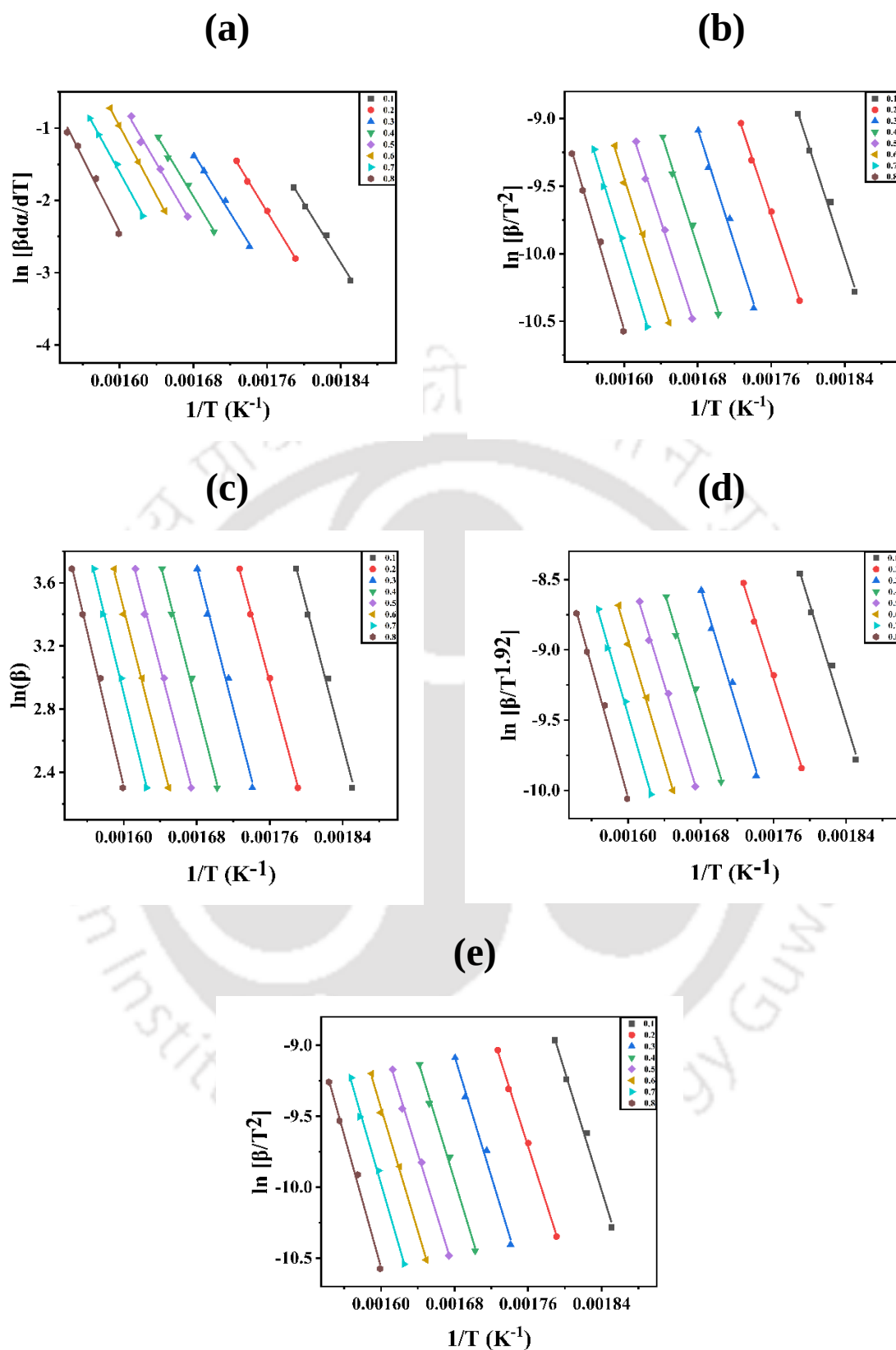


Figure 6.8.4 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:3: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.

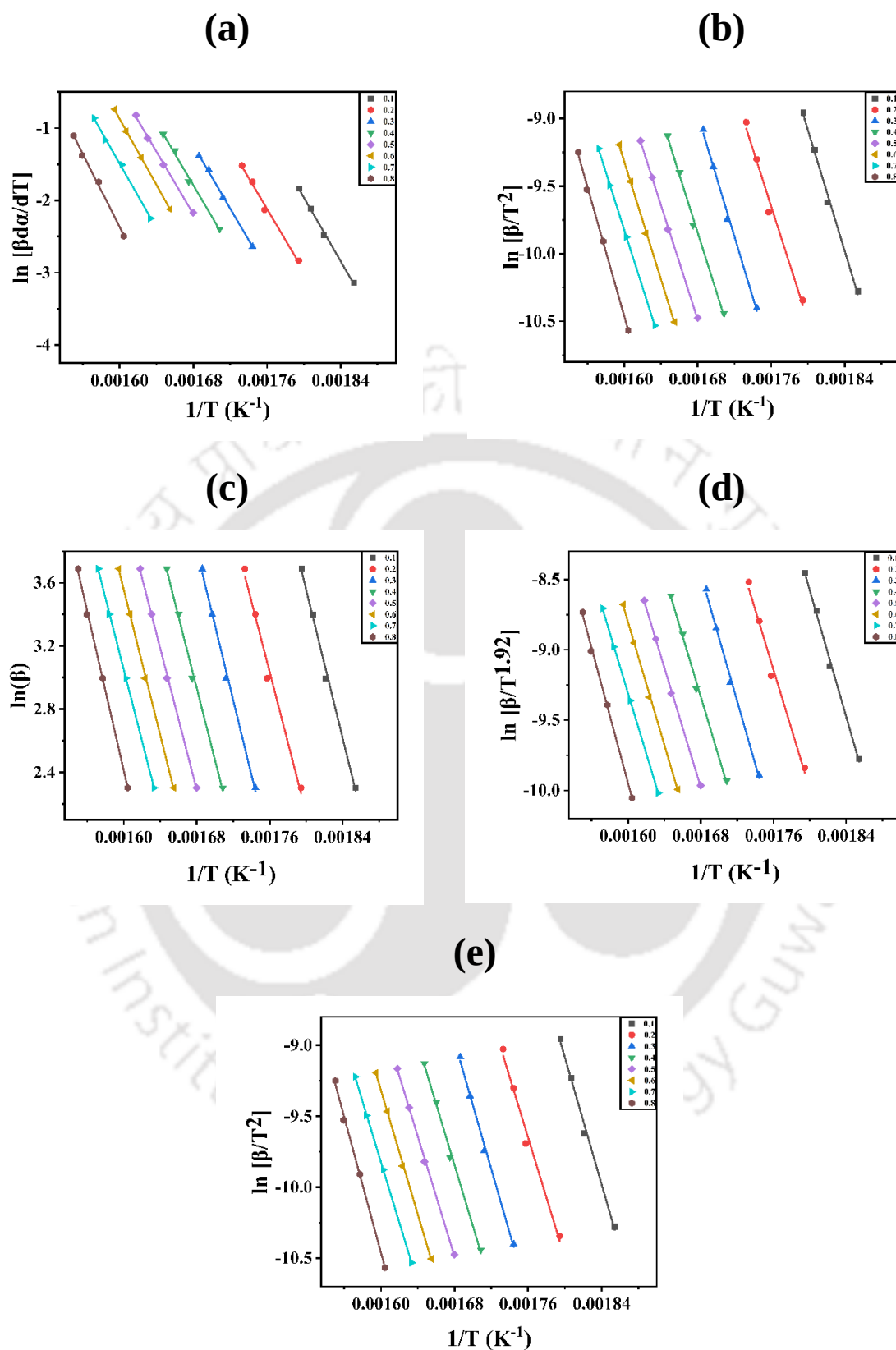


Figure 6.8.5 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:2: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.

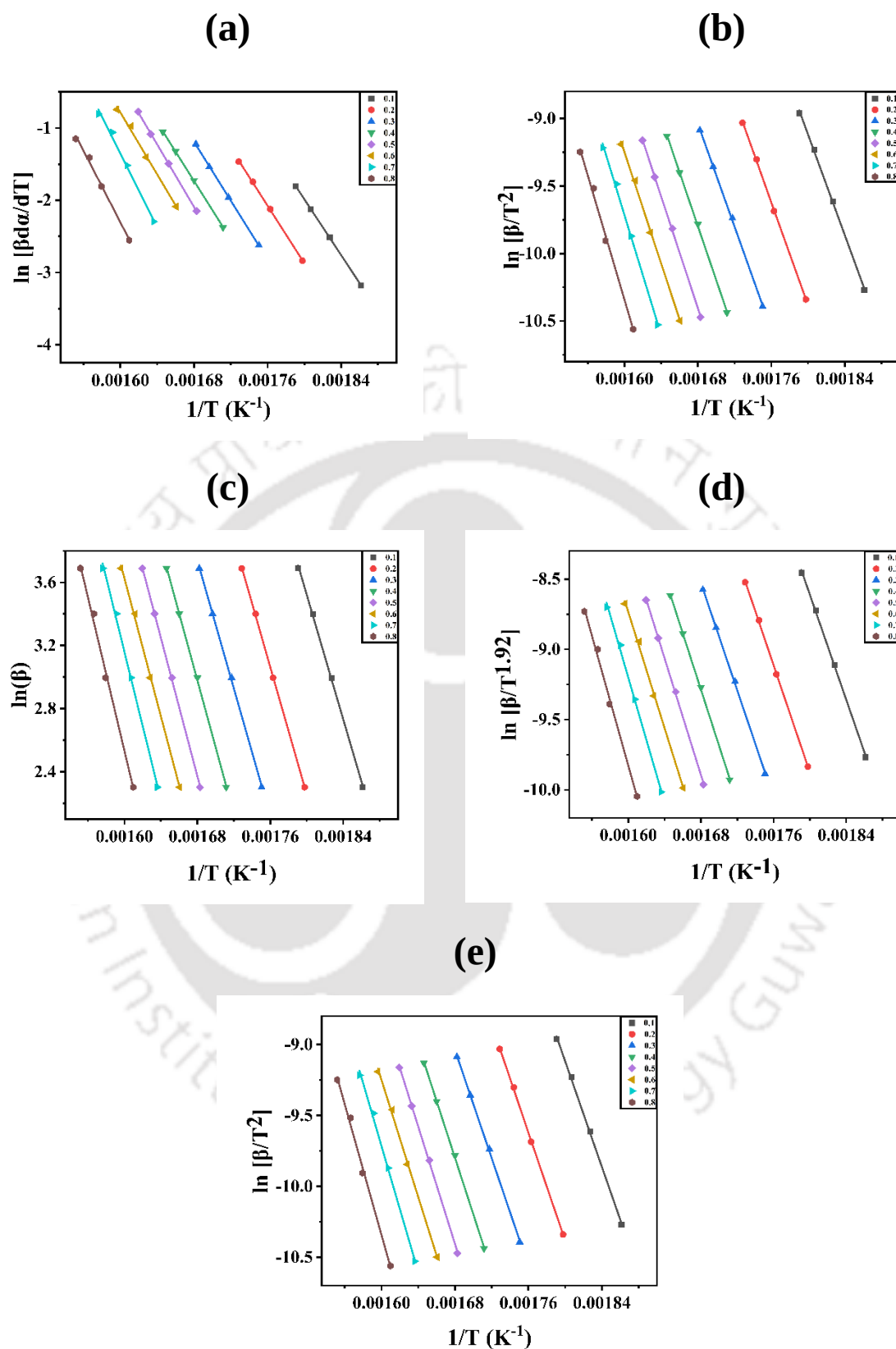


Figure 6.8.6 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:1: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.

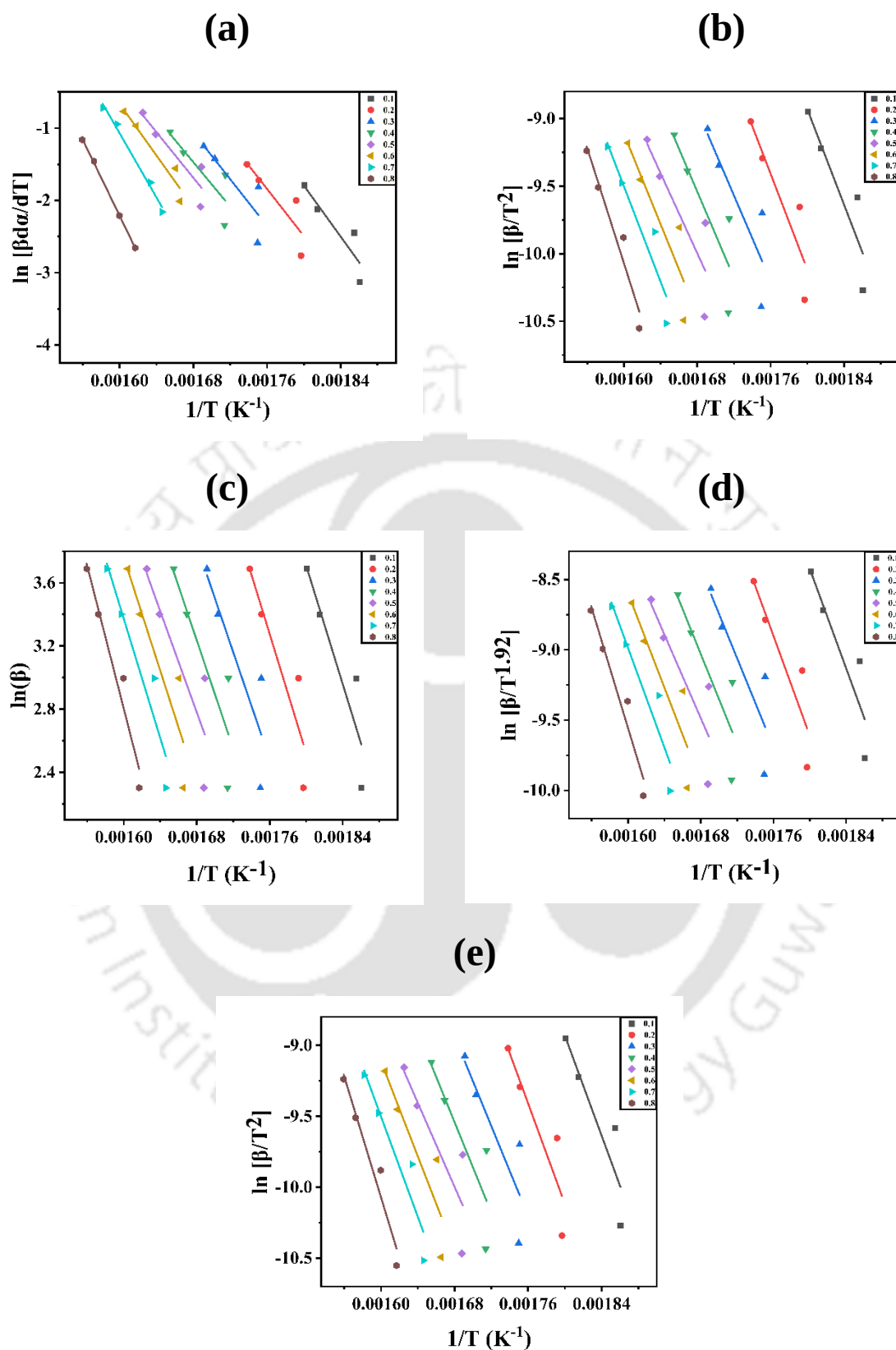


Figure 6.8.7 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 2:1: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.

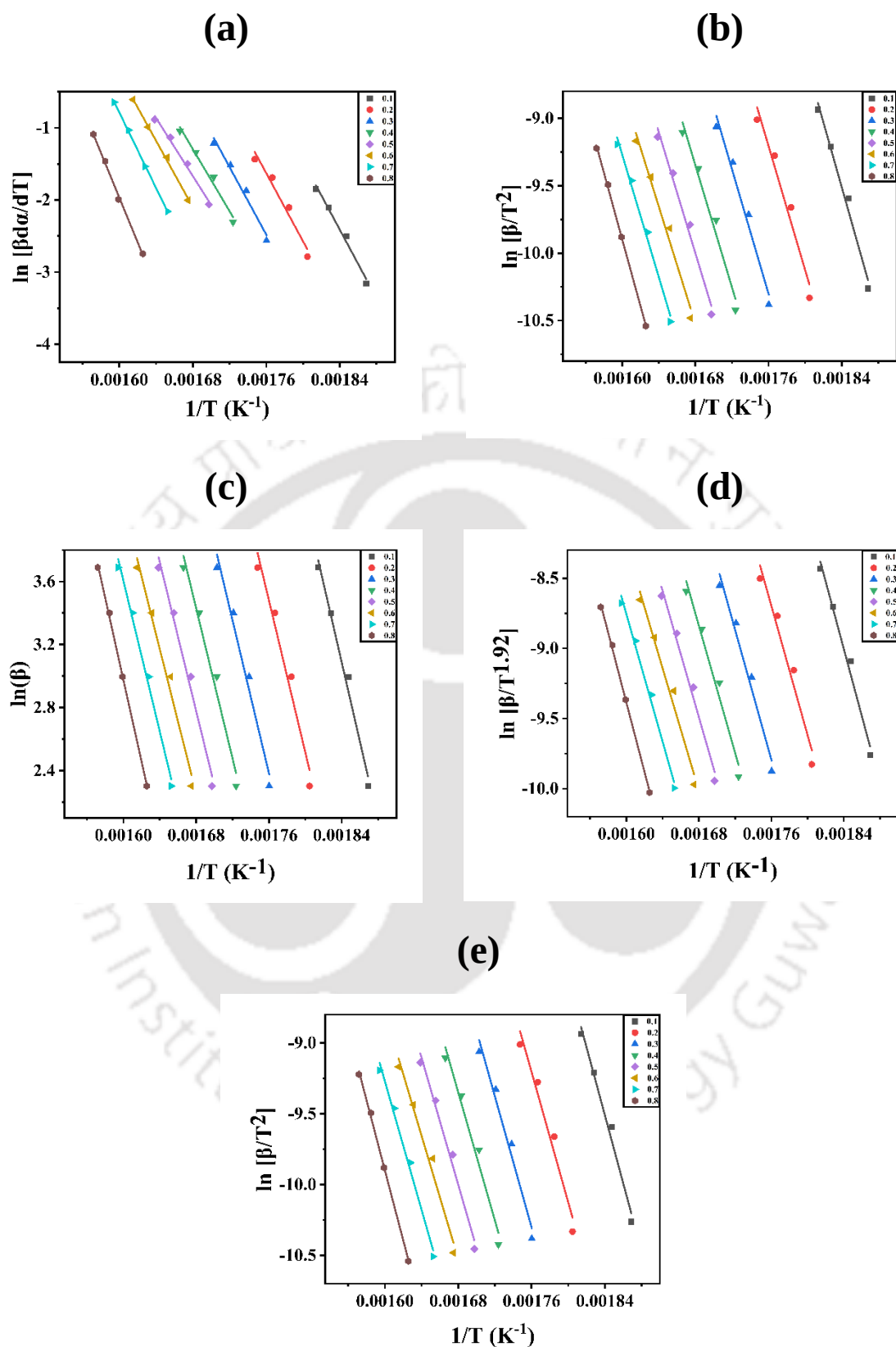


Figure 6.8.8 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 3:1: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.

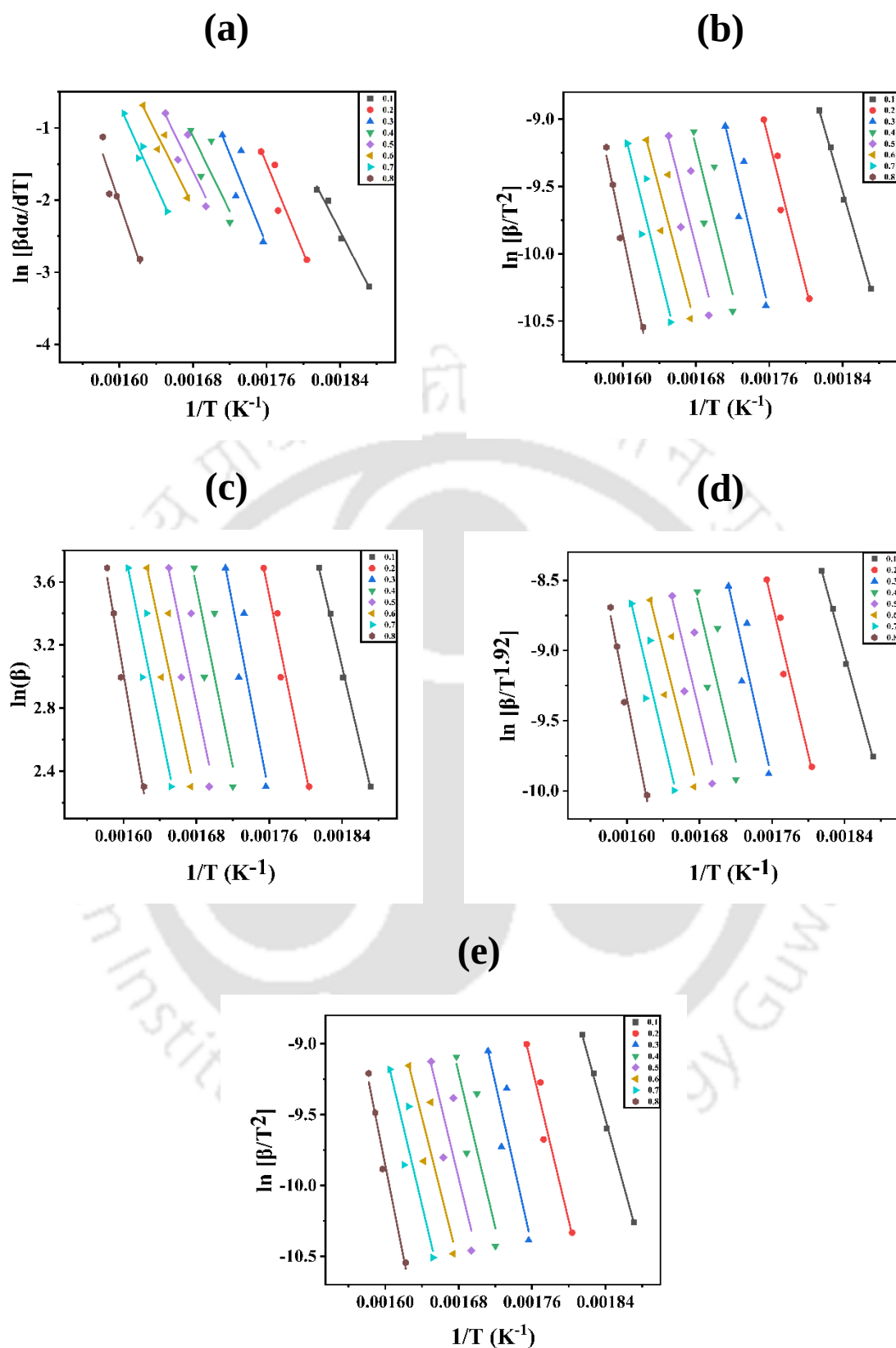


Figure 6.8.9 (a-e) Iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 4:1: (a) DFM, (b) KAS, (c) OFW, (d) STK and (e) DAEM.

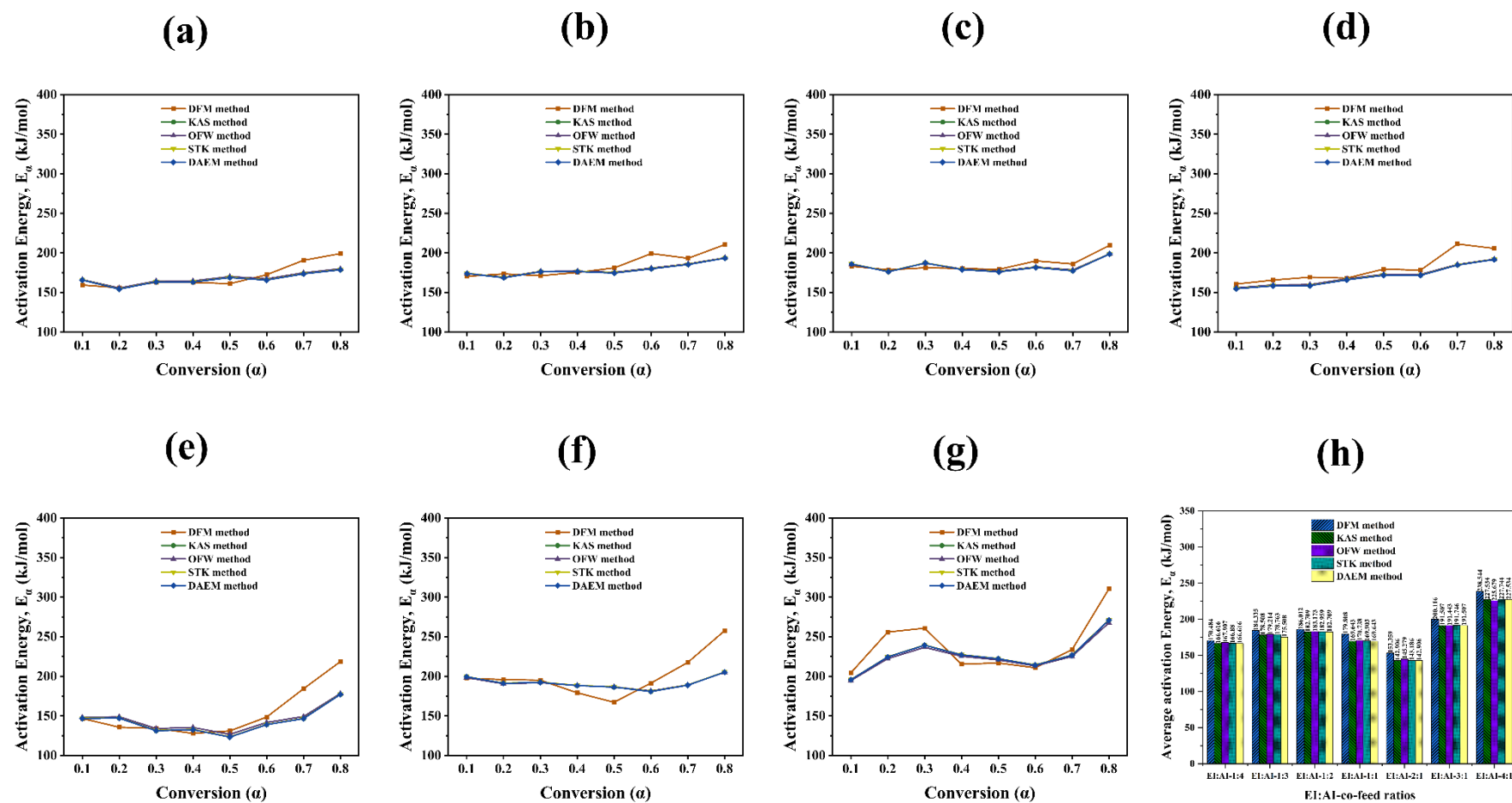


Figure 6.8.10 (a-g) Apparent activation energy vs. conversion of co-feed pyrolysis of EI:AI at (a) 1:4, (b) 1:3, (c) 1:2, (d) 1:1, (e) 2:1, (f) 3:1 and (g) 4:1; and (h) average activation energy using different iso-conversional models at various co-feed ratios.

Table 6.8.1 Average values of activation energy (kJ/mol), pre-exponential factor (min⁻¹) and R² for EI and AI biomass pyrolysis at various co-feed ratios.

Co-feed ratios	DFM			KAS			OFW			STK			DAEM		
	E_a	k_o	R ²	E_a	k_o	R ²	E_a	k_o	R ²	E_a	k_o	R ²	E_a	k_o	R ²
EI:AI-1:4	170.484	3.362×10^{15}	0.997	166.616	3.187×10^{14}	0.999	167.907	1.995×10^{12}	0.999	166.880	2.606×10^{14}	0.999	166.616	1.188×10^{15}	0.999
EI:AI-1:3	184.335	2.899×10^{16}	0.994	178.508	3.761×10^{15}	0.995	179.214	2.091×10^{13}	0.995	178.763	3.060×10^{15}	0.995	178.508	9.697×10^{15}	0.995
EI:AI-1:2	186.012	2.522×10^{16}	0.997	182.709	2.053×10^{16}	0.996	183.173	9.883×10^{13}	0.997	182.959	1.660×10^{16}	0.996	182.709	1.135×10^{17}	0.996
EI:AI-1:1	179.808	5.898×10^{16}	0.997	169.643	2.243×10^{15}	0.998	170.738	1.272×10^{13}	0.999	169.903	1.826×10^{15}	0.998	169.643	1.770×10^{15}	0.998
EI:AI-2:1	153.359	1.267×10^{17}	0.844	142.906	1.171×10^{14}	0.813	145.279	7.554×10^{11}	0.832	143.186	9.585×10^{13}	0.813	142.906	9.502×10^{13}	0.813
EI:AI-3:1	200.116	2.926×10^{20}	0.986	191.507	4.344×10^{17}	0.981	191.443	1.727×10^{15}	0.983	191.746	3.484×10^{17}	0.981	191.507	3.515×10^{18}	0.981
EI:AI-4:1	238.544	7.232×10^{24}	0.852	227.534	1.579×10^{22}	0.857	225.679	4.340×10^{19}	0.866	227.744	1.247×10^{22}	0.857	227.534	1.079×10^{22}	0.857

6.8.2.3 Reaction mechanism

6.8.2.3.1 Criado's master plots method

The reaction mechanisms revealed through Criado's master plots for the co-feed pyrolysis of EI and AI biomass at various co-feed ratios are illustrated in Figures 6.8.11-6.8.17. The Criado's master plots unveiled a similar intricate solid-state reaction mechanism for the co-feed pyrolysis processes as observed for their individual counterparts. Similar to the single-feed pyrolysis processes, the co-feed pyrolysis process also did not follow a single reaction model rather it followed a combination of various models including power law, Avrami-Erofeev, contracting area, diffusion and various order reaction models. These intricacies arose due to the influence of biomass components, synergistic effects of co-feeding EI and AI biomass and effect of heating rates, especially at higher conversions. For instance, the co-feed ratio of 1:1, the pyrolysis process followed P2, P3, P4, D1 and F0 models from 0.1 to 0.6 at all heating rates. However, at higher conversion levels of 0.7 and 0.8 variations in the reaction mechanisms were observed. For instance, at heating rate of 10°C/min, the process followed R3 models at 0.7 and 0.8 conversion, respectively, while for the heating rates of 20, 30 and 40°C/min, the process followed D3 and R2, D3 and R3, D2 and R3 models, respectively. Similar kind of reaction mechanism was followed at other ratios of pyrolysis co-feed as evident from the Criado's master plots.

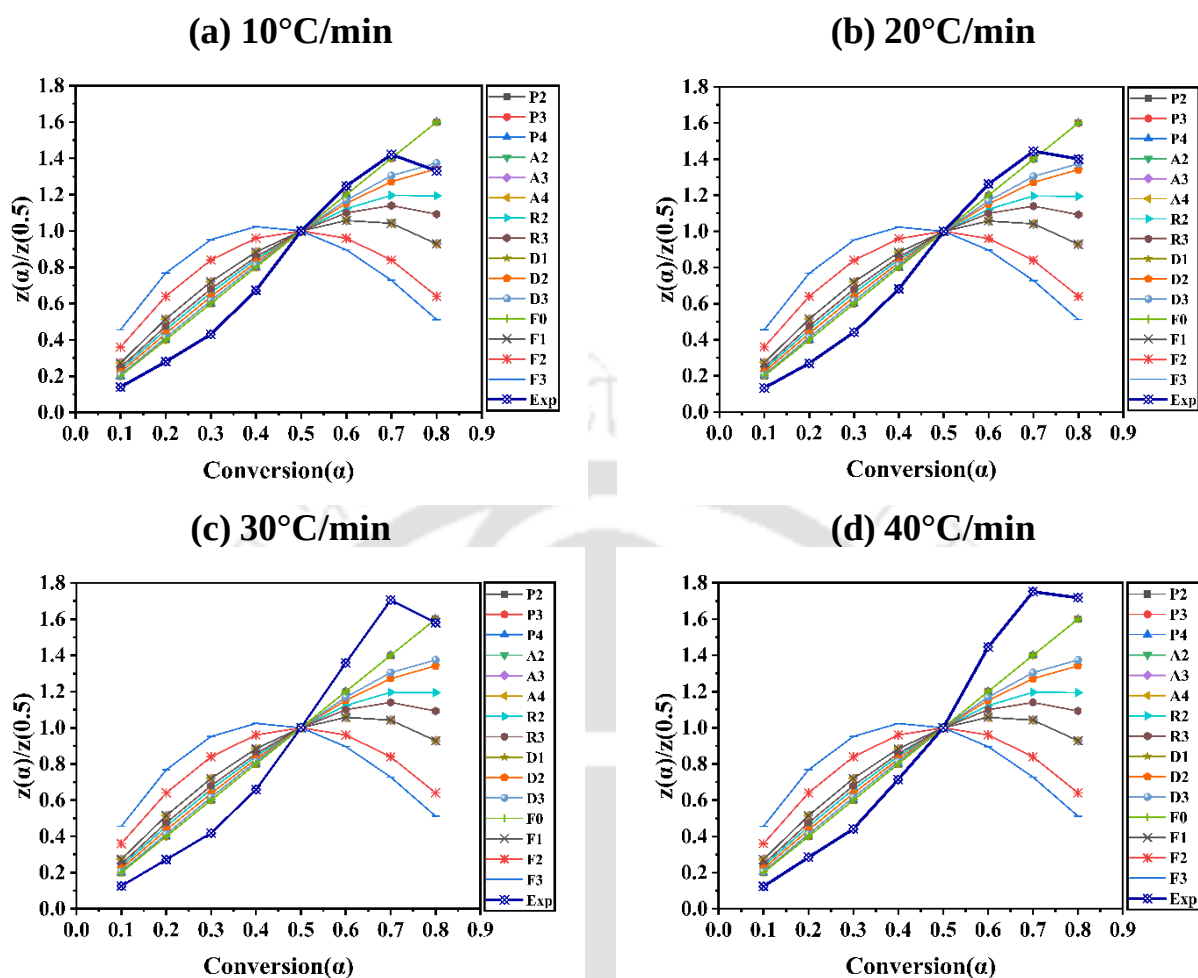
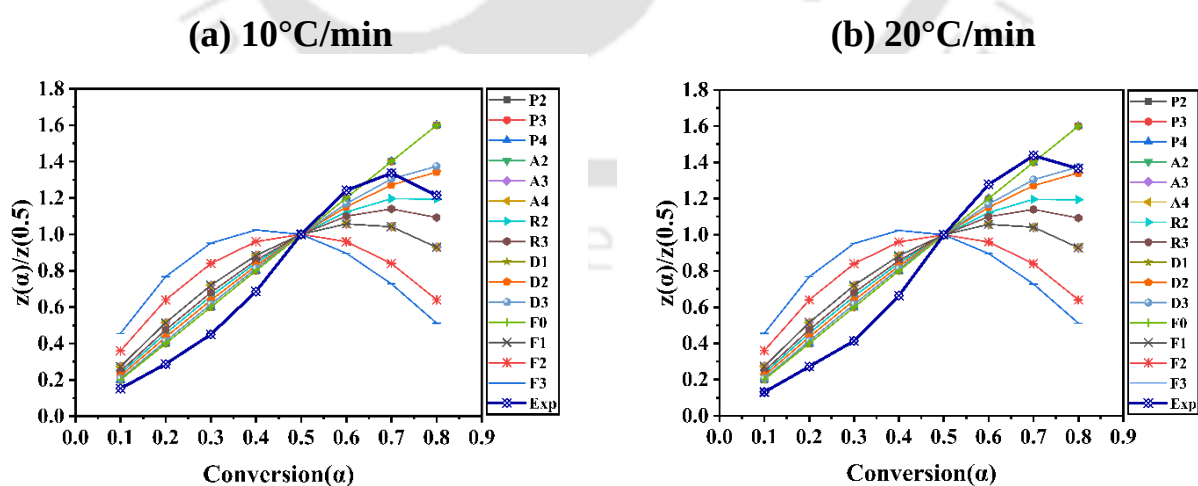


Figure 6.8.11 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:4.



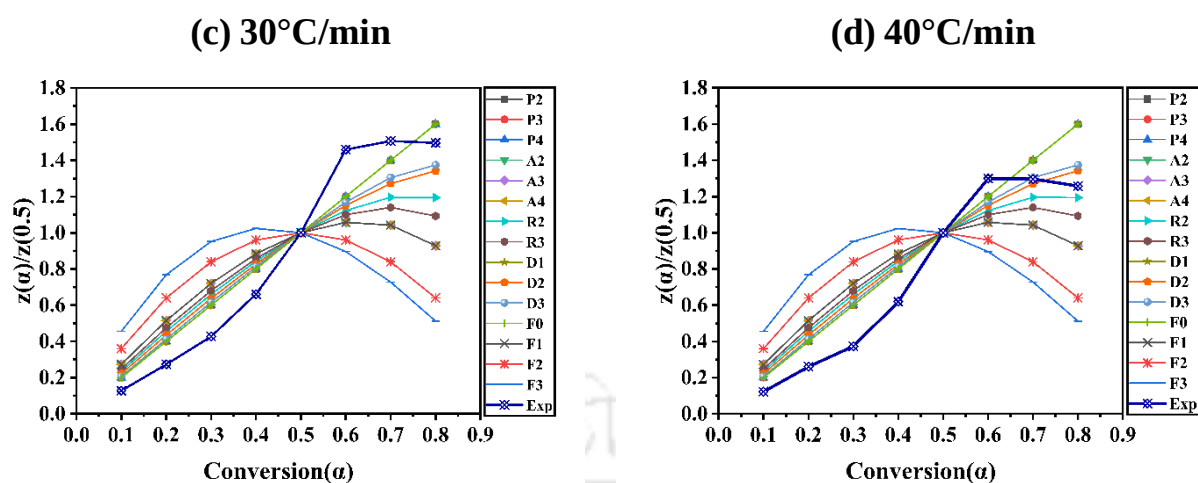


Figure 6.8.12 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:3.

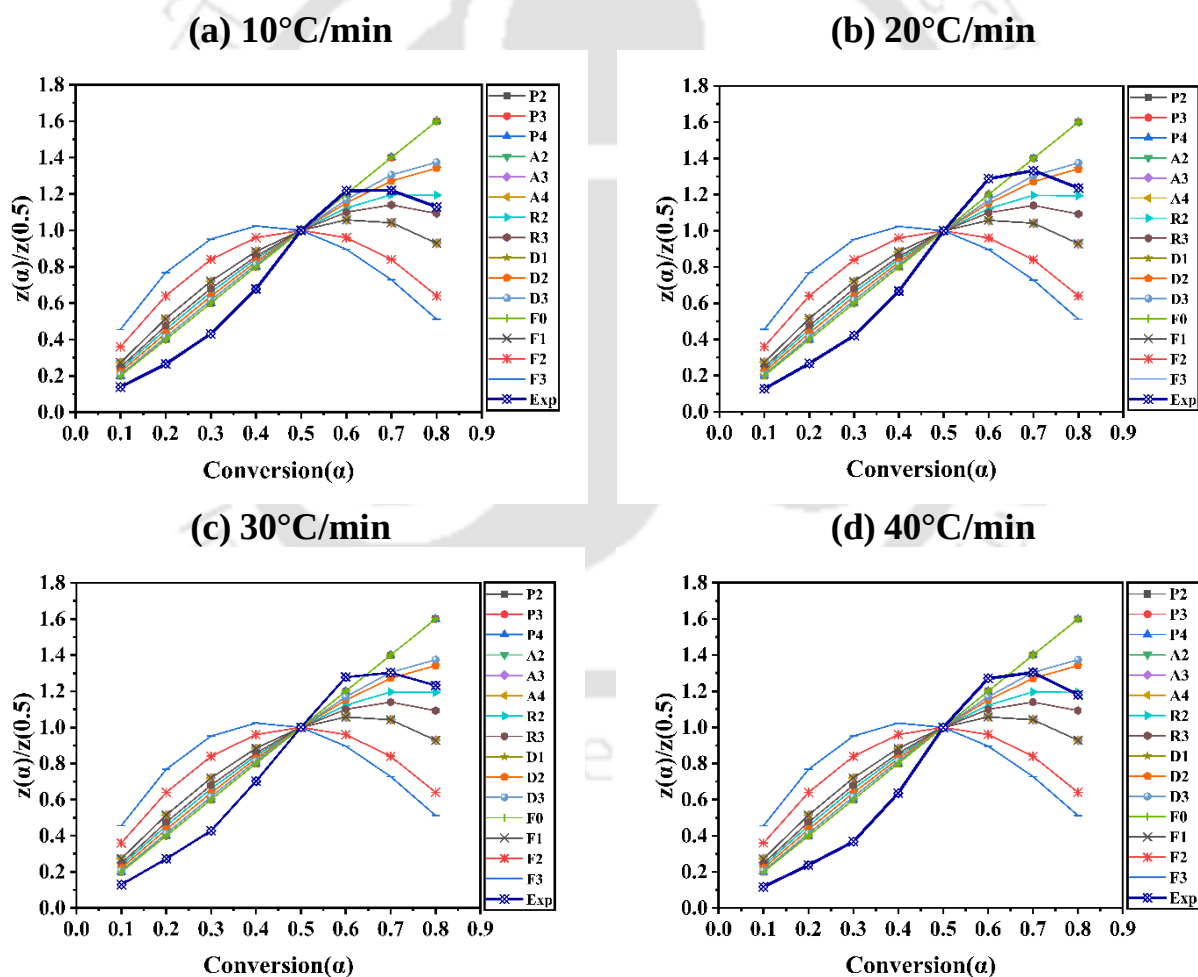


Figure 6.8.13 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:2.

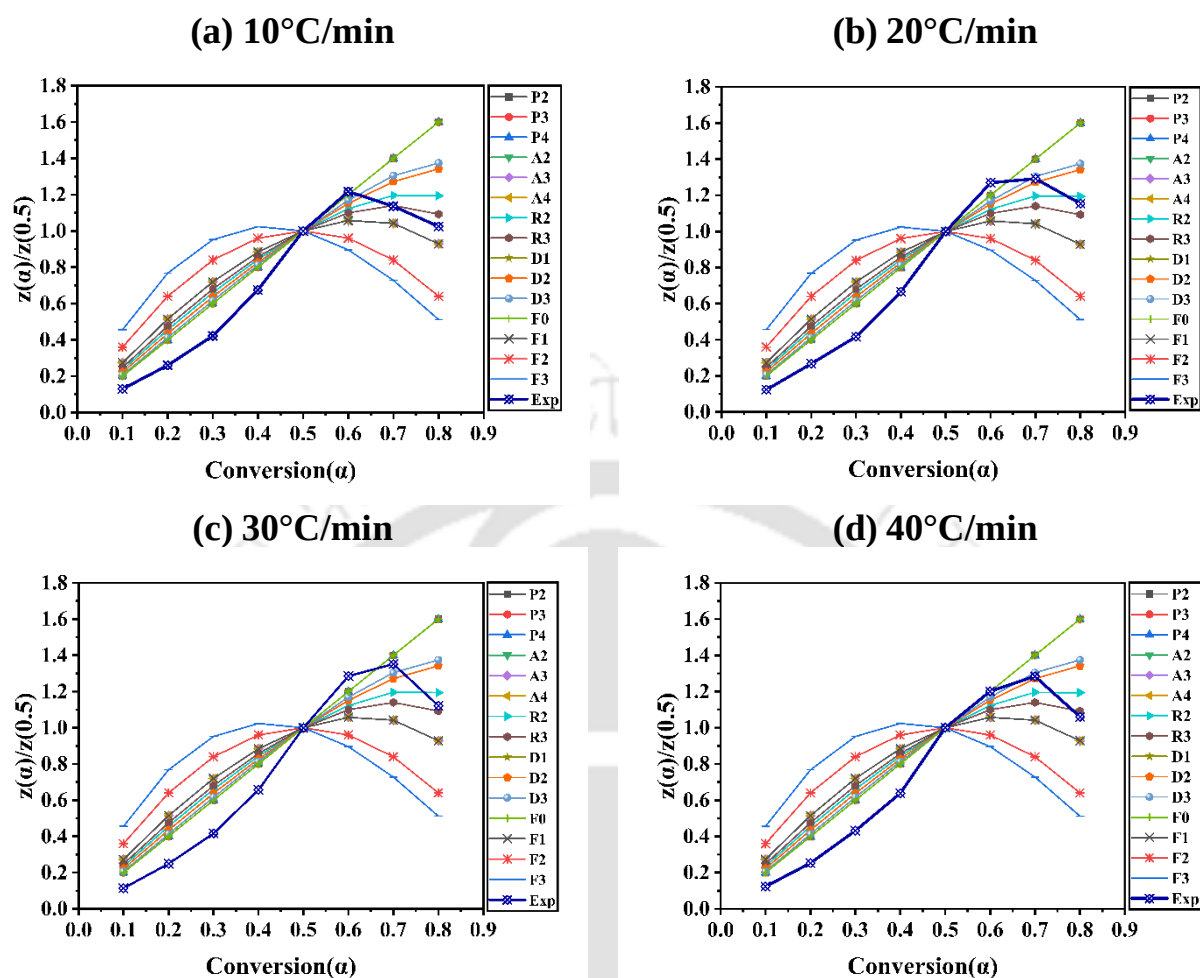
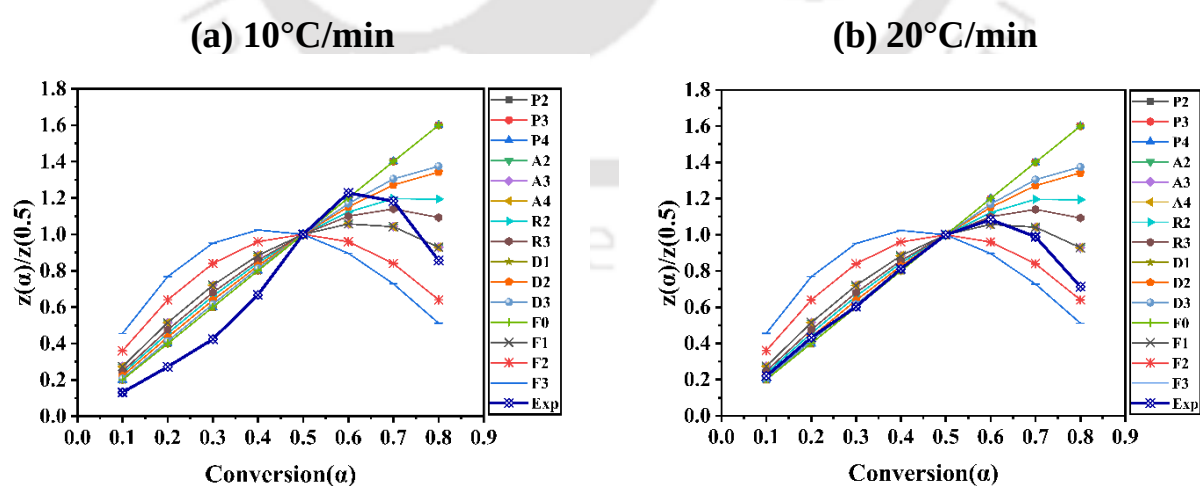


Figure 6.8.14 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:1.



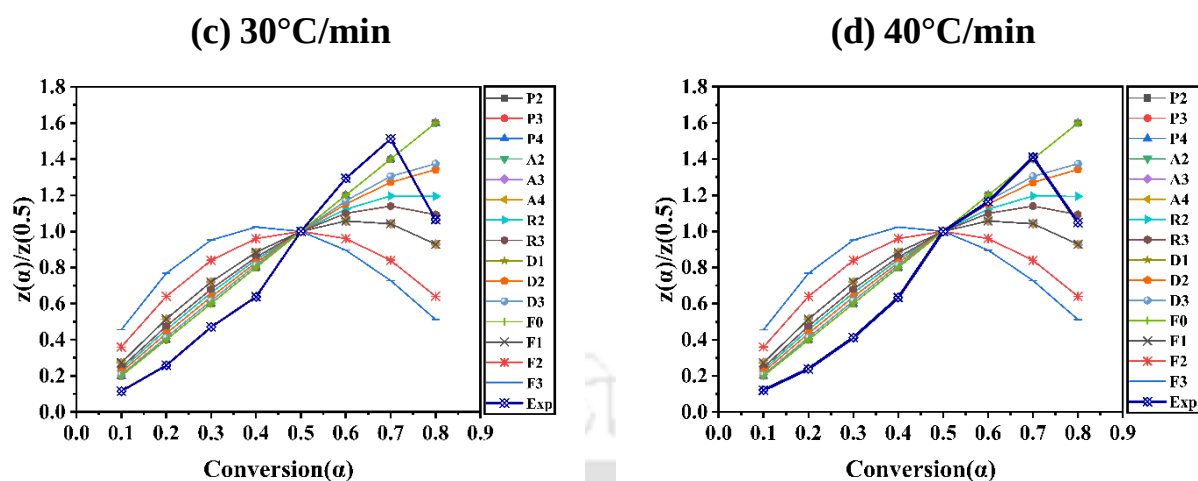


Figure 6.8.15 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 2:1.

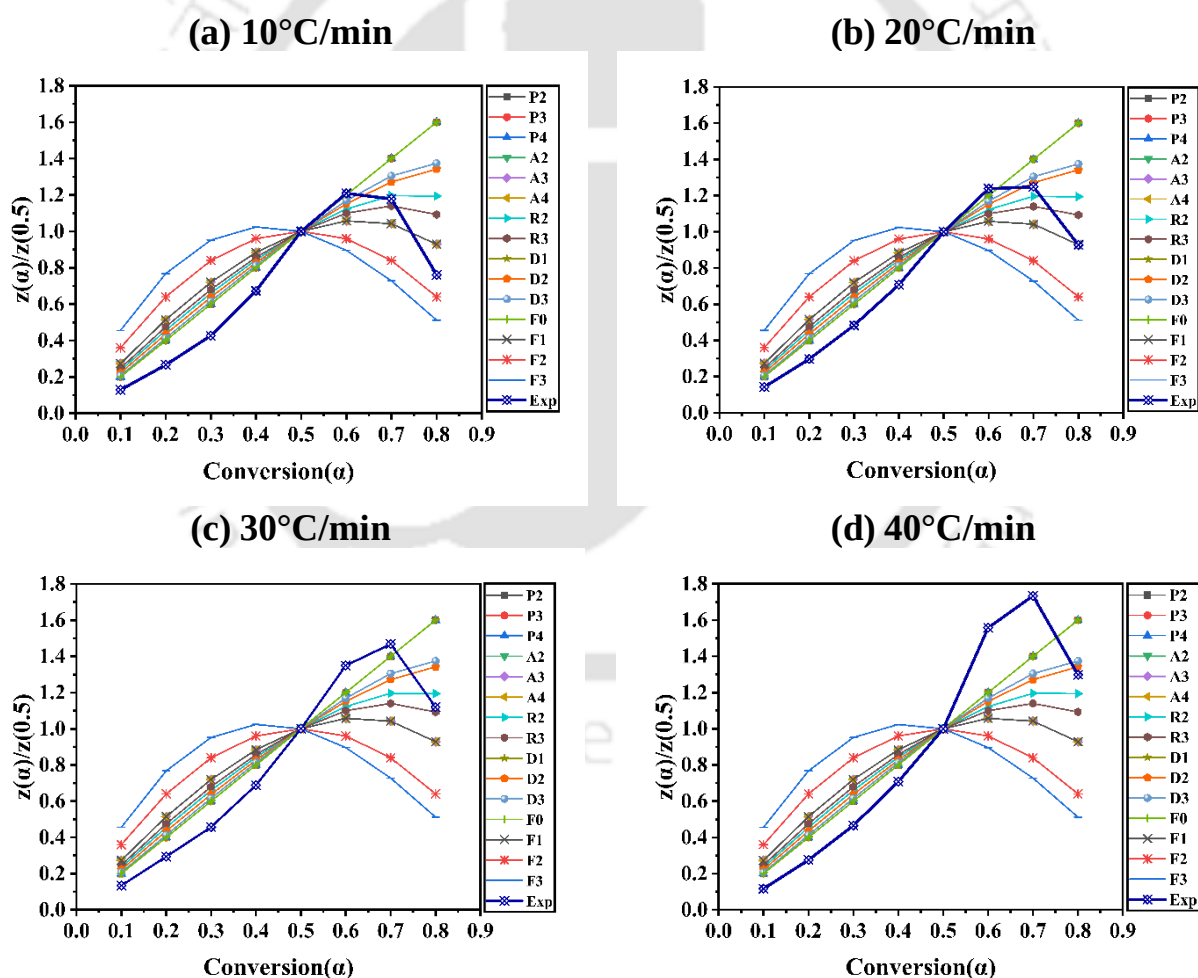


Figure 6.8.16 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 3:1.

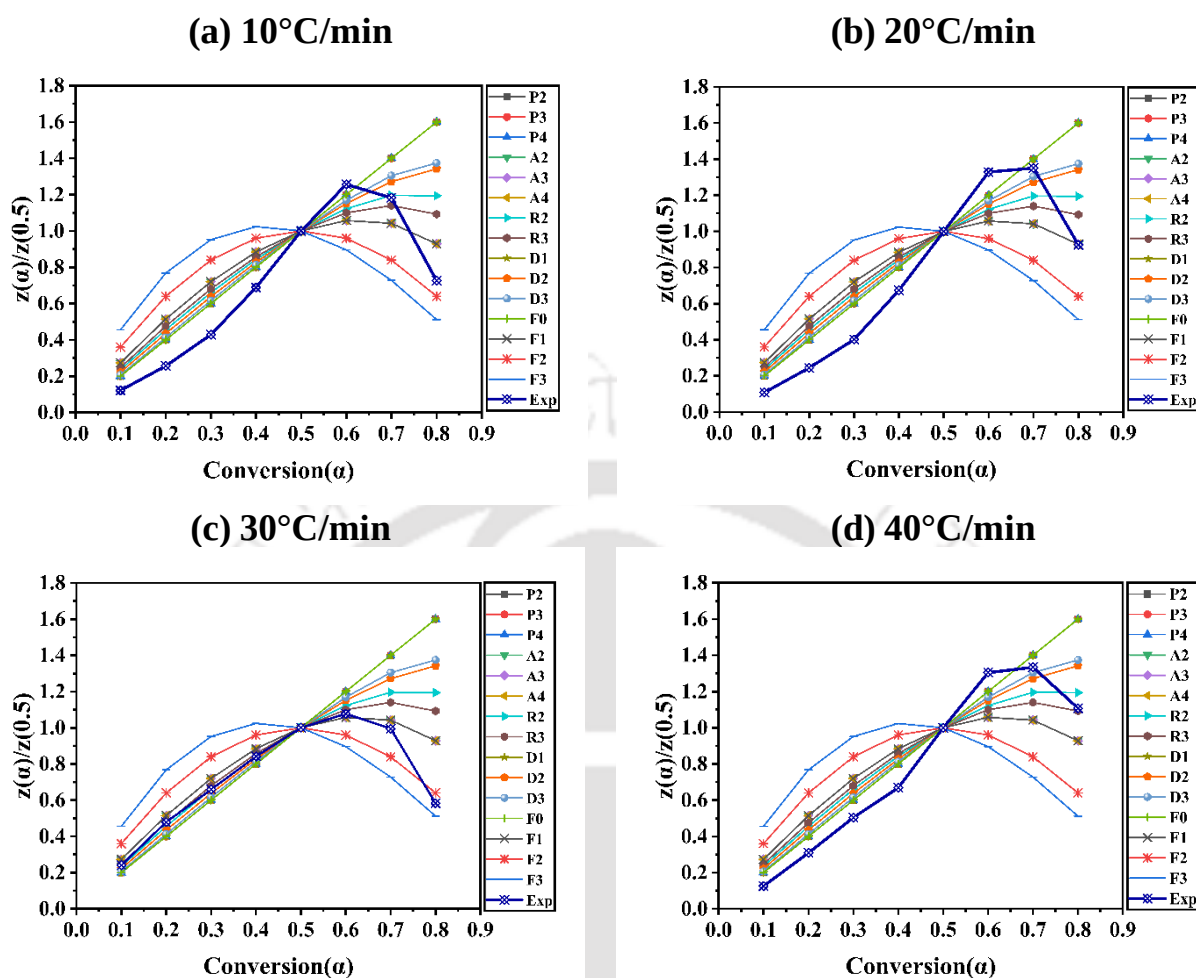


Figure 6.8.17 (a-d) Criado's master plots for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 4:1.

6.8.2.3.2 Master plots based on integral form of kinetic data

The graphical representations of the reaction mechanism revealed through the integral method for the co-feed pyrolysis of EI and AI biomass of different co-feed are illustrated in Figures 6.8.18-6.8.24. Unlike the Criado's master plots the integral master plot depicted consistency in the reaction models involved in the co-feed pyrolysis process. For instance, for the co-feed ratio of 1:1, regardless of the heating rate applied, the pyrolysis process consistently adhered to A2 model. Similar kind of trends were followed for other co-feed ratios.

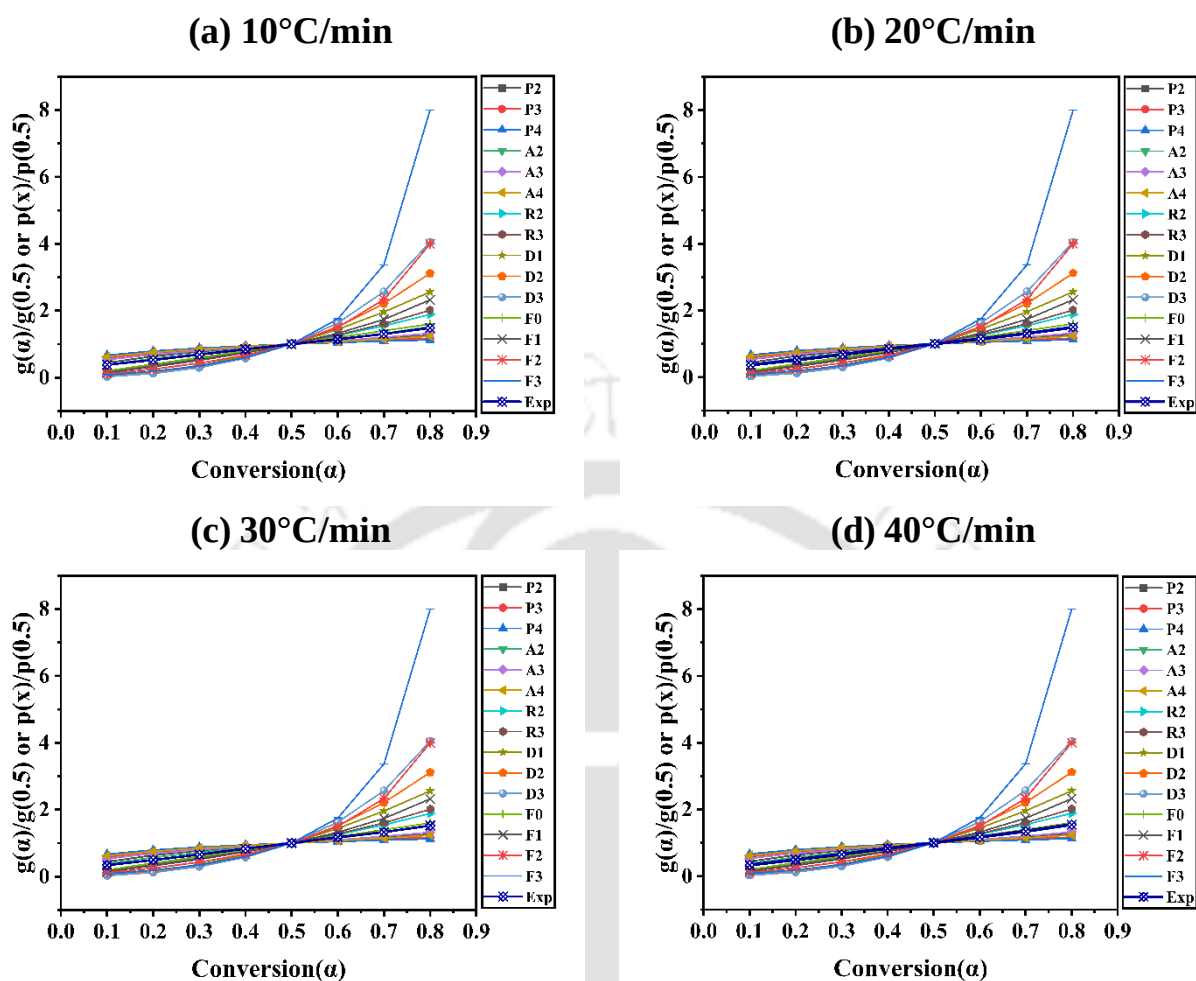
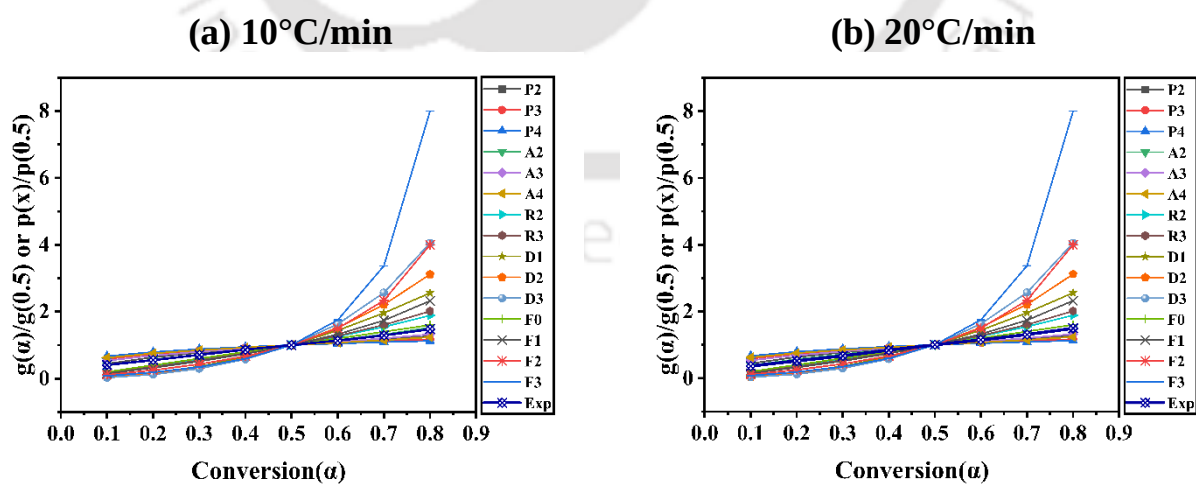


Figure 6.8.18 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:4.



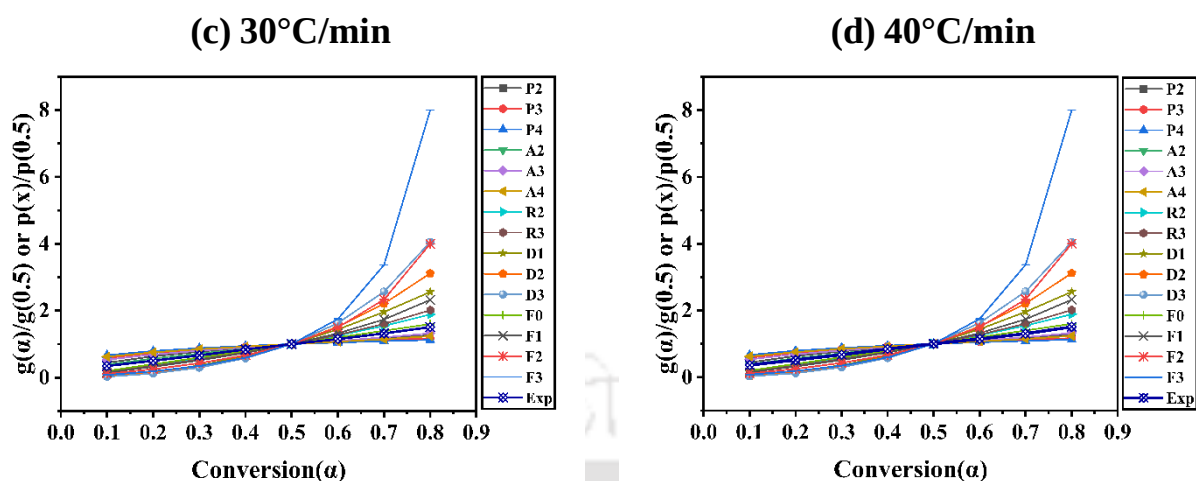


Figure 6.8.19 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:3.

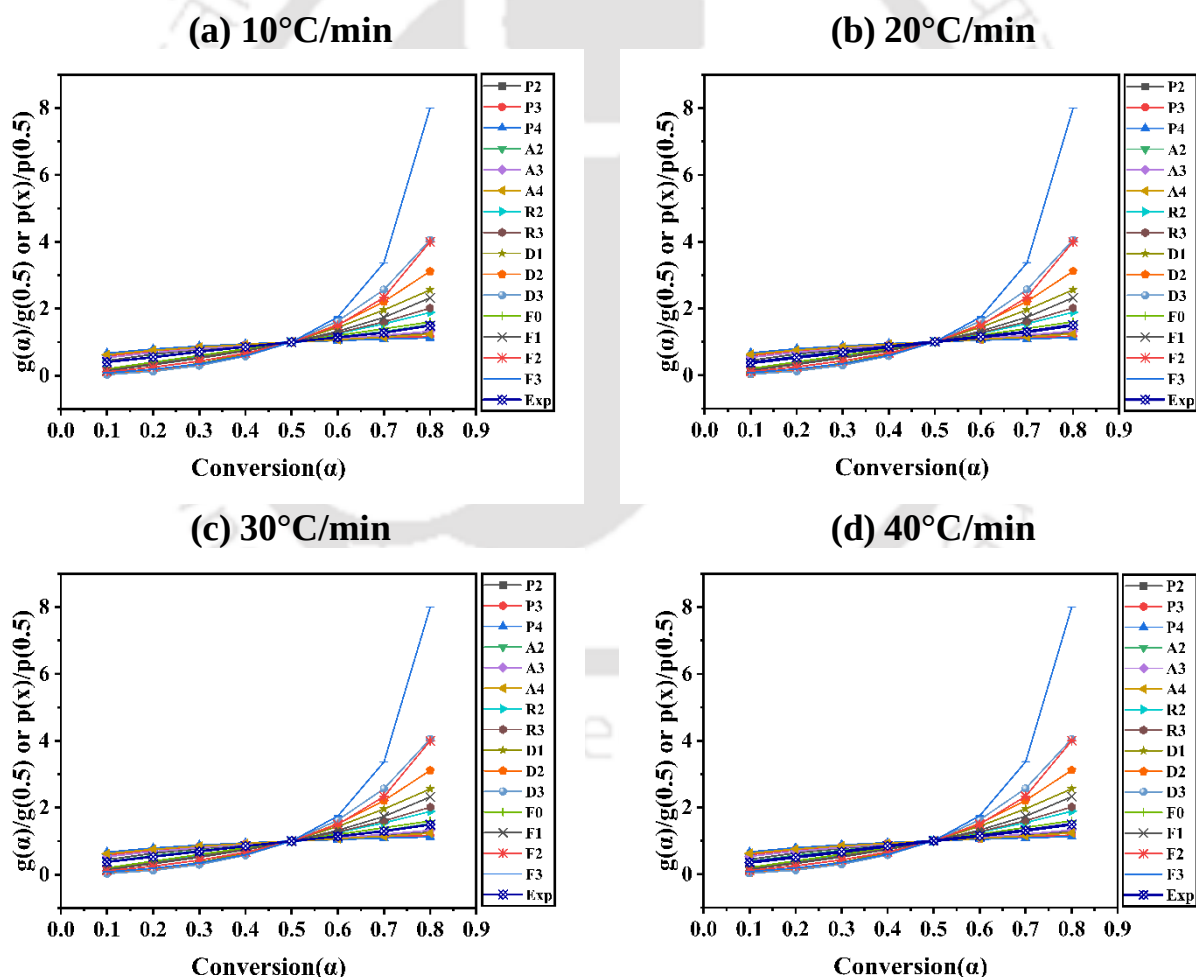


Figure 6.8.20 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:2.

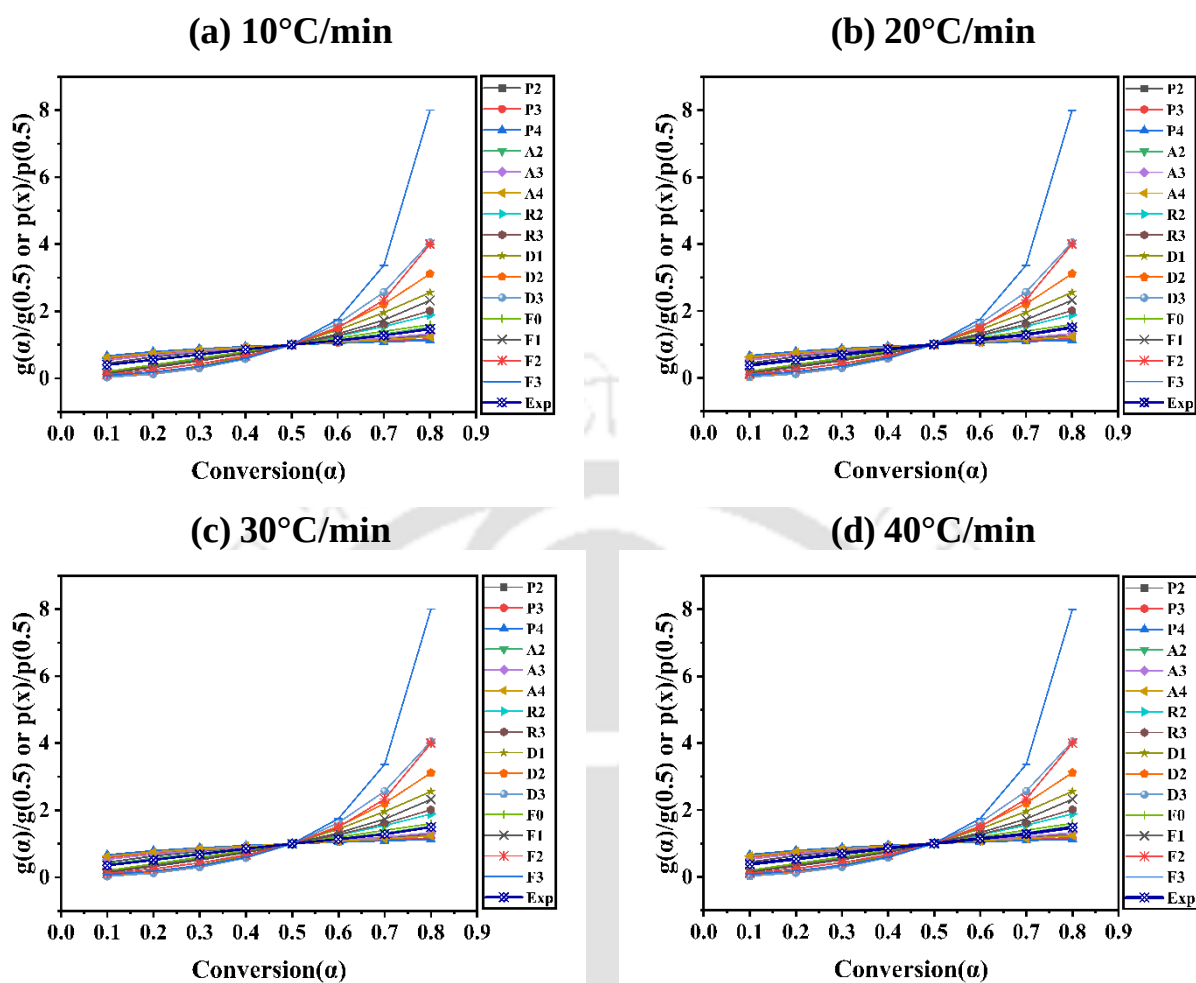
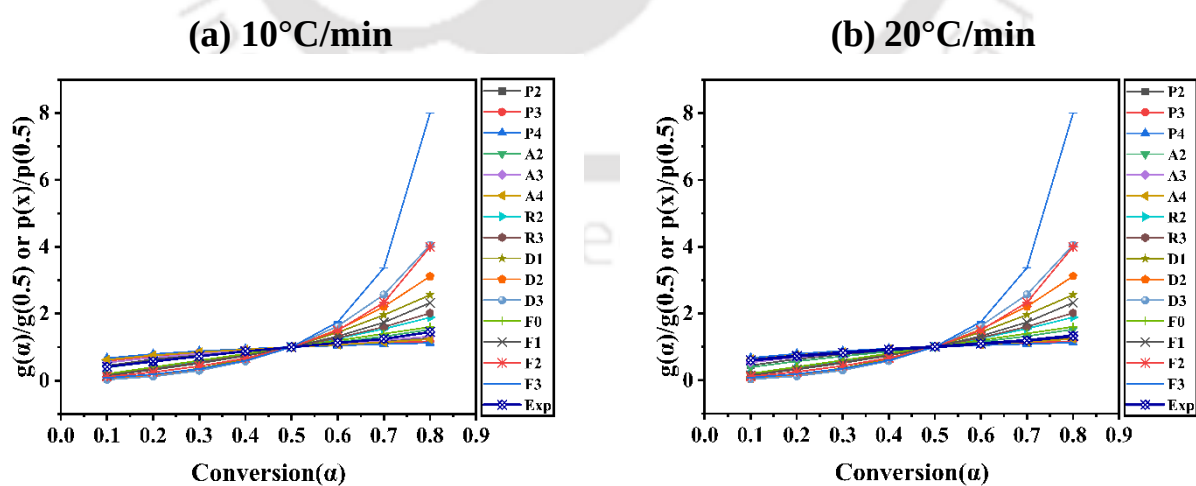


Figure 6.8.21 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 1:1.



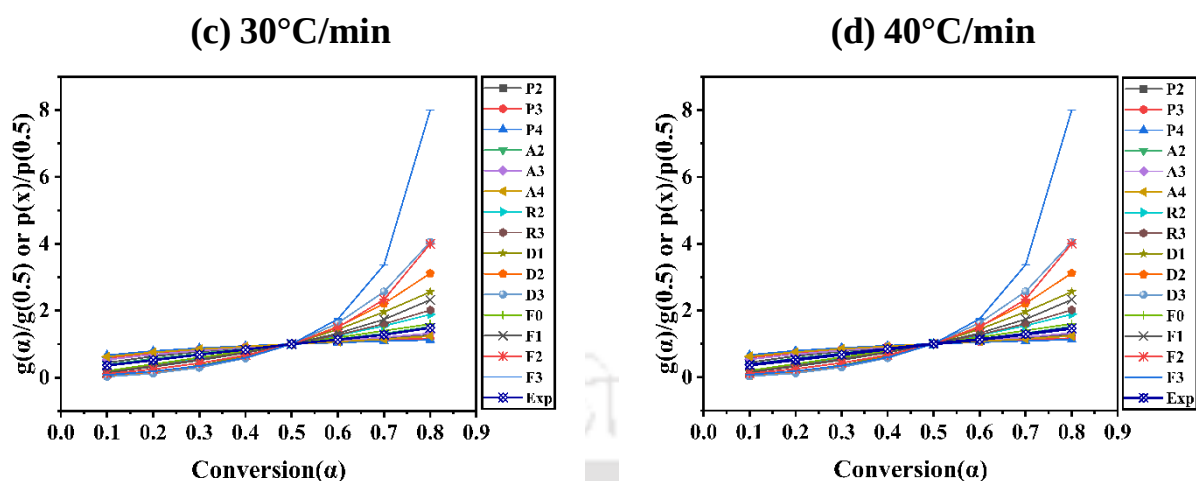


Figure 6.8.22 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 2:1.

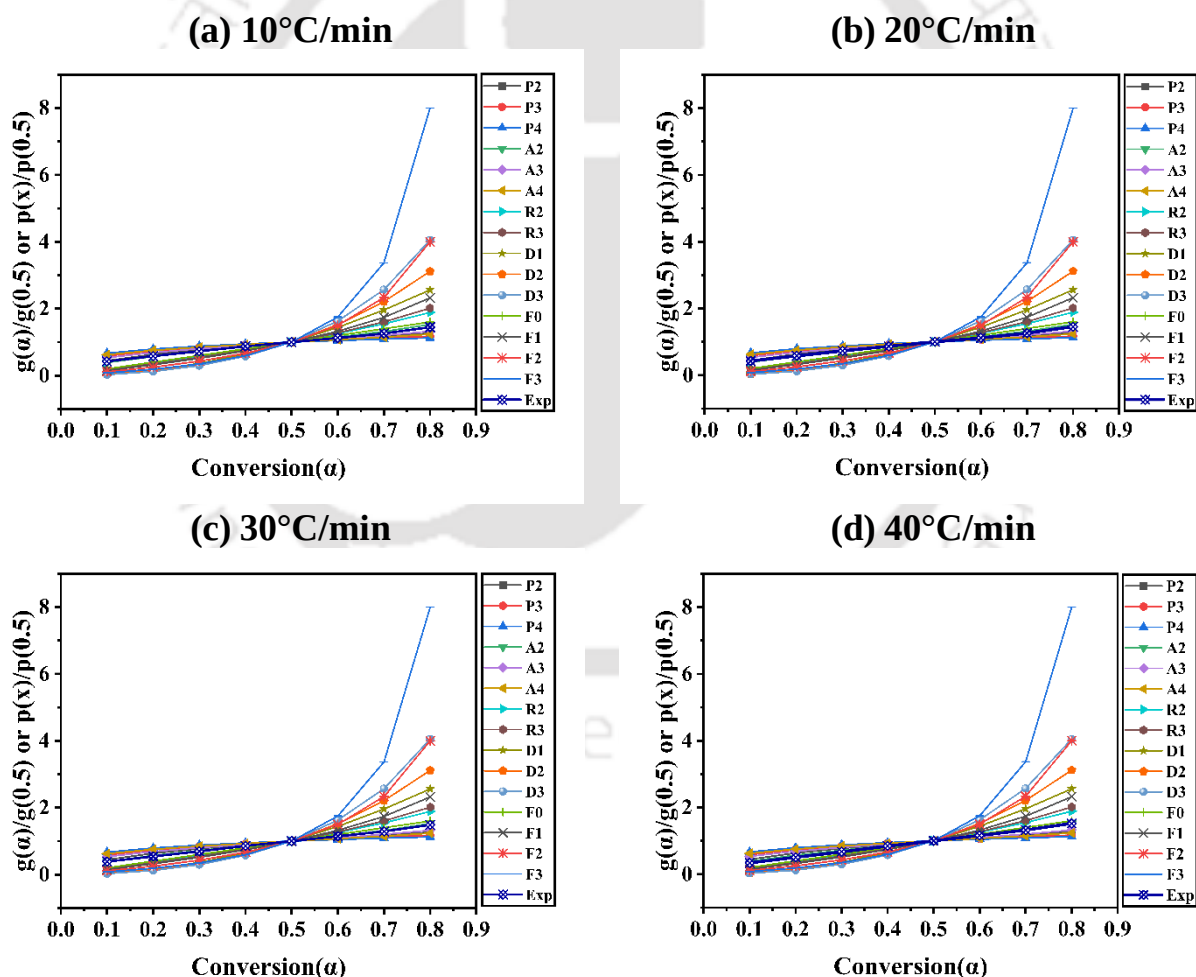


Figure 6.8.23 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 3:1.

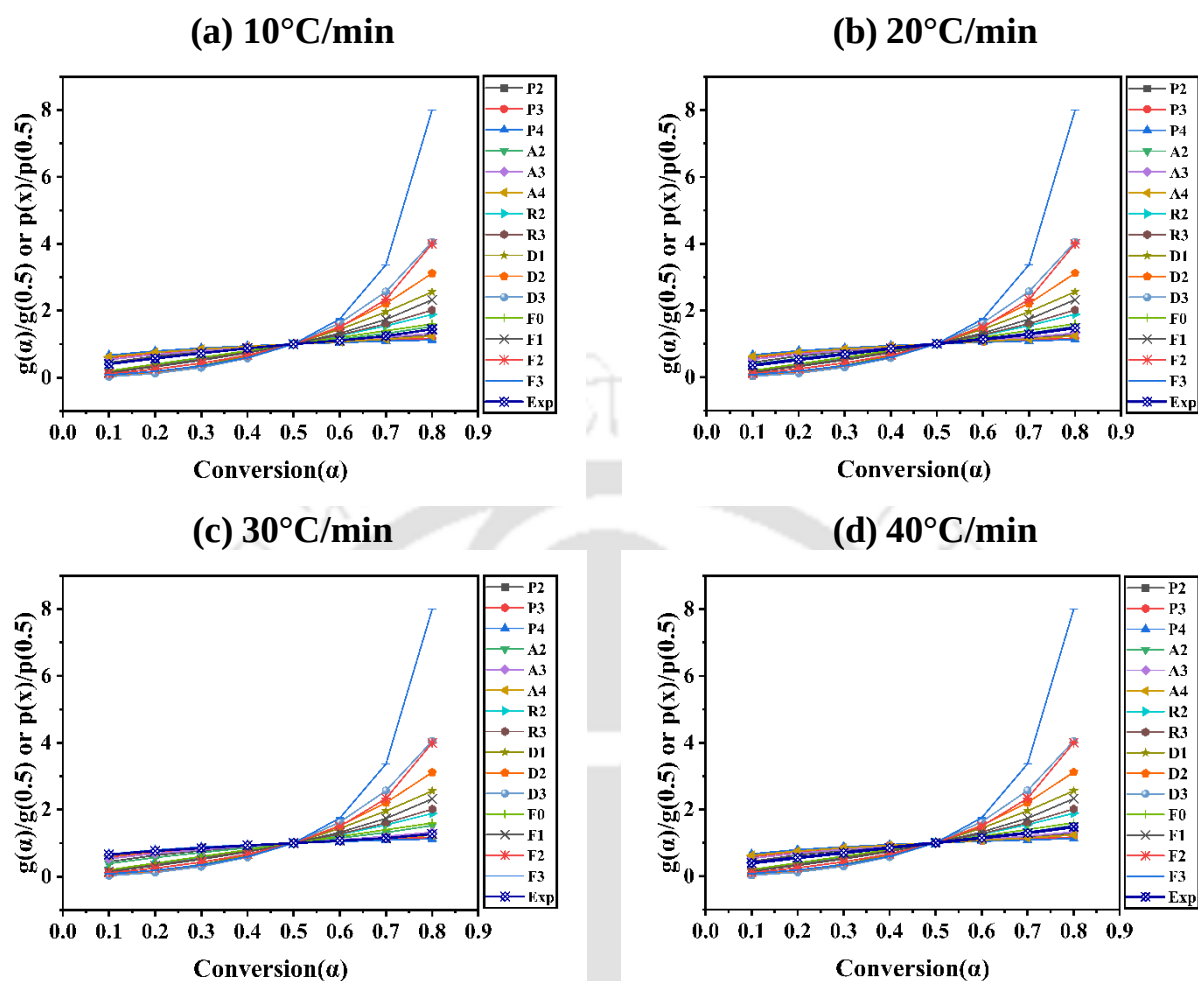


Figure 6.8.24 (a-d) Master plot based on integral method for reaction mechanism of pyrolysis of EI and AI biomass at co-feed ratio of 4:1.

6.8.3 Thermodynamic properties

The thermodynamic properties including the enthalpy change (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS) were also evaluated for the co-feed pyrolysis processes. The graphical illustrations of these properties are illustrated in Figures 6.8.25-6.8.45 while their details have been reported in Tables C21-C27 of Appendix C. The average values of the thermodynamic properties are also presented in Table 6.8.2.

Figures 6.8.25-6.8.31 illustrate the graphical representations of ΔH for the co-feed pyrolysis processes using iso-conversional methods at various conversions and heating rates. Except the DFM method, the average enthalpy changes using the iso-conversional methods for the various co-feed ratios followed a similar trend and were relatively consistent with minimal variations like the average activation energy. However, the synergistic effect of co-feeding was

observed in the ΔH values. The pyrolysis with co-feed ratio of 4:1 depicted the maximum average enthalpy change (kJ/mol) values of 233.581, 233.481, 233.564, 233.415 for DFM; 222.571, 222.471, 222.554, 222.405 for KAS; 220.715, 220.616, 220.699, 220.549 for OFW; 222.780, 222.647, 222.764, 222.614 for STK; 222.571, 222.471, 222.554, 222.405 for DAEM at heating rates of $\beta=10, 20, 30$ and $40^\circ\text{C}/\text{min}$, respectively. On the other hand, pyrolysis with co-feed ratio of 2:1 depicted the minimum enthalpy change (kJ/mol) values of 148.388, 148.404, 148.221, 148.163 for DFM; 137.934, 137.950, 137.767, 137.700 for KAS; 140.307, 140.324, 140.141, 140.083 for OFW; 138.214, 138.089, 138.048, 137.990 for STK; 137.934, 137.950, 137.767, 137.709 for DAEM at the corresponding heating rates of $\beta=10, 20, 30$ and $40^\circ\text{C}/\text{min}$, respectively. At heating rates of $\beta=10, 20, 30$ and $40^\circ\text{C}/\text{min}$, the average enthalpy change (kJ/mol) values for the co-feed ratio of 1:1 were found to be 174.819, 174.711, 174.653, 174.587 for DFM; 164.654, 164.546, 164.488, 164.421 for KAS; 165.750, 165.642, 165.583, 165.517 for OFW; 164.614, 164.806, 164.748, 164.682 for STK; 164.654, 164.546, 164.488, 164.421 for DAEM, respectively. Analysis of the graphical representations of ΔH values revealed that the ΔH values were minimally affected by the heating rate. Positive ΔH values were observed at all conversions and co-feed ratios, indicating the endothermic nature of the co-feed pyrolysis process, with an increased endothermic effect towards the end of the process.

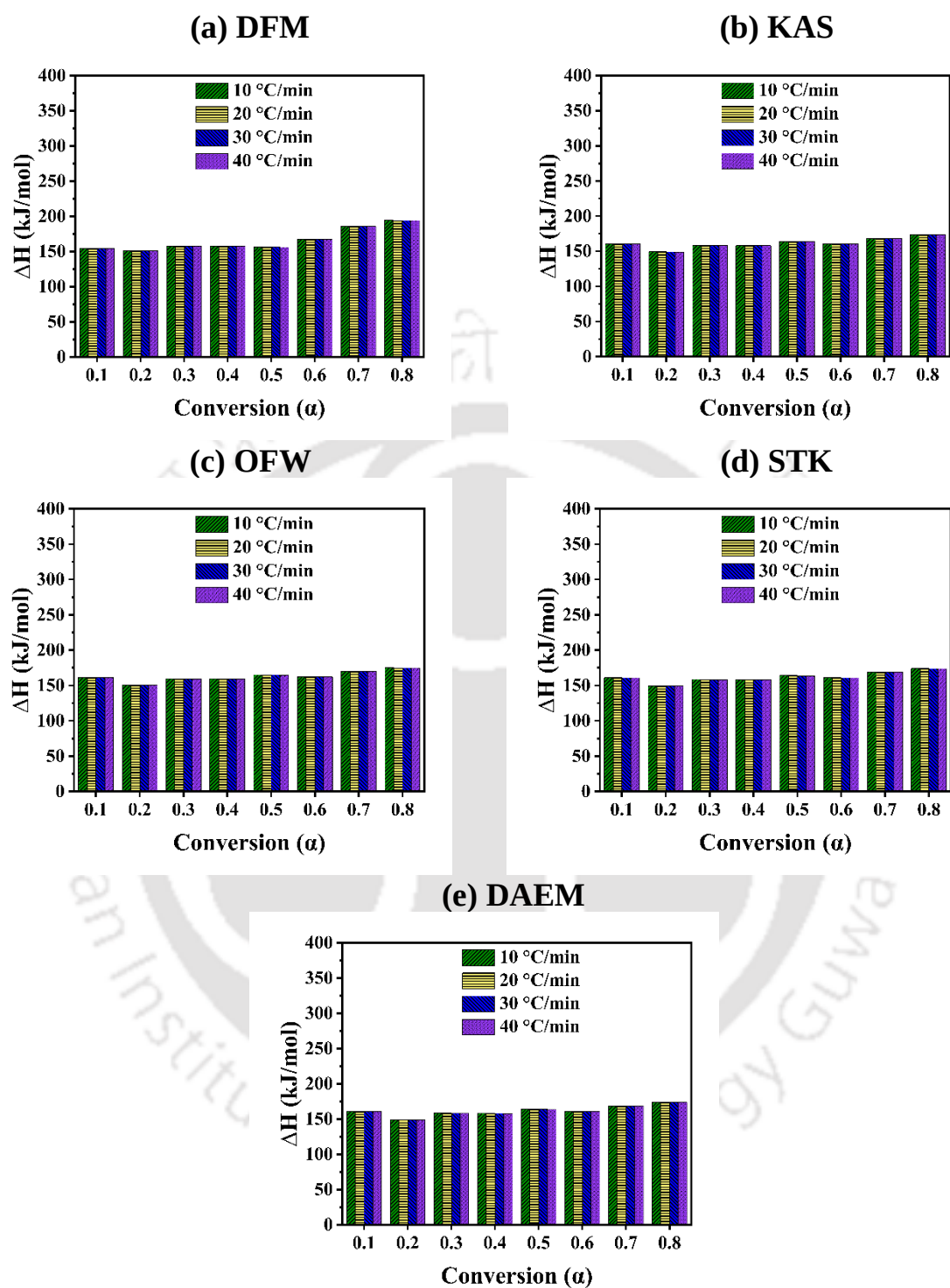


Figure 6.8.25 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 1:4.

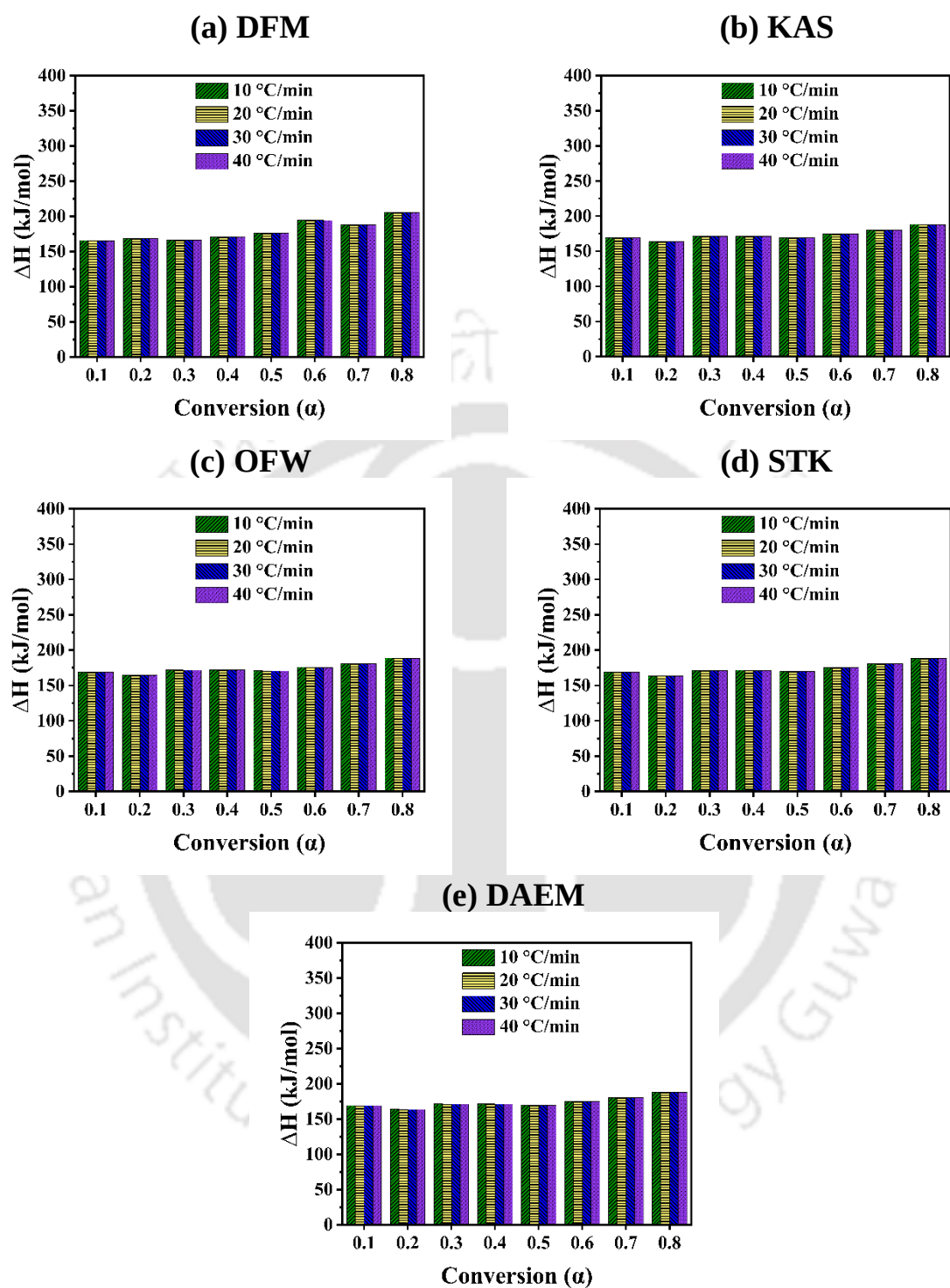


Figure 6.8.26 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 1:3.

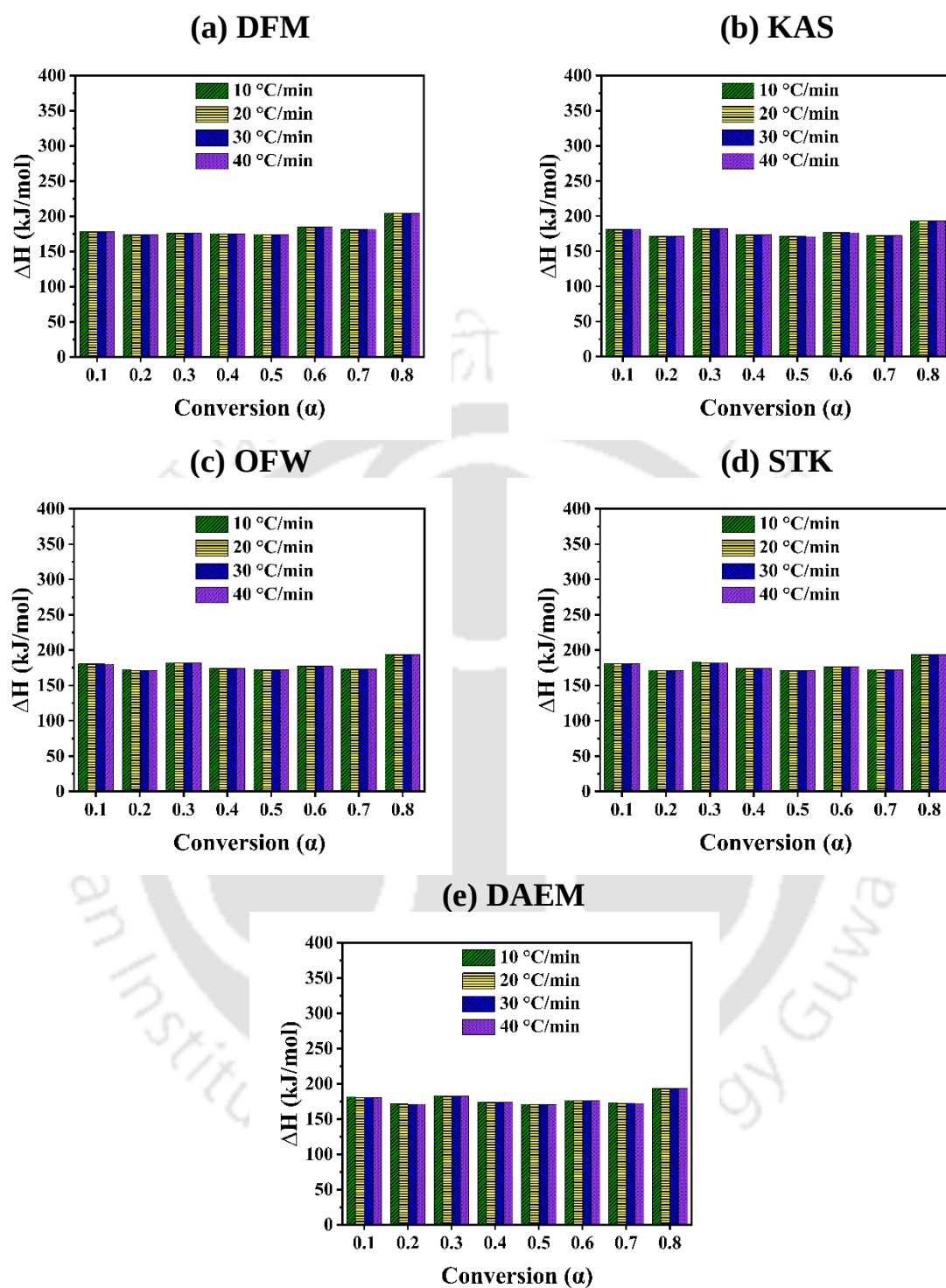


Figure 6.8.27 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 1:2.

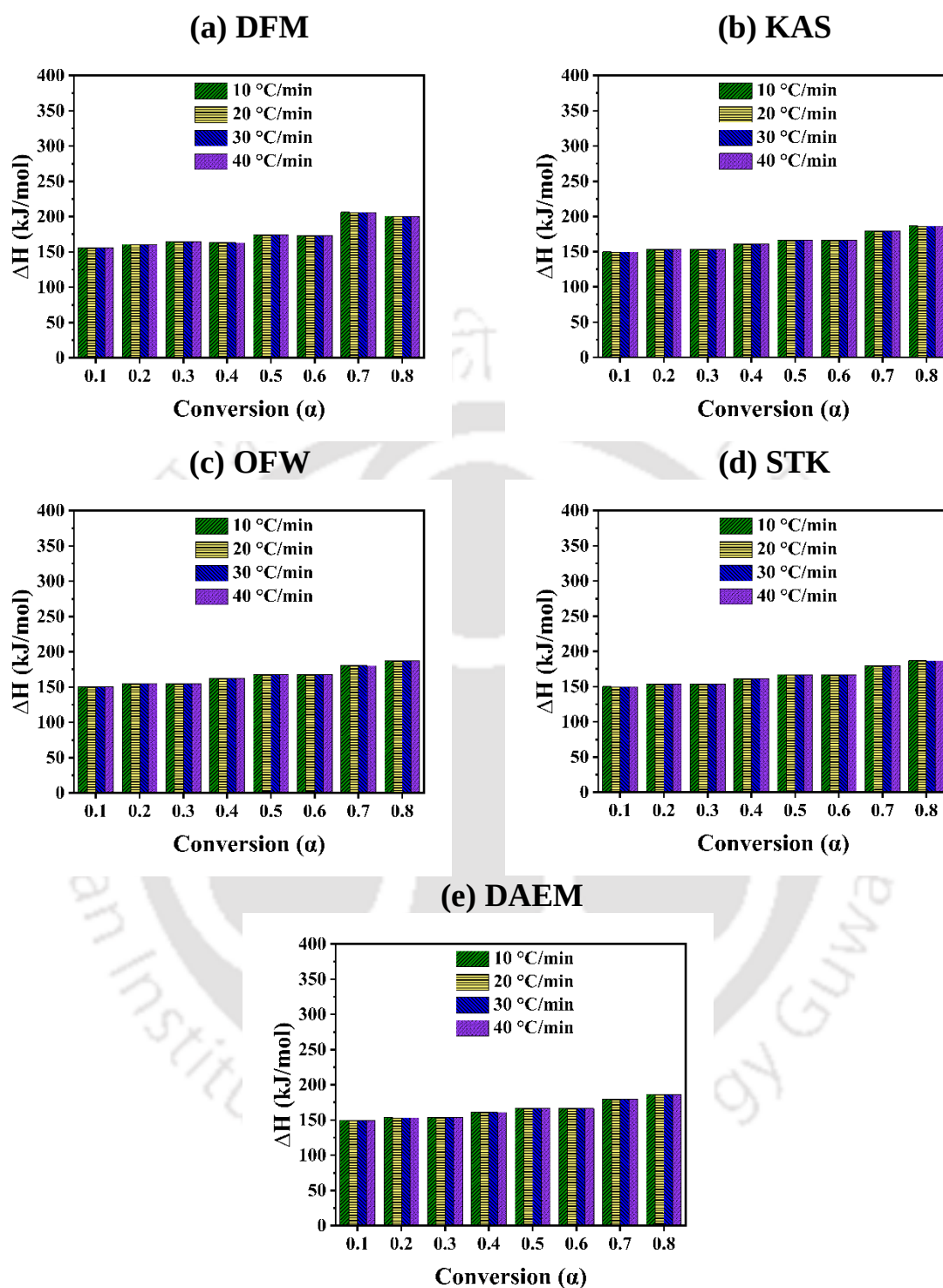


Figure 6.8.28 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 1:1.

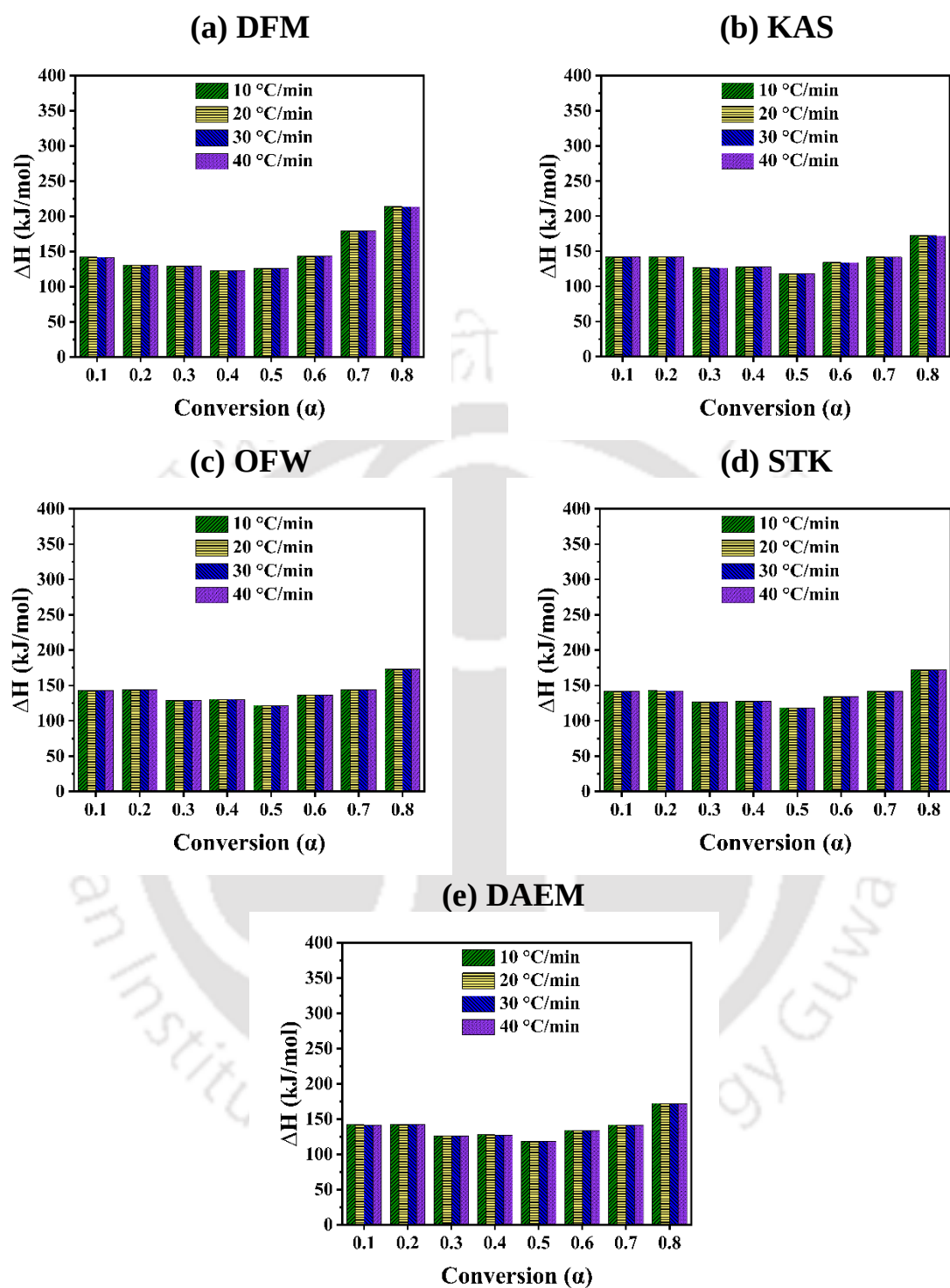


Figure 6.8.29 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 2:1.

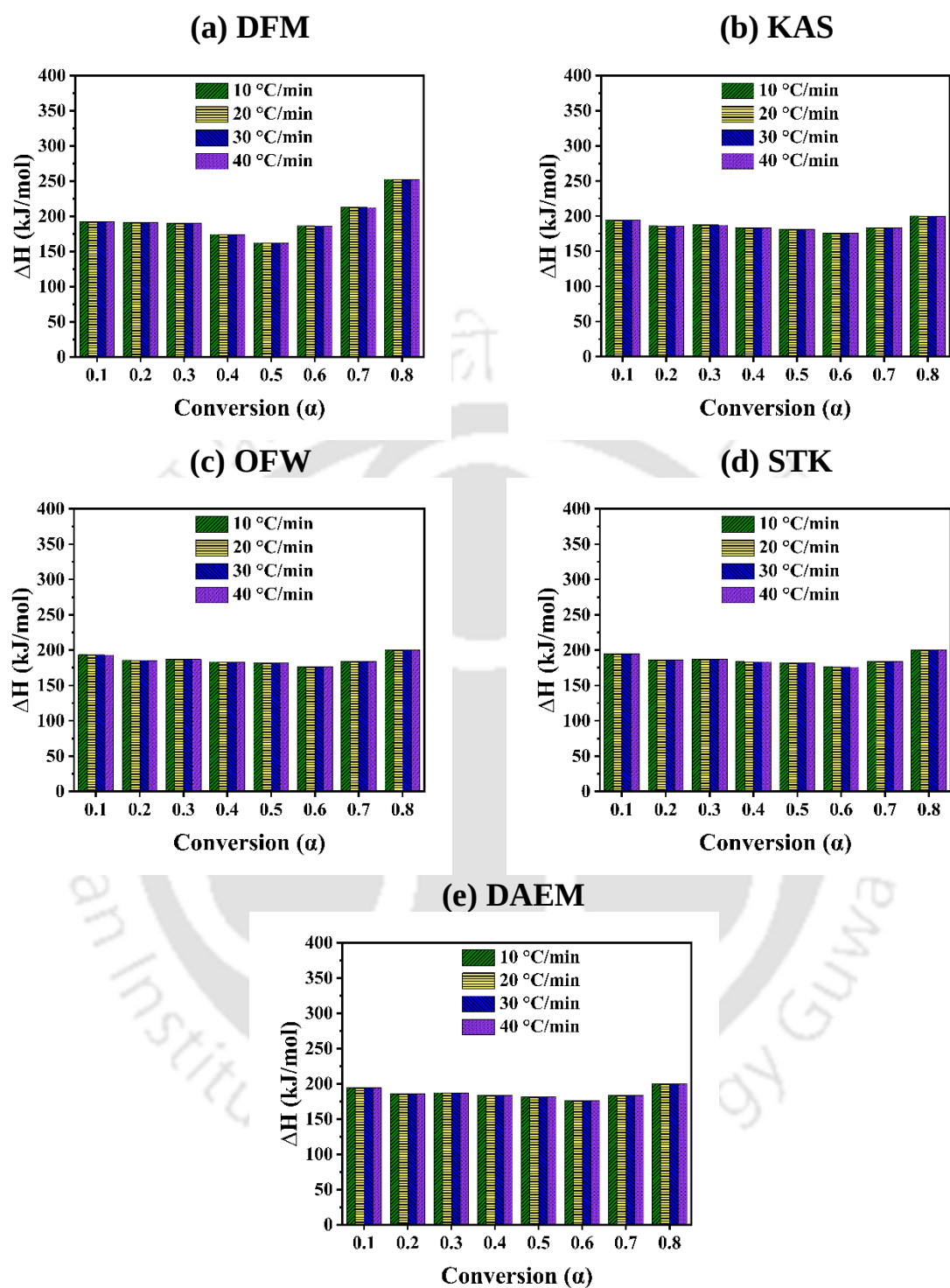


Figure 6.8.30 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 3:1.

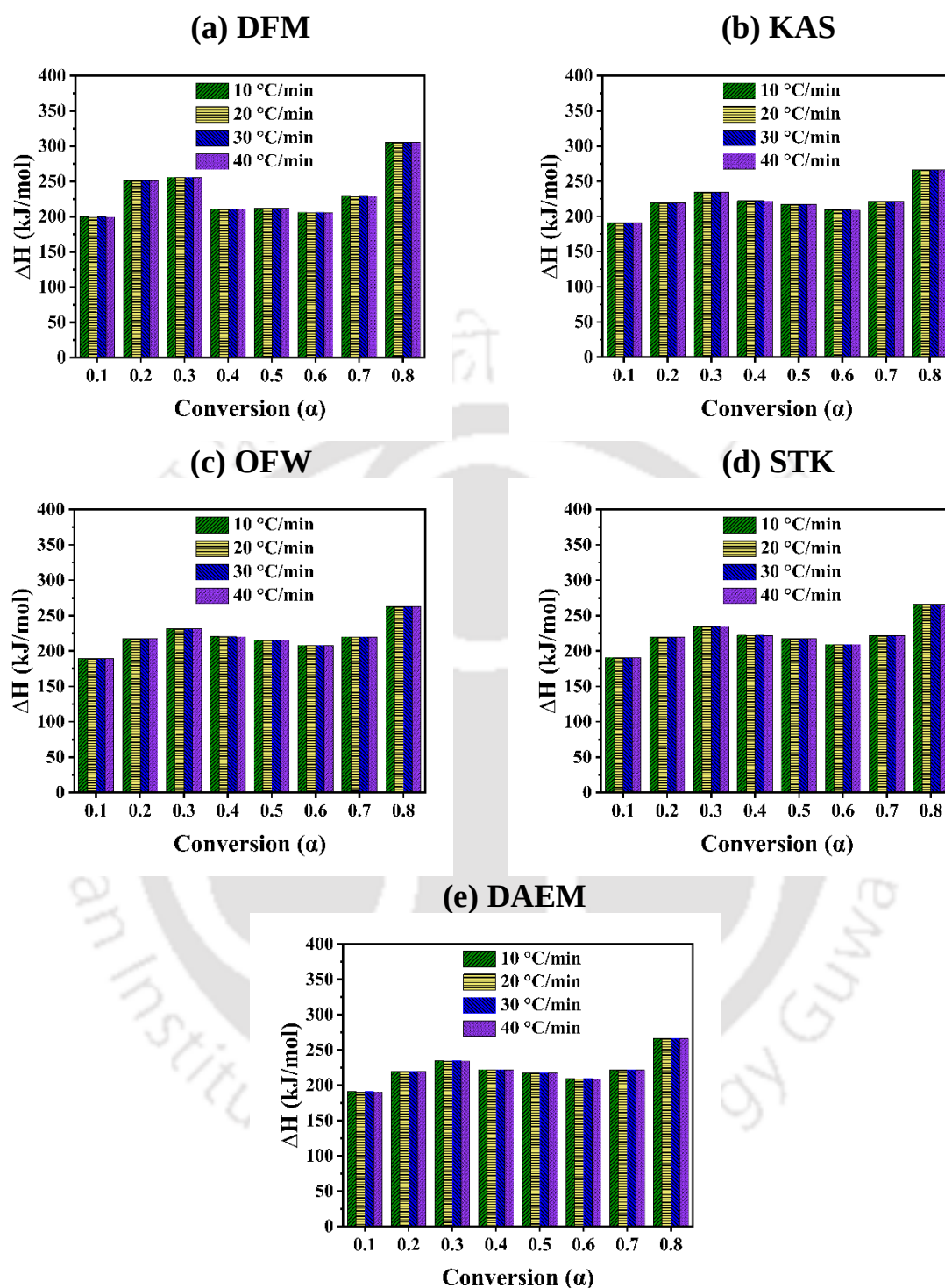


Figure 6.8.31 (a-e) Change in enthalpy (ΔH) vs. conversion (α) plots of EI and AI biomass pyrolysis at co-feed ratio of 4:1.

Figures 6.8.32-6.8.38 illustrate the graphical representations of ΔG for the co-feed pyrolysis processes using iso-conversional methods at various conversions and heating rates. The average Gibbs free energy change (kJ/mol) values at heating rates of $\beta=10, 20, 30$ and

40°C/min for the pyrolysis with co-feed ratio 1:1 were found to be 173.425, 173.978, 174.050, 174.994 for DFM; 173.705, 174.264, 174.339, 175.288 for KAS; 173.687, 174.231, 174.306, 175.254 for OFW; 173.698, 174.256, 174.332, 175.280 for STK; 173.705, 174.264, 174.339, 175.288 for DAEM, respectively. Positive ΔG values suggest that the active pyrolysis zone of the pyrolysis process demands an input of energy for the reaction to take place and does not occur spontaneously [198,199]. High ΔG values indicate a less favorable thermodynamic reaction, necessitating a higher energy input for its breakdown. Minimal variations in the ΔG values were noted as the conversion progressed under various heating rates for all the co-feed ratios, but no substantial change in the ΔG values were observed with the change in co-feed ratios. This suggests a consistent energy requirement throughout the process irrespective of feed ratio.



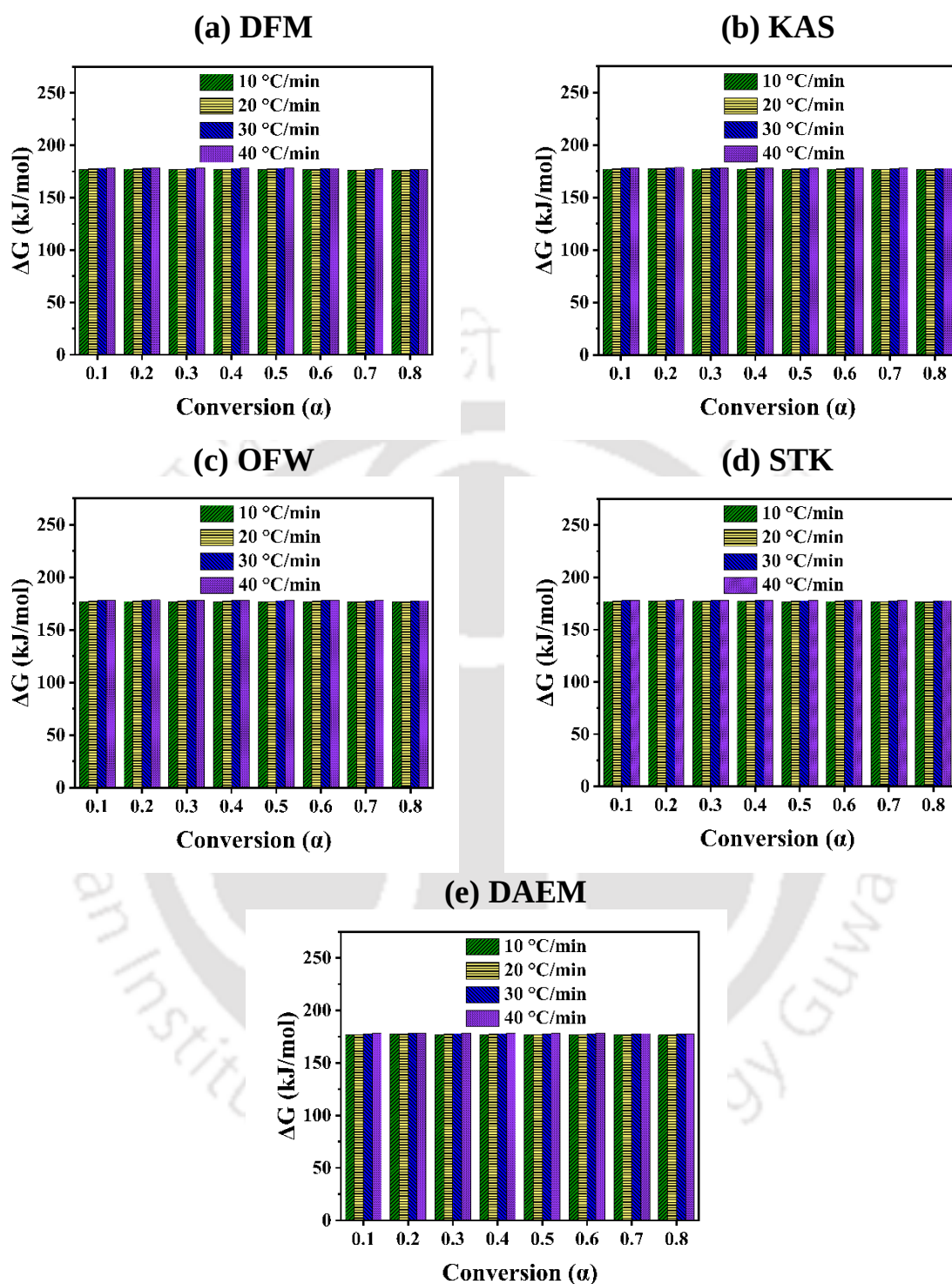


Figure 6.8.32 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:4.

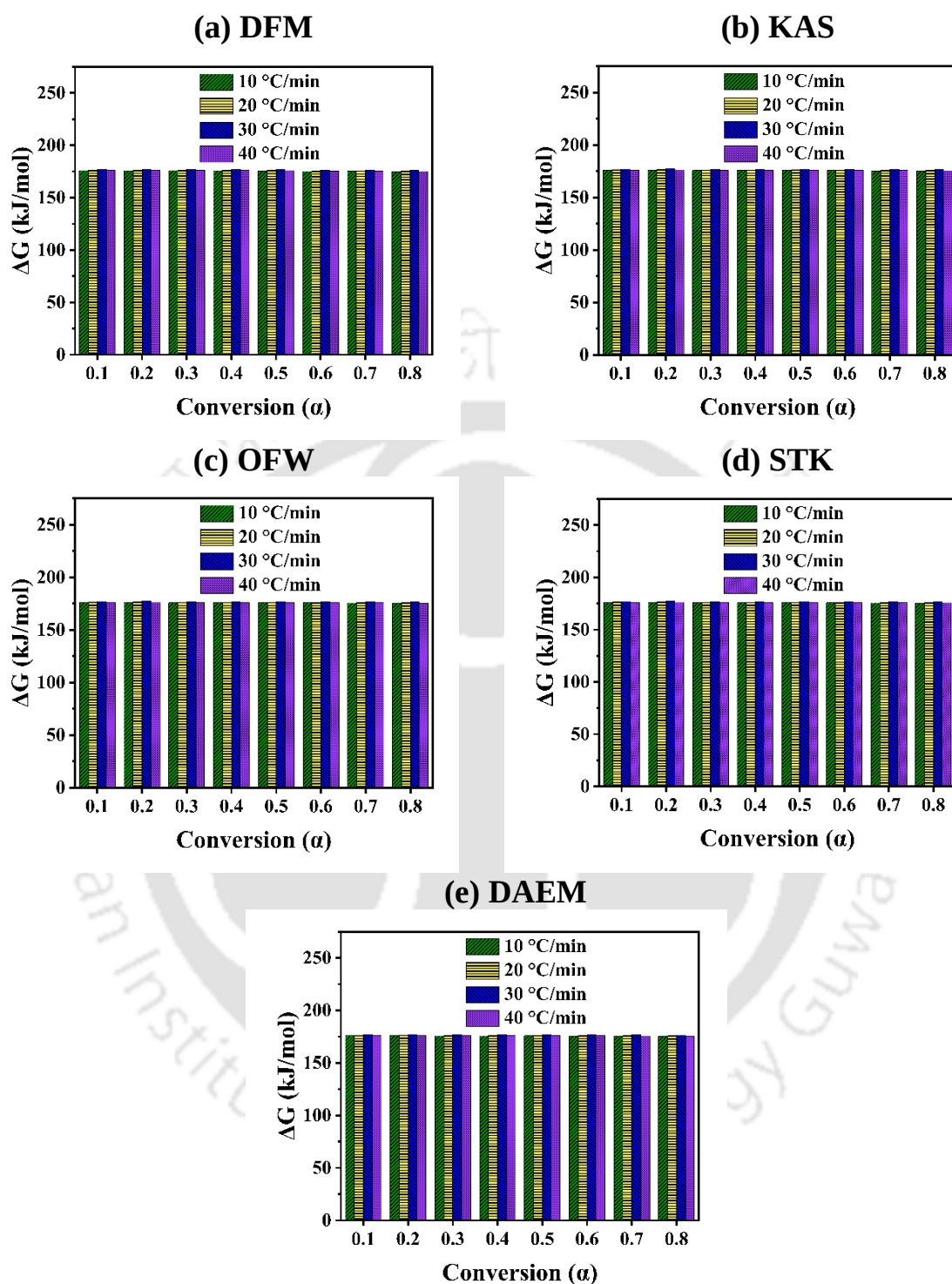


Figure 6.8.33 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:3.

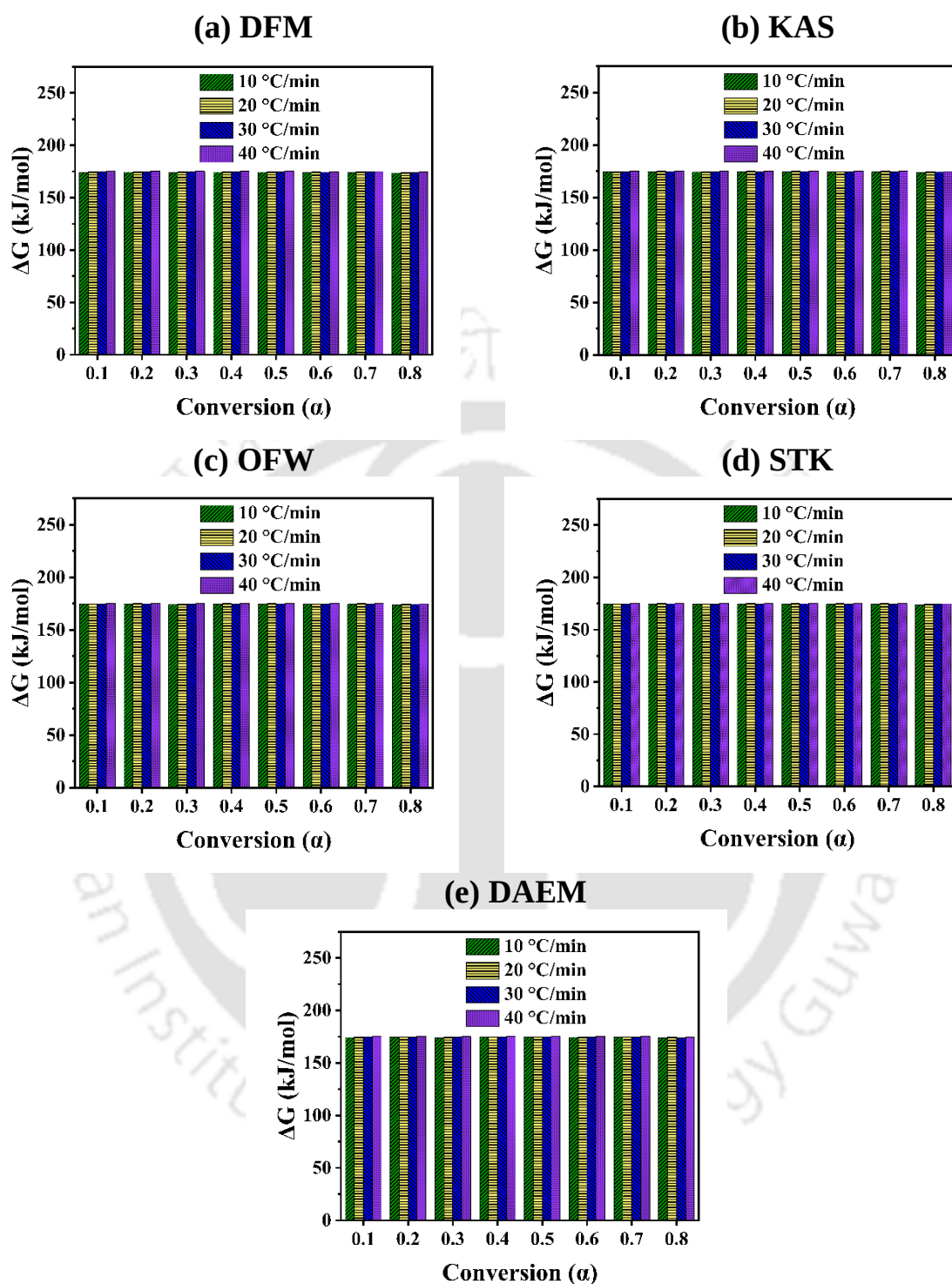


Figure 6.8.34 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:2.

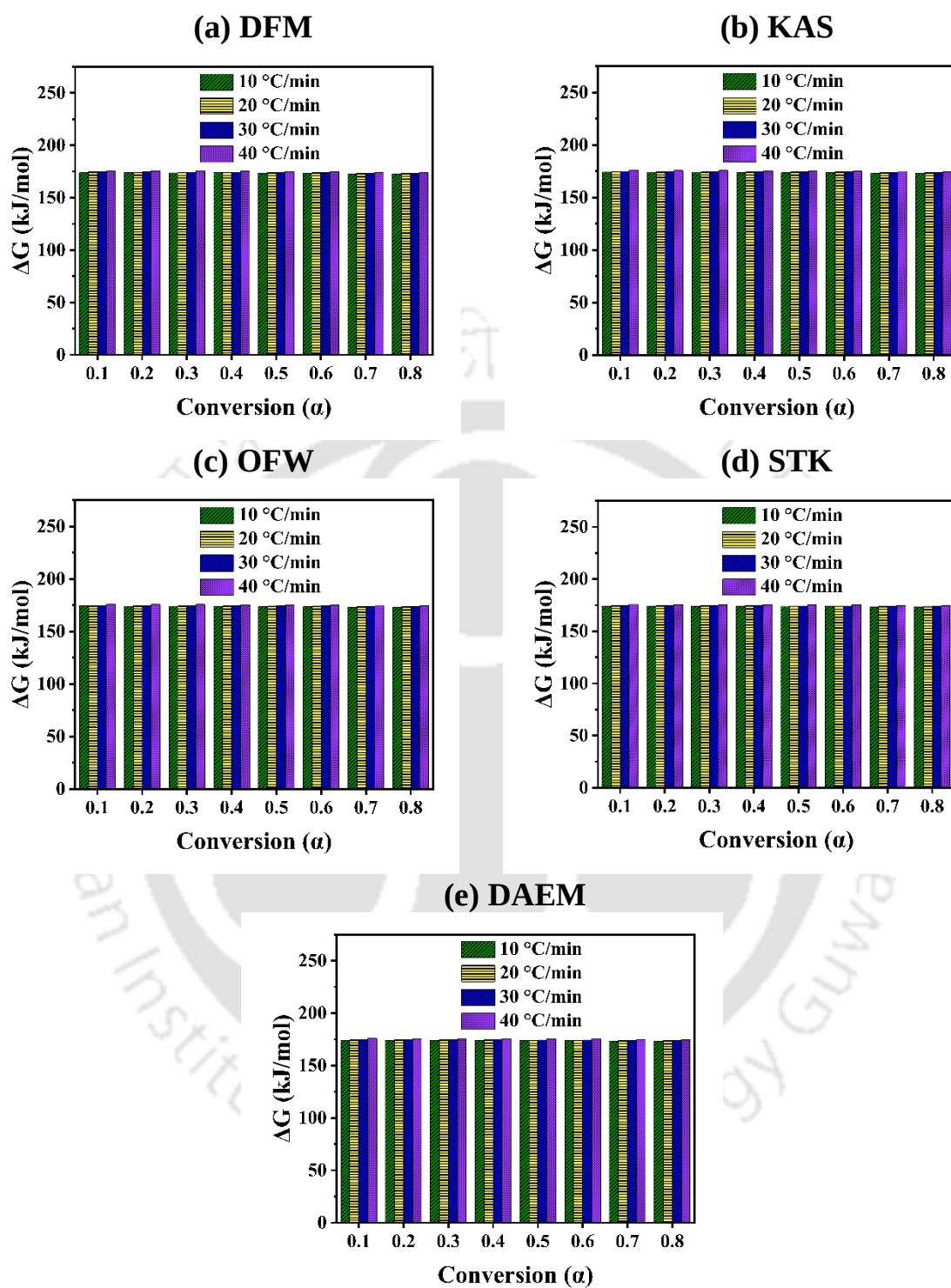


Figure 6.8.35 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:1.

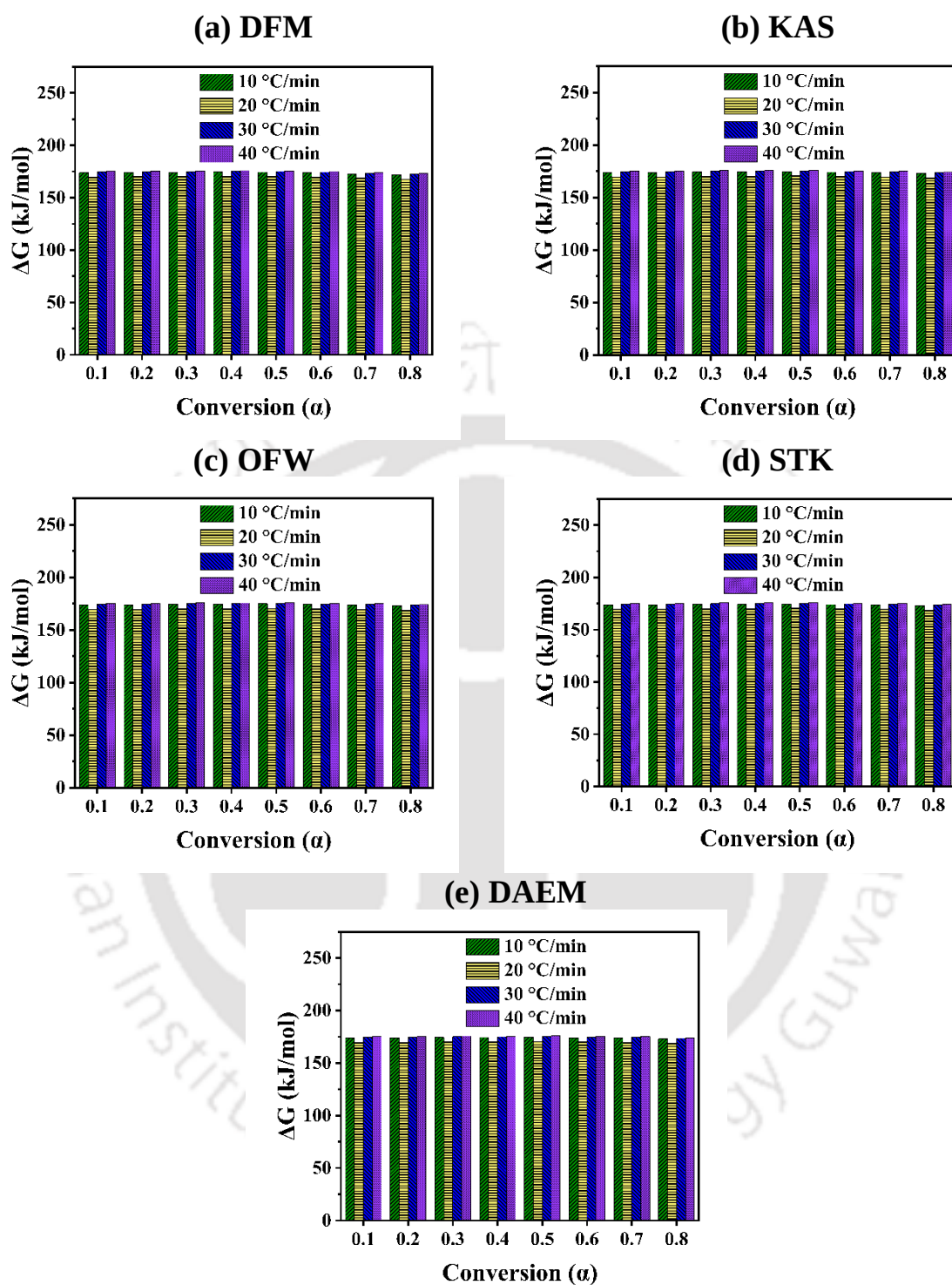


Figure 6.8.36 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 2:1.

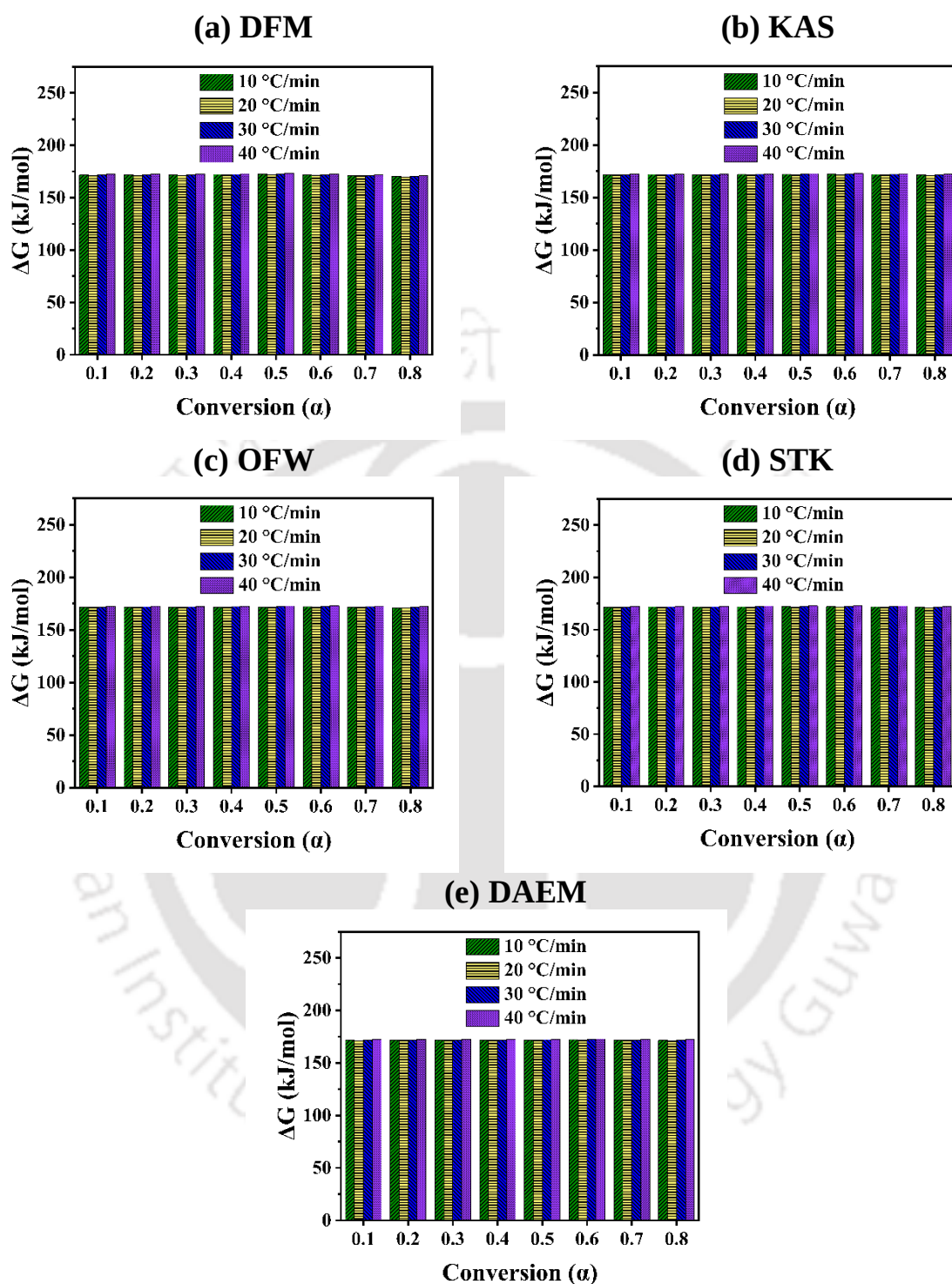


Figure 6.8.37 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 3:1.

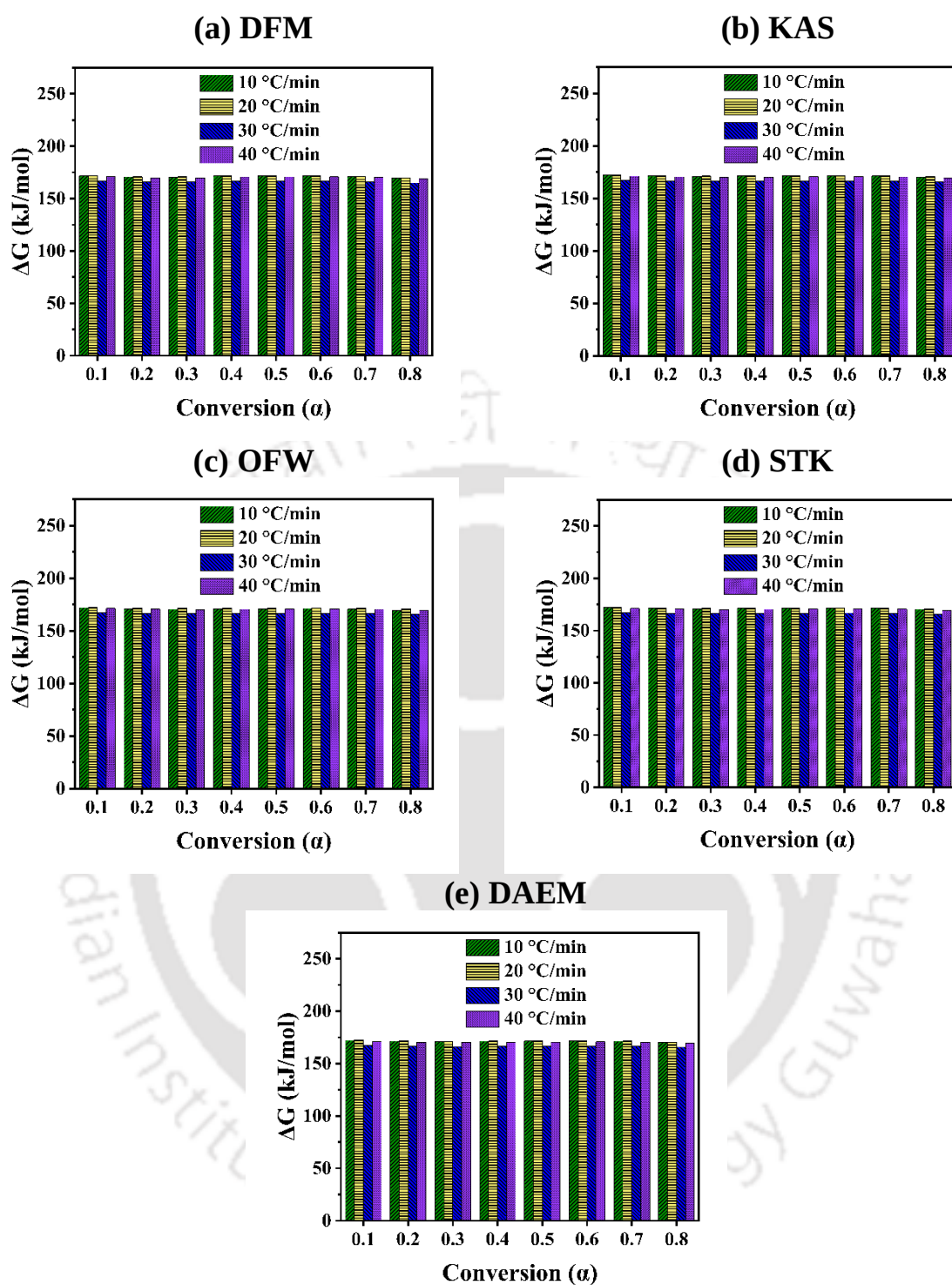


Figure 6.8.38 (a-e) Change in Gibbs free energy (ΔG) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 4:1.

Figures 6.8.39-6.8.45 illustrate the graphical representation of ΔS for the co-feed pyrolysis processes using iso-conversional methods at various conversions and heating rates. Significant synergistic effect of co-feeding was observed with the variation of ΔS values. For the pyrolysis with co-feed ratios of 4:1 and 3:1 the ΔS were found to be positive while for the co-feed ratios of 2:1, 1:1 and 1:4 the ΔS were found to be negative. For the pyrolysis with co-

feed ratio of 1:2, the ΔS showed a mixed trend of positive and negative entropies at various conversion. The average entropy change (kJ/mol·K) values at heating rates of $\beta=10, 20, 30$ and $40^\circ\text{C}/\text{min}$ for the pyrolysis with co-feed ratio of 1:1 were 0.002, 0.001, 0.001, -0.001 for DFM; -0.015, -0.016, -0.016, -0.017 for KAS; -0.013, -0.014, -0.014, -0.016 for OFW; -0.015, -0.015, -0.017 for STK; -0.015, -0.016, -0.016, -0.017 for DAEM, respectively.

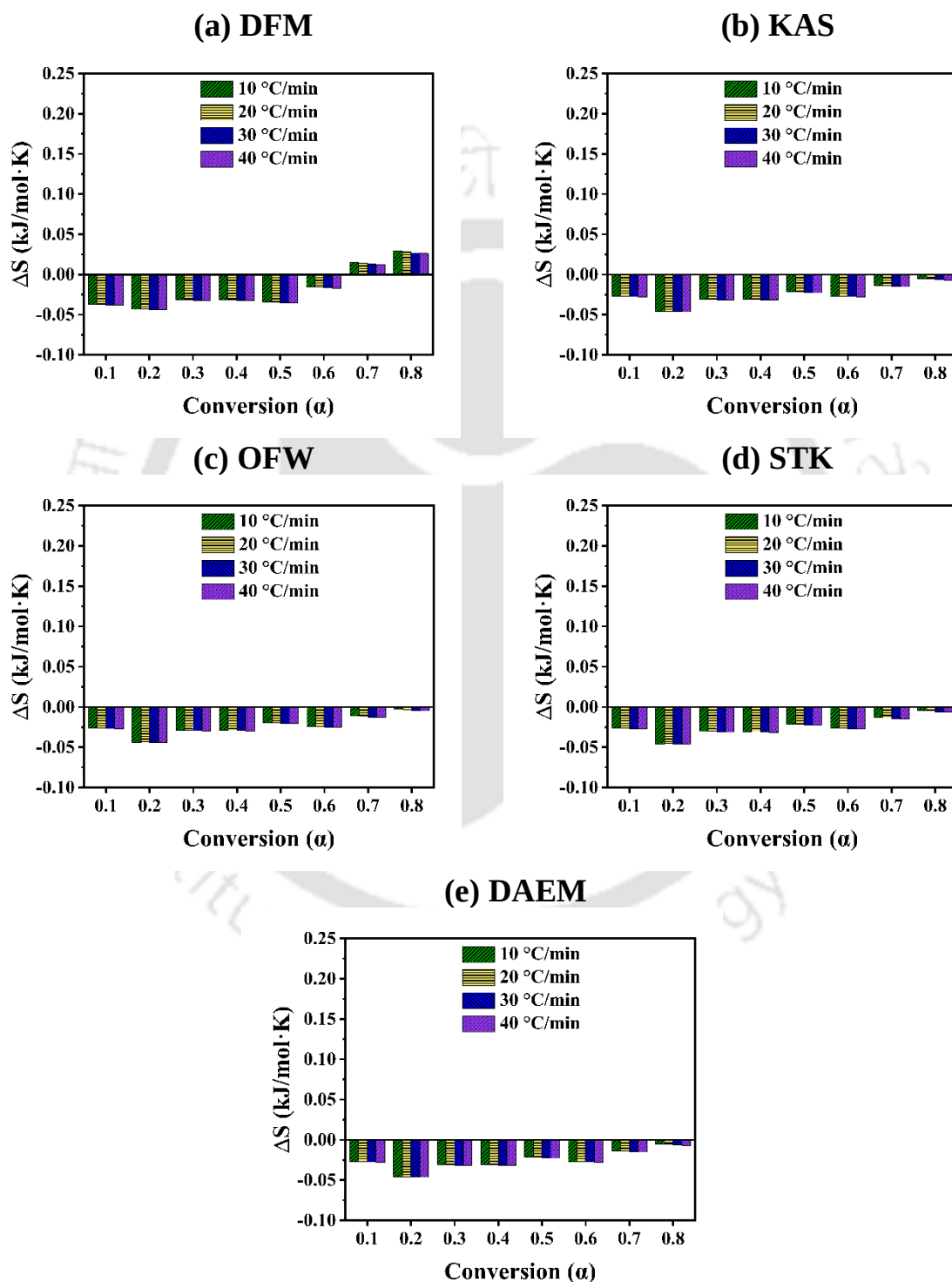


Figure 6.8.39 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:4.

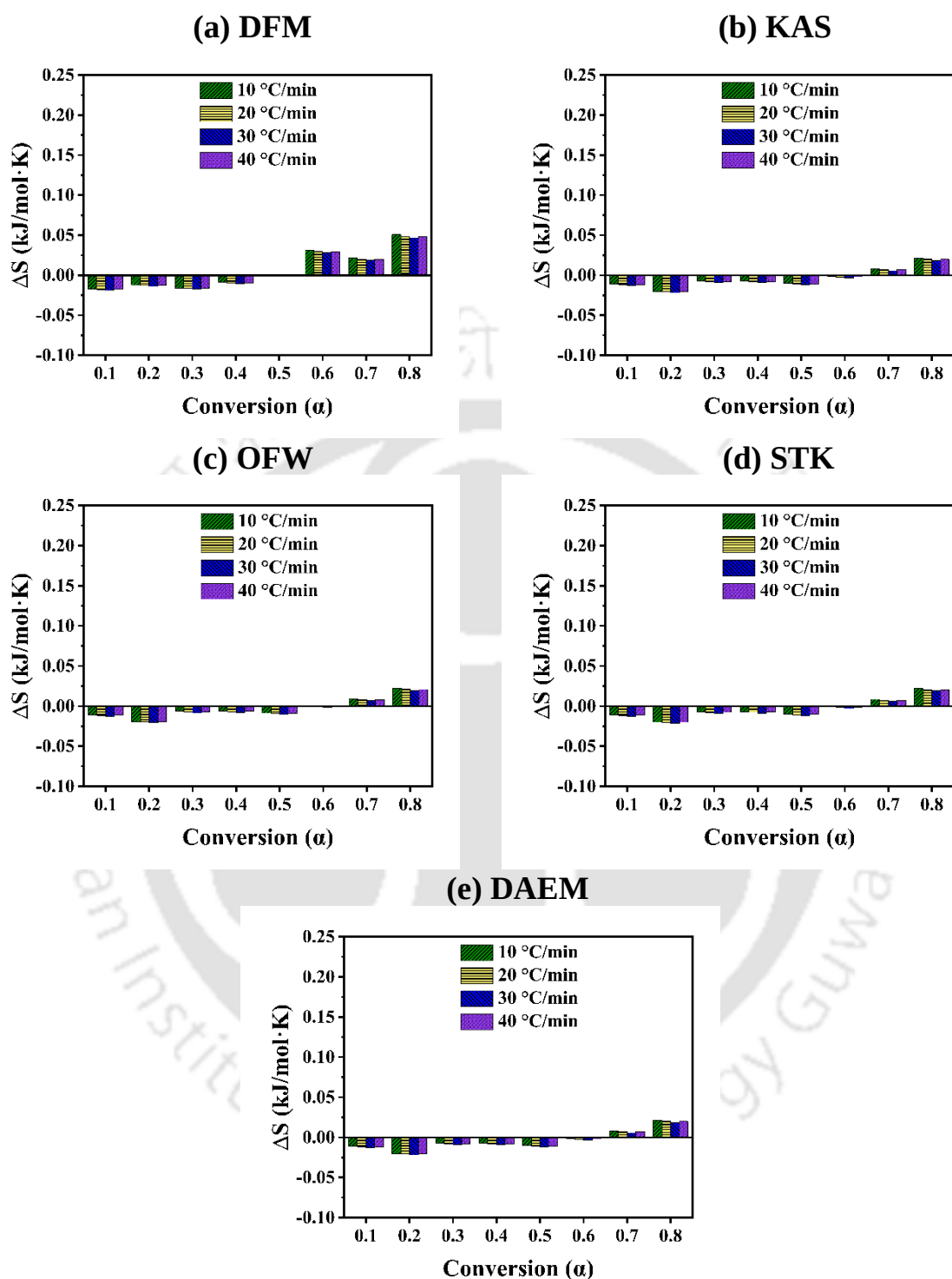


Figure 6.8.40 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:3.

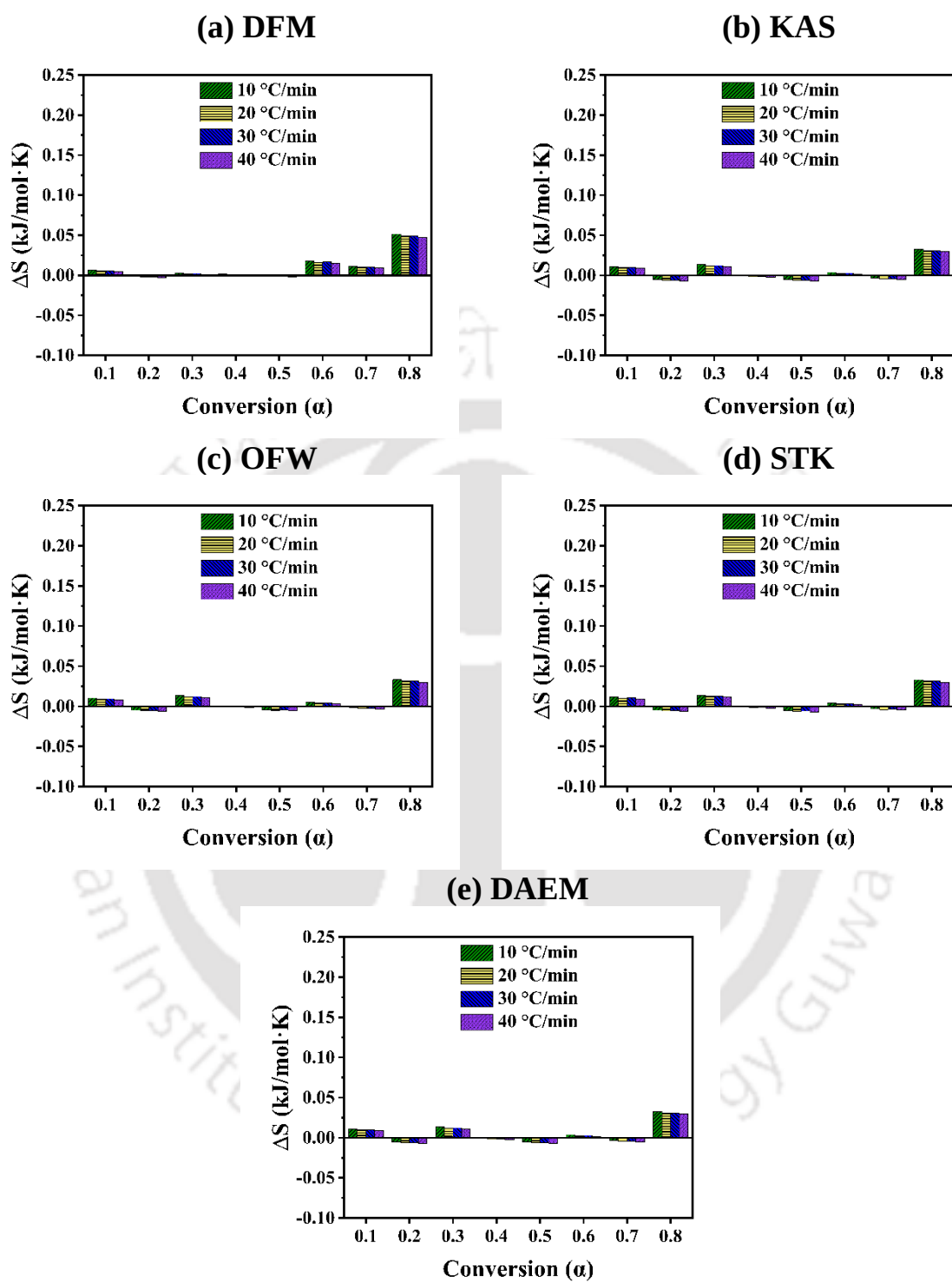


Figure 6.8.41 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:2.

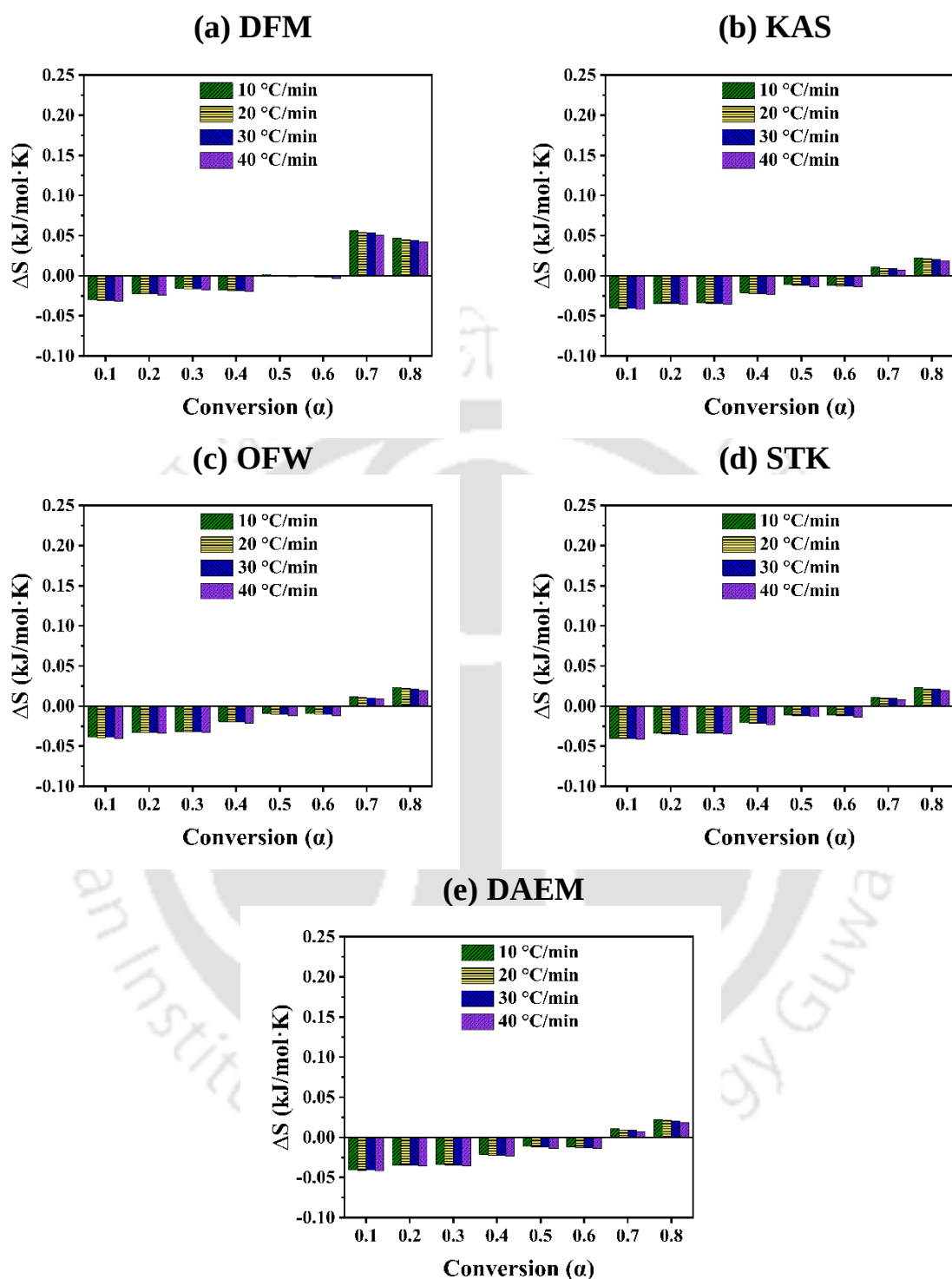


Figure 6.8.42 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 1:1.

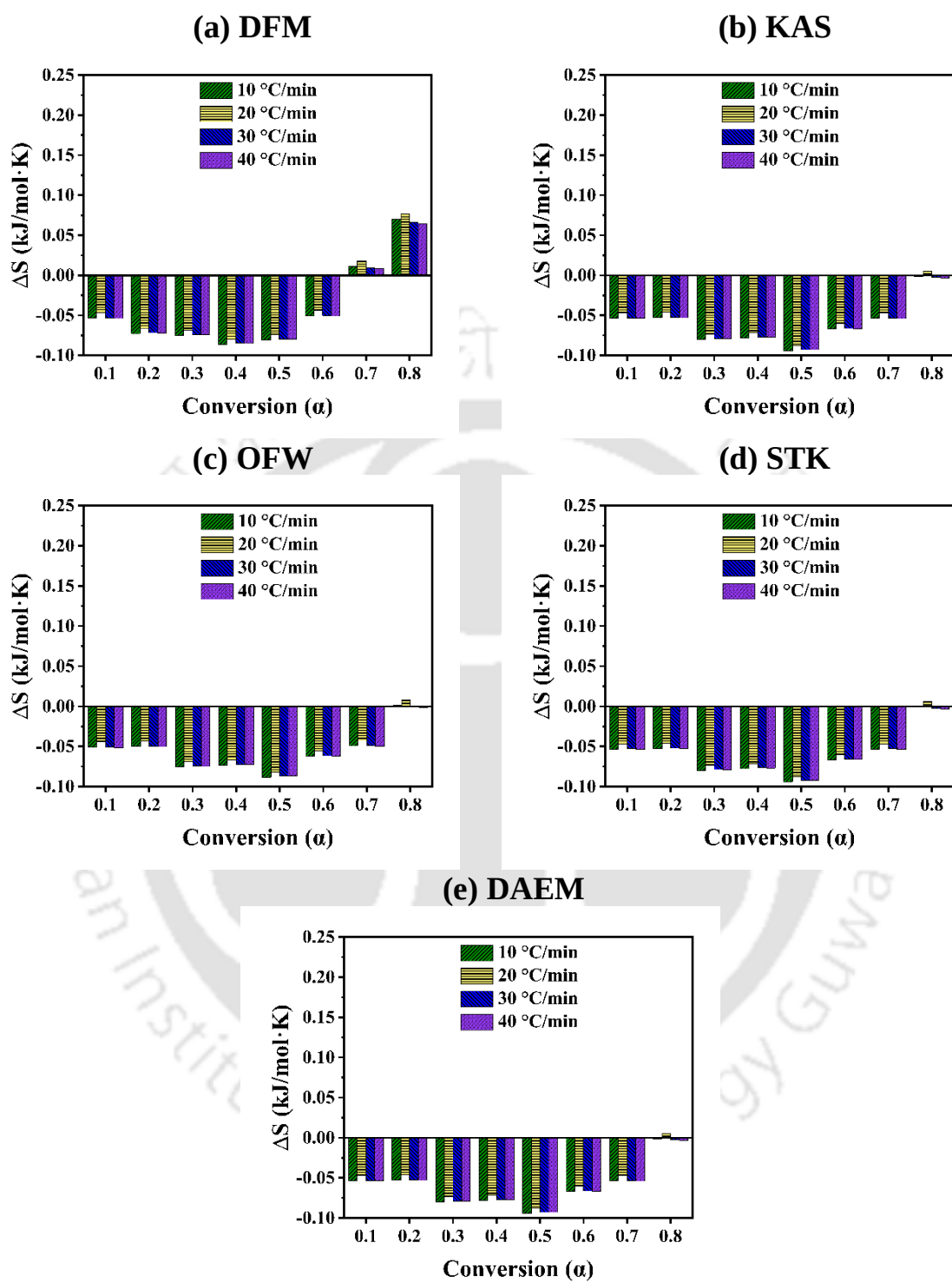


Figure 6.8.43 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 2:1.

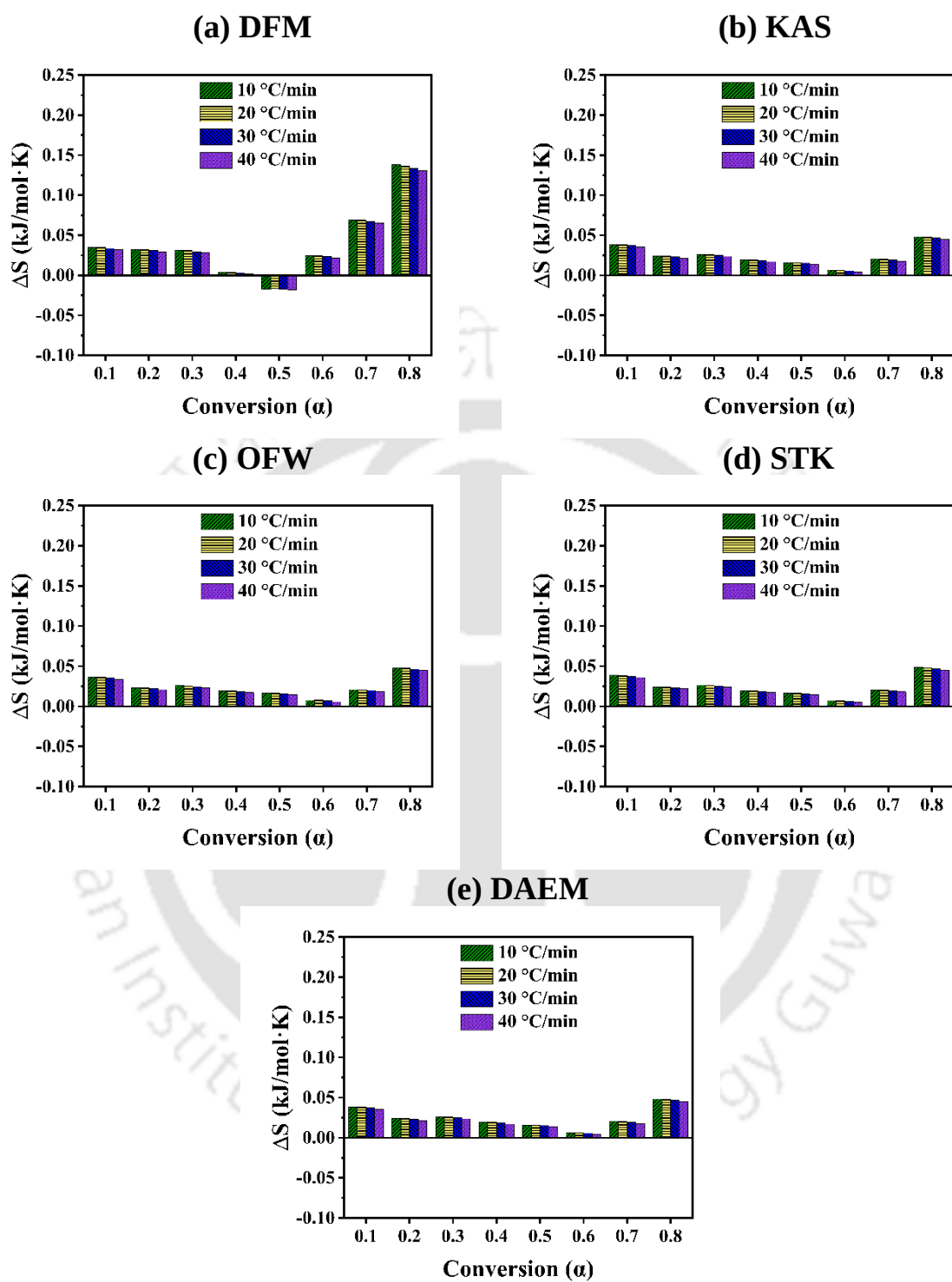


Figure 6.8.44 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 3:1.

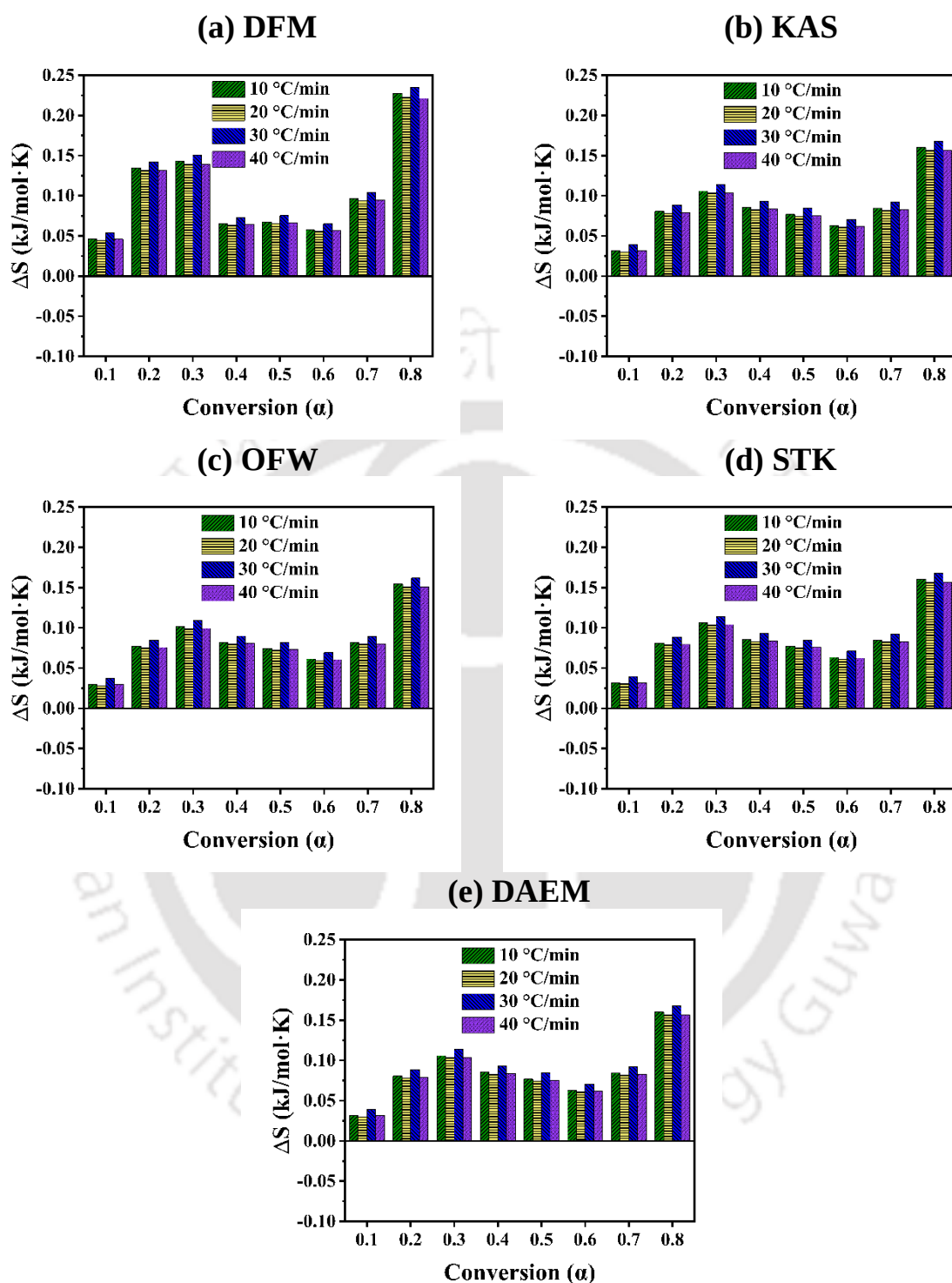


Figure 6.8.45 (a-e) Change in entropy (ΔS) vs. conversion (α) of EI and AI biomass pyrolysis at co-feed ratio of 4:1.

Table 6.8.2 Average values of enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI and AI biomass pyrolysis at various co-feed ratios.

Co-feed ratios	Iso-conversional methods	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
		ΔH	ΔG	ΔS	ΔH	ΔH	ΔG	ΔS	ΔH	ΔH	ΔG	ΔS	ΔH
EI:AI-1:4	DFM	165.412	176.832	-0.019	165.313	177.029	-0.019	165.238	177.689	-0.020	165.188	178.005	-0.020
	KAS	161.544	176.934	-0.025	161.444	177.133	-0.025	161.369	177.795	-0.026	161.320	178.112	-0.026
	OFW	162.835	176.792	-0.023	162.735	177.093	-0.023	162.661	177.754	-0.024	162.611	178.071	-0.024
	STK	161.809	176.926	-0.025	161.784	177.125	-0.025	161.634	177.787	-0.026	161.584	178.104	-0.026
	DAEM	161.544	176.934	-0.025	161.444	177.133	-0.025	161.369	177.795	-0.026	161.320	178.112	-0.026
EI:AI-1:3	DFM	179.288	175.489	0.006	179.180	176.003	0.005	179.105	176.663	0.004	179.089	175.766	0.005
	KAS	173.461	175.641	-0.004	173.353	176.158	-0.005	173.278	176.821	-0.006	173.262	175.924	-0.004
	OFW	174.167	175.645	-0.002	174.059	176.138	-0.003	173.984	176.800	-0.004	173.968	175.903	-0.003
	STK	173.717	175.634	-0.003	173.667	176.151	-0.004	173.534	176.813	-0.005	173.517	175.916	-0.004
	DAEM	173.461	175.641	-0.004	173.353	176.158	-0.005	173.278	176.821	-0.006	173.262	175.924	-0.004
EI:AI-1:2	DFM	180.999	174.180	0.011	180.891	174.713	0.010	180.841	174.469	0.010	180.783	175.103	0.009
	KAS	177.696	174.268	0.006	177.587	174.803	0.005	177.538	174.559	0.005	177.479	175.194	0.004
	OFW	178.160	174.255	0.006	178.052	174.789	0.005	178.002	174.545	0.006	177.944	175.181	0.004
	STK	177.946	174.261	0.006	177.863	174.796	0.005	177.788	174.552	0.005	177.730	175.187	0.004
	DAEM	177.696	174.268	0.006	177.587	174.803	0.005	177.538	174.559	0.005	177.479	175.194	0.004
EI:AI-1:1	DFM	174.819	173.425	0.002	174.711	173.978	0.001	174.653	174.050	0.001	174.587	174.994	-0.001
	KAS	164.654	173.705	-0.015	164.546	174.264	-0.016	164.488	174.339	-0.016	164.421	175.288	-0.017
	OFW	165.750	173.687	-0.013	165.642	174.231	-0.014	165.583	174.306	-0.014	165.517	175.254	-0.016
	STK	164.914	173.698	-0.015	164.806	174.256	-0.015	164.748	174.332	-0.015	164.682	175.280	-0.017
	DAEM	164.654	173.705	-0.015	164.546	174.264	-0.016	164.488	174.339	-0.016	164.421	175.288	-0.017

EI:AI-2:1	DFM	148.388	173.648	-0.042	148.404	169.583	-0.036	148.221	174.318	-0.042	148.163	174.973	-0.043
	KAS	137.934	173.943	-0.060	137.950	169.877	-0.054	137.767	174.623	-0.060	137.709	175.282	-0.060
	OFW	140.307	174.097	-0.056	140.324	169.792	-0.049	140.141	174.535	-0.056	140.083	175.193	-0.056
	STK	138.214	173.933	-0.060	138.089	169.867	-0.053	138.048	174.613	-0.059	137.990	175.271	-0.060
	DAEM	137.934	173.943	-0.060	137.950	169.877	-0.054	137.767	174.623	-0.060	137.709	175.282	-0.060
EI:AI-3:1	DFM	195.161	171.654	0.039	195.078	171.294	0.039	195.011	171.686	0.038	194.953	172.334	0.036
	KAS	186.551	171.838	0.025	186.468	171.480	0.025	186.402	171.875	0.024	186.344	172.525	0.022
	OFW	186.487	171.609	0.025	186.404	171.482	0.025	186.338	171.876	0.024	186.280	172.526	0.022
	STK	186.791	171.832	0.025	186.649	171.474	0.025	186.641	171.869	0.024	186.583	172.518	0.023
	DAEM	186.551	171.838	0.025	186.468	171.480	0.025	186.402	171.875	0.024	186.344	172.525	0.022
EI:AI-4:1	DFM	233.581	171.103	0.105	233.481	171.335	0.102	233.564	166.255	0.112	233.415	170.231	0.102
	KAS	222.571	171.311	0.086	222.471	171.547	0.084	222.554	166.464	0.094	222.405	170.446	0.084
	OFW	220.715	170.805	0.083	220.616	171.588	0.081	220.699	166.503	0.090	220.549	170.487	0.081
	STK	222.780	171.306	0.086	222.647	171.543	0.084	222.764	166.459	0.094	222.614	170.441	0.085
	DAEM	222.571	171.311	0.086	222.471	171.547	0.084	222.554	166.464	0.094	222.405	170.446	0.084

6.9 SUMMARY OF THIS CHAPTER

Fuel phase extraction of bio-oil obtained from single-feed pyrolysis of *Erythrina indica* (EI) and *Azadirachta indica* (AI) biomass was carried out using dichloromethane and n-hexane individually at four different vol.% (10, 20, 30 and 40%) of solvent relative to the volume of the raw bio-oil and compared to those extracted without using any solvent. Out of the two solvents, n-hexane proved to be the more effective solvent for isolating fuel phases. It demonstrated enhanced physiochemical properties, including improved density, viscosity and calorific value, compared to those extracted without using any solvent and extracted using dichloromethane. Physiochemical properties of the fuel phases extracted using 30 vol.% and 40 vol.% n-hexane were comparable to conventional gasoline. Biochar produced from EI and AI biomass exhibited physiochemical properties comparable to conventional coal and possessed a fair flowability and combustibility indices. The non-condensable gases produced from EI and AI biomass possessed approximately 50-65% of combustible gases which included H₂, CO and CH₄. The co-feed pyrolysis of EI and AI biomass proved successful in improving both the yield and quality of pyrolysis oil and biochar, with optimal outcomes observed at the EI:AI-1:1 co-feed ratio. The fuel phase extracted (from raw bio-oil obtained with 1:1 co-feed ratio) using 10 vol.% of n-hexane, at the co-feed ratio of 1:1 exhibited the maximum calorific value of 36.798 MJ/kg. The biochar obtained at the EI:AI-1:1 co-feed ratio also displayed the maximum calorific value of 29.233 MJ/kg. An economic analysis for establishing a 10-ton batch-type pyrolysis plant for single-feed pyrolysis of EI and AI biomass, as well as their co-feed pyrolysis at a 1:1 ratio, was conducted. The initial investment was calculated to be INR 2,16,61,887, while the operating costs for single-feed pyrolysis of EI and AI biomasses were INR 2,82,97,013 and INR 2,83,71,750, respectively. For co-feed pyrolysis, the operating cost was INR 2,91,22,915. The minimum fuel selling price of the fuel phase obtained from single-feed pyrolysis of EI and AI was INR 10.88 and 22.54, respectively, while for the co-feed ratio of 1:1, it was INR 18.36. However, the calculations for determining the payback period, net present value and internal rate of return were based on a fuel phase price of INR 50 per litre (consistent with furnace oil price) and a biochar cost of INR 20 per kg. The analysis revealed viable projects with positive net present values with returns exceeding the initial investment for all the scenarios. The payback periods were found to be 3.90 years for the single-feed pyrolysis of EI biomass and 6.45 years for AI biomass. For the co-feed pyrolysis at a 1:1 ratio, the payback period was determined to be 4.02 years. The kinetics and thermodynamics of single-feed and co-feed non-isothermal pyrolysis of EI and AI biomass were investigated at

heating rates of 10, 20, 30 and 40°C/min using five different iso-conversional methods, viz. the differential Friedman method (DFM), Kissinger-Akharria-Sunose (KAS), Ozawa-Flynn-Wall (OFW), Starink (STK) and distributed activation energy model (DAEM). Strong correlations ($R^2 > 0.98$) in kinetic plots indicated excellent agreement of the iso-conversional methods for both biomasses. Complex reaction mechanisms were unveiled by Criado's master plots and integral approach for both EI and AI biomass pyrolysis. The synergistic effect of co-feed pyrolysis was evident in the average activation energy required at various co-feed ratios. Average activation energy (kJ/mol) values for the co-feed ratio of EI:AI-1:1 ranged from 169.643 kJ/mol to 179.808 kJ/mol, while the average values for the change in enthalpy ranged from 164.421 kJ/mol to 174.819 kJ/mol. Nevertheless, considering the properties of pyrolytic products, as well as kinetics and thermodynamics, co-feed ratio of EI:AI-1:1 ratio is found to be the optimal ratio for producing biofuels through pyrolysis.

6.10 LIMITATIONS AND CHALLENGES ENCOUNTERED DURING THIS RESEARCH WORK

While no research is immune to challenges and limitations, this study has effectively addressed the majority of them. Nevertheless, a few limitations and challenges persisted throughout the research process. The most significant challenge was recovering the solvent used for separating the fuel phase. During solvent recovery, volatile compounds with low boiling points were also removed from the fuel phase, resulting in a denser and more viscous fuel. However, avoiding solvent recovery proved advantageous, significantly enhancing the physicochemical properties of the fuel phase, making it comparable to conventional gasoline.

In the kinetic study, several limitations were encountered. Firstly, the heat and mass transfer limitations were an issue. In TGA experiments, especially with smaller sample sizes, these limitations were minimum whereas in practical applications with larger sample sizes, these can cause temperature gradients within the sample, affecting the accuracy of the kinetic data. Secondly, the inherent heterogeneity of biomass, which comprises different components such as cellulose, hemicellulose and lignin, each with distinct thermal behaviors, complicates kinetic analysis. The observed weight loss is a combined effect of the decomposition of all components. Thirdly, the heating rate significantly influences observed kinetics. Slow heating rates can lead to more pronounced secondary reactions, while fast heating rates might not allow sufficient time for complete reaction steps, complicating the extrapolation of lab-scale TGA results to real-world pyrolysis conditions.

Additionally, kinetic models used to interpret TGA data often rely on assumptions, such as single-step reactions or specific reaction orders, which might not accurately reflect the complex nature of biomass pyrolysis. TGA typically operates under non-equilibrium conditions, especially at higher heating rates, making it difficult to obtain accurate thermodynamic data that assume equilibrium conditions. Secondary reactions, such as char formation and gas-phase reactions, can interfere with the primary decomposition reactions, complicating the extraction of clear thermodynamic parameters. Lastly, the preparation of biomass samples, including grinding and drying, can impact the TGA results. Ensuring consistent sample preparation is essential but can be difficult to standardize.



Chapter 7: Conclusions

Single and co-feed pyrolysis of EI and AI biomass have been carried out with aim to produce biofuels, biochar and non-condensable gases at 600°C. Extraction of fuel phase of the pyrolytic bio-oil was carried out using two different solvent at various ratio of solvent relative to the volume of the raw bio-oil. In addition to analysis of feeds and products, the kinetics and thermodynamics of corresponding processes have also been accomplished. The average yield of bio-oil, biochar and non-condensable gases from the single-feed pyrolysis of EI biomass were found to be 26.873 wt.%, 42.870 wt.% and 30.257 wt.%, respectively whereas for AI biomass pyrolysis the corresponding values were found to be 27.286 wt.%, 41.053 wt.% and 31.662 wt.%, respectively. The fuel phase separation from the raw bio-oil obtained from the single-feed pyrolysis of EI and AI biomass was carried out using dichloromethane and n-hexane at four vol.% (10, 20, 30 and 40%) of solvent relative to the volume of raw bio-oil and compared to those without using solvents. Out of the two solvents, n-hexane emerged out to be the superior solvent for extracting the fuel phase. The fuel phases separated using n-hexane depicted better physiochemical properties in terms of density, viscosity and calorific value viewpoint as compared to those extracted without using any solvent and extracted using dichloromethane. Fuel phases separated using 30 and 40 vol.% n-hexane depicted properties similar to commercial gasoline especially in terms of calorific value, density and pH. Fuel phases indicated the presence of aliphatics, ketones, aromatics, isopropyl compounds, aliphatic ethers, alcohols, hydrocarbons and alkyl groups in the fuel phases obtained from EI and AI biomass. The average calorific values of biochar and non-condensable gases obtained from EI and AI biomass were found to be 28.030 MJ/kg and 14.486 MJ/Nm³ and 28.500 MJ/kg and 14.882 MJ/Nm³, respectively. Physiochemical properties of EI and AI biochar along with flowability and combustion indices indicated that the biochar produced is comparable to conventional coal. Fixed carbon emerged out to be the chief component of the biochar. The non-condensable gases obtained from EI and AI biomass constituted approximately 50-65% (by volume) of combustible gases including H₂, CO and CH₄. The volumetric compositions of non-condensable gases from pyrolysis of EI biomass included 16.822% H₂, 24.664% CO, 23.183% CH₄ and 35.329% CO₂, whereas those obtained from pyrolysis of AI biomass comprised 15.874% H₂, 26.656% CO, 23.849% CH₄ and 33.620% CO₂.

The co-feed pyrolysis of EI and AI biomass resulted raw bio-oil yield varying in the range 29.512 wt.% and 32.399 wt.%, while biochar and non-condensable gas yield varied between 38.249 wt.% to 42.480 wt.% and 26.901 wt.% to 30.730 wt.%, respectively. The physicochemical properties of the fuel phase showed improvement especially in terms of density and calorific value. The fuel phase of bio-oil (from raw bio-oil of 1:1 co-feed pyrolysis) extracted with 10 vol.% of n-hexane solvent exhibited the highest calorific value of 36.798 MJ/kg. The corresponding volumetric percentage composition of non-condensable gases included 7.452% H₂, 34.257% CO, 21.322% CH₄ and 36.969% CO₂ with a calorific value of 13.761 MJ/Nm³. The biochar produced at co-feed ratio of 1:1 had a calorific value of 29.233 MJ/kg. The co-feed pyrolysis of EI and AI biomass was successful in enhancing the yield and product quality of the pyrolysis oil and the biochar with optimal results observed at co-feed ratio of 1:1, especially in terms of calorific value.

In order to establish techno-economic feasibility, an economic analysis for establishing a 10-ton batch-type pyrolysis plant was also conducted for single-feed pyrolysis of EI and AI biomass, as well as their co-feed pyrolysis at 1:1 ratio using the annual cost method. The payback periods were found to be 3.90 years for the single-feed pyrolysis of EI biomass and 6.46 years for AI biomass. For the co-feed pyrolysis at a 1:1 ratio, the payback period was determined to be 4.05 years. The economic analysis revealed that all scenarios are viable projects with positive net present values and returns exceeding the initial investment by the end of the project.

Since the kinetics and thermodynamics are essential for the design of suitable pyrolyzer, the same of single and co-feed pyrolysis of EI and AI biomass were also studied at four different heating rates of 10, 20, 30 and 40°C/min using five different iso-conversional methods; and the outcomes are as below. The average activation energy values for EI and AI biomass pyrolysis varied from 176.861 kJ/mol to 184.787 kJ/mol and 187.613 kJ/mol to 196.635 kJ/mol, respectively. The corresponding average values of enthalpy change, Gibbs free energy change and entropy change of pyrolysis of EI biomass varied from 171.781 kJ/mol to 179.890 kJ/mol, 168.191 kJ/mol to 170.083 kJ/mol and 0.003 kJ/mol·K to 0.019 kJ/mol·K, respectively, whereas for pyrolysis of AI biomass, the corresponding values varied from 182.425 kJ/mol to 191.638 kJ/mol, 167.288 kJ/mol to 173.742 kJ/mol and 0.014 kJ/mol·K to 0.039 kJ/mol·K, respectively. The kinetic plots from all methods displayed a strong correlation with R² values exceeding 0.98 for both the biomass, indicating excellent agreement of the iso-conversional methods. Criado's master plots and an integral approach indicate the complex

reaction mechanism of EI and AI biomass pyrolysis process. It was observed that the biomass pyrolysis did not follow a single reaction model rather it followed a complex reaction mechanism with combination of various reaction models. The synergistic effect of co-feed pyrolysis of EI and AI biomass evident from the kinetic study as well. The average activation energy (kJ/mol) values for the co-feed ratio of EI:AI-1:1 ranged from 169.643 kJ/mol to 179.808 kJ/mol, while the average values for the change in enthalpy were found to be between 164.421 kJ/mol and 174.819 kJ/mol, respectively.

Finally, considering the physiochemical properties of the pyrolytic products, potential applications and economic analysis, the co-feed pyrolysis of EI and AI at a 1:1 ratio emerges to be more favourable option.





Chapter 8: Future Scope of this Work

Research is a continuous process and there may be possible “n” no. of future works or scopes. However, following are found to be requiring immediate future work attraction, especially from commercialization viewpoint.

- Performance testing of the biofuels produced through pyrolysis in IC engines.
- Technological study on scaling up of the pyrolysis processes for commercialization beyond 10-ton batch and continuous plants.
- Integration with upgradation processes like hydrodeoxygenation to further improve the quality of the fuel phase and check whether it is more important than solvent extraction, especially in terms of techno-economic feasibility.
- Studies on environmental and social impacts of the commercial plants producing biofuels by pyrolysis.



Research Output

Research Papers (Published):

1. **G. Ahmed**, N. Kishore, Separation and extensive evaluation of properties of fuel and non-fuel portions of pyrolytic bio-oil obtained from *Erythrina indica* biomass, J. Renew. Sustain. Energy. 15 (2023).
2. **G. Ahmed**, N. Kishore, Fuel phase extraction from pyrolytic liquid of *Azadirachta indica* biomass followed by subsequent characterization of pyrolysis products, Renew. Energy. 219 (2023) 119460.
3. **G. Ahmed**, P.K.R. Annapureddy, N. Kishore, Study on non-isothermal pyrolysis of *Azadirachta indica* for kinetic triplets and thermodynamics evaluation, Bioresour. Technol. Reports. 25 (2024) 101794.
4. **G. Ahmed**, N. Kishore, Synergistic effects on properties of biofuel and biochar produced through co-feed pyrolysis of *Erythrina indica* and *Azadirachta indica* biomass, Renew. Energy. 227 (2024) 120508.

Research Papers (Under review/Under preparation):

5. **G. Ahmed**, P.K.R. Annapureddy, N. Kishore, Elucidation of kinetics and thermodynamic properties of *Erythrina indica* biomass pyrolysis. (Under review)
6. **G. Ahmed**, P.K.R. Annapureddy, N. Kishore, Exploration of synergistic influences on kinetics and thermodynamic properties of *Erythrina indica* and *Azadirachta indica* biomass co-feed pyrolysis. (Under review)

Conference Paper:

7. **G. Ahmed**, N. Kishore, Characterization of biofuel obtained by pyrolysis of *A. indica*, Sustainable Energy Generation and Storage: Proceedings of NERC 2022. Singapore: Springer Nature Singapore. (2023). 145-153.
8. **G. Ahmed**, N. Kishore, The Co-Pyrolysis of *Erythrina indica* and *Azadirachta indica* in a Tubular Reactor, Sustainability in Chemical Processes through Digitalization and Green Chemistry Approaches: Nova Science Publishers, Inc. New York, USA. (2023).

Conference proceedings:

1. **G. Ahmed**, N. Kishore, Thermochemical conversion of *E. indica* biomass in a tubular batch reactor, Industrial Conclave 2022, IIT Guwahati, 20-23rd January, (2022).
2. **G. Ahmed**, N. Kishore, Pyrolysis of *A. indica* in a benchtop tubular reactor: Fuel characterization, North East Research Conclave (NERC) 2022, IIT Guwahati, 20-22nd May, (2022).
3. **G. Ahmed**, N. Kishore, Effect of co-pyrolysis of *Erythrina Indica* and *Azadirachta indica* in a tubular reactor, CHEMCON-2022, Harcourt Butler Technical University, Kanpur, 27-30th December, (2022).
4. **G. Ahmed**, N. Kishore, Thermogravimetric analysis of *Erythrina indica* biomass: Insights into the kinetics of heat treatment through pyrolysis, ChEmference-2023, BITS Pilani, K.K. Birla Goa Campus, 30th September, -2nd October, (2023).

Bibliography

- [1] Rasam S, Moshfegh Haghighi A, Azizi K, Soria-Verdugo A, Keshavarz Moraveji M. Thermal behavior, thermodynamics and kinetics of co-pyrolysis of binary and ternary mixtures of biomass through thermogravimetric analysis. *Fuel* 2020;280:118665. doi:10.1016/j.fuel.2020.118665.
- [2] Ahmad T, Zhang D. A critical review of comparative global historical energy consumption and future demand: The story told so far. *Energy Reports* 2020;6:1973–91. doi:10.1016/j.egyr.2020.07.020.
- [3] Himeur Y, Ghanem K, Alsalemi A, Bensaali F, Amira A. Artificial intelligence based anomaly detection of energy consumption in buildings: A review, current trends and new perspectives. *Appl Energy* 2021;287:116601. doi:10.1016/j.apenergy.2021.116601.
- [4] Ma N, Zhao W, Wang W, Li X, Zhou H. Large scale of green hydrogen storage: Opportunities and challenges. *Int J Hydrogen Energy* 2023. doi:10.1016/j.ijhydene.2023.09.021.
- [5] Tian J, Yu L, Xue R, Zhuang S, Shan Y. Global low-carbon energy transition in the post-COVID-19 era. *Appl Energy* 2022;307:118205. doi:10.1016/j.apenergy.2021.118205.
- [6] Qiu B, Tao X, Wang J, Liu Y, Li S, Chu H. Research progress in the preparation of high-quality liquid fuels and chemicals by catalytic pyrolysis of biomass: A review. *Energy Convers Manag* 2022;261:115647. doi:10.1016/j.enconman.2022.115647.
- [7] Ryu HW, Kim DH, Jae J, Lam SS, Park ED, Park YK. Recent advances in catalytic co-pyrolysis of biomass and plastic waste for the production of petroleum-like hydrocarbons. *Bioresour Technol* 2020;310:123473. doi:10.1016/j.biortech.2020.123473.
- [8] Hwang Y, Farooq A, Park SH, Kim KH, Lee MH, Choi SC, et al. NH₃-induced removal of NO_x from a flue gas stream by silent discharge ozone generation in a double reactor system. *Korean J Chem Eng* 2019;36:1291–7. doi:10.1007/s11814-019-0325-8.

- [9] Ali Qamar O, Jamil F, Hussain M, Al-Muhtaseb AH, Inayat A, Waris A, et al. Feasibility-to-applications of value-added products from biomass: Current trends, challenges, and prospects. *Chem Eng J* 2023;454:140240. doi:10.1016/j.cej.2022.140240.
- [10] Hood R. *Global Warming. A Companion to Appl Ethics* 2007:674–84. doi:10.1002/9780470996621.ch50.
- [11] Ahmed G, Acharya S, Kawale H, Singh A, Kishore N, Pal S. Thermochemical conversion of *Polyalthia longifolia* leaves at different temperatures and characterization of their products. *Fuel* 2020;280. doi:10.1016/j.fuel.2020.118574.
- [12] Rammohan D, Kishore N, Uppaluri RVS. Pyro–catalytic co–pyrolysis of Delonix regia and butyl rubber tube: Kinetic modelling and thermodynamic insights. *Renew Energy* 2022;201:194–203. doi:10.1016/j.renene.2022.10.099.
- [13] Wu Y, Wang H, Li H, Han X, Zhang M, Sun Y, et al. Applications of catalysts in thermochemical conversion of biomass (pyrolysis, hydrothermal liquefaction and gasification): A critical review. *Renew Energy* 2022;196:462–81. doi:10.1016/j.renene.2022.07.031.
- [14] Global Energy Review 2021, Renewables bucked the trend in 2020 2021:2020–1. <https://www.iea.org/reports/global-energy-review-2021/renewables>. (Accessed 13th November 2022).
- [15] Alper K, Tekin K, Karagöz S, Ragauskas AJ. Sustainable energy and fuels from biomass: A review focusing on hydrothermal biomass processing. *Sustain Energy Fuels* 2020;4:4390–414. doi:10.1039/d0se00784f.
- [16] GoI. Renewable Energy in India - Indian Power Industry Investment. Invest India 2021. <https://www.investindia.gov.in/sector/renewable-energy>. (Accessed 19th November 2022).
- [17] Kim JY, Lee HW, Lee SM, Jae J, Park YK. Overview of the recent advances in lignocellulose liquefaction for producing biofuels, bio-based materials and chemicals. *Bioresour Technol* 2019;279:373–84. doi:10.1016/j.biortech.2019.01.055.
- [18] Yang Z, Wu Y, Zhang Z, Li H, Li X, Egorov RI, et al. Recent advances in co-thermochemical conversions of biomass with fossil fuels focusing on the synergistic

- effects. *Renew Sustain Energy Rev* 2019;103:384–98. doi:10.1016/j.rser.2018.12.047.
- [19] Low YW, Yee KF. A review on lignocellulosic biomass waste into biochar-derived catalyst: Current conversion techniques, sustainable applications and challenges. *Biomass and Bioenergy* 2021;154:106245. doi:10.1016/j.biombioe.2021.106245.
- [20] Gaudreau K. Biofuel basics. *Altern J* 2009;35:14–9.
- [21] Lee D, Nam H, Won Seo M, Hoon Lee S, Tokmurzin D, Wang S, et al. Recent progress in the catalytic thermochemical conversion process of biomass for biofuels. *Chem Eng J* 2022;447:137501. doi:10.1016/j.cej.2022.137501.
- [22] IREDA 2020. <https://www.ireda.in/biomass-power-generation>. (Accessed 25 November 2022).
- [23] Zoghلامي A, Paës G. Lignocellulosic Biomass: Understanding Recalcitrance and Predicting Hydrolysis. *Front Chem* 2019;7. doi:10.3389/fchem.2019.00874.
- [24] Zheng Y, Zhao J, Xu F, Li Y. Pretreatment of lignocellulosic biomass for enhanced biogas production. *Prog Energy Combust Sci* 2014;42:35–53. doi:10.1016/j.pecs.2014.01.001.
- [25] Somerville C. Cellulose synthesis in higher plants. *Annu Rev Cell Dev Biol* 2006;22:53–78. doi:10.1146/annurev.cellbio.22.022206.160206.
- [26] Davison BH, Parks J, Davis MF, Donohoe BS. Plant Cell Walls: Basics of Structure, Chemistry, Accessibility and the Influence on Conversion. *Aqueous Pretreat Plant Biomass Biol Chem Convers to Fuels Chem* 2013:23–38. doi:10.1002/9780470975831.ch3.
- [27] Zakzeski J, Bruijninx PCA, Jongerius AL, Weckhuysen BM. The catalytic valorization of lignin for the production of renewable chemicals. *Chem Rev* 2010;110:3552–99. doi:10.1021/cr900354u.
- [28] Jensen CU, Rodriguez Guerrero JK, Karatzos S, Olofsson G, Iversen SB. Fundamentals of Hydrofaction™: Renewable crude oil from woody biomass. *Biomass Convers Biorefinery* 2017;7:495–509. doi:10.1007/s13399-017-0248-8.
- [29] Kumar A, Lingadurai S, Jain A, Barman N. *Erythrina variegata* Linn: A review on morphology, phytochemistry, and pharmacological aspects. *Pharmacogn Rev*

- 2010;4:147–52. doi:10.4103/0973-7847.70908.
- [30] Martins J, Brijesh S. Anti-depressant activity of *Erythrina variegata* bark extract and regulation of monoamine oxidase activities in mice. *J Ethnopharmacol* 2020;248:112280. doi:10.1016/j.jep.2019.112280.
 - [31] Kumar VS, Navaratnam V. Neem (*Azadirachta indica*): Prehistory to contemporary medicinal uses to humankind. *Asian Pac J Trop Biomed* 2013;3:505–14. doi:10.1016/S2221-1691(13)60105-7.
 - [32] Sowmya Dhanalakshmi C, Madhu P. Biofuel production of neem wood bark (*Azadirachta indica*) through flash pyrolysis in a fluidized bed reactor and its chromatographic characterization. *Energy Sources, Part A Recover Util Environ Eff* 2021;43:428–43. doi:10.1080/15567036.2019.1624893.
 - [33] V.K. Gupta, S.K. Dhyani, S.P. Akhrawat RVK. *Neem Germplasm catalogue* 2011.
 - [34] Nanda S, Vo DVN, Sarangi PK. Biorefinery of alternative resources: Targeting green fuels and platform chemicals. 2020. doi:10.1007/978-981-15-1804-1.
 - [35] Adams P, Bridgwater T, Lea-Langton A, Ross A, Watson I. *Biomass Conversion Technologies*. Elsevier Inc.; 2017. doi:10.1016/B978-0-08-101036-5.00008-2.
 - [36] Gebremariam SN, Marchetti JM. Economics of biodiesel production: Review. *Energy Convers Manag* 2018;168:74–84. doi:10.1016/j.enconman.2018.05.002.
 - [37] McKendry P. Energy production from biomass (part 2): conversion technologies. *Bioresour Technol* 2001;83:47–54. doi:https://doi.org/10.1016/S0960-8524(01)00119-5.
 - [38] Zhang Z, Li Y, Luo L, Yellezuome D, Rahman MM, Zou J, et al. Insight into kinetic and Thermodynamic Analysis methods for lignocellulosic biomass pyrolysis. *Renew Energy* 2023;202:154–71. doi:10.1016/j.renene.2022.11.072.
 - [39] Kartal F, Dalbudak Y, Özveren U. Prediction of thermal degradation of biopolymers in biomass under pyrolysis atmosphere by means of machine learning. *Renew Energy* 2023;204:774–87. doi:10.1016/j.renene.2023.01.017.
 - [40] Aravind SV, Ahmed G, Kishore N. Results in Engineering Pyrolysis of *Delonix regia* using metal oxide catalysts and solvent effect on fuel fraction of bio-oil. *Results Eng*

- 2023;17:100876. doi:10.1016/j.rineng.2023.100876.
- [41] Nawaz A, Kumar P. Pyrolysis behavior of low value biomass (*Sesbania bispinosa*) to elucidate its bioenergy potential: Kinetic, thermodynamic and prediction modelling using artificial neural network. *Renew Energy* 2022;200:257–70. doi:10.1016/j.renene.2022.09.110.
- [42] Tekin K, Karagöz S, Bektaş S. A review of hydrothermal biomass processing. *Renew Sustain Energy Rev* 2014;40:673–87. doi:10.1016/j.rser.2014.07.216.
- [43] Patel M, Zhang X, Kumar A. Techno-economic and life cycle assessment on lignocellulosic biomass thermochemical conversion technologies: A review. *Renew Sustain Energy Rev* 2016;53:1486–99. doi:10.1016/j.rser.2015.09.070.
- [44] Raheem A, Wan Azlina WAKG, Taufiq Yap YH, Danquah MK, Harun R. Thermochemical conversion of microalgal biomass for biofuel production. *Renew Sustain Energy Rev* 2015;49:990–9. doi:10.1016/j.rser.2015.04.186.
- [45] Zaman CZ, Pal K, Yehye WA, Sagadevan S, Shah ST, Adebisi GA, et al. Pyrolysis: A Sustainable Way to Generate Energy from Waste. *Pyrolysis* 2017:1–29. doi:10.5772/intechopen.69036.
- [46] Sun Y, Liu L, Wang Q, Yang X, Tu X. Pyrolysis products from industrial waste biomass based on a neural network model. *J Anal Appl Pyrolysis* 2016;120:94–102. doi:10.1016/j.jaap.2016.04.013.
- [47] Titirici MM, Funke A, Kruse A. Hydrothermal Carbonization of Biomass. *Recent Adv Thermochem Convers Biomass* 2015:325–52. doi:10.1016/B978-0-444-63289-0.00012-0.
- [48] Elliott DC, Biller P, Ross AB, Schmidt AJ, Jones SB. Hydrothermal liquefaction of biomass: Developments from batch to continuous process. *Bioresour Technol* 2015;178:147–56. doi:10.1016/j.biortech.2014.09.132.
- [49] Biller P, Sharma BK, Kunwar B, Ross AB. Hydroprocessing of bio-crude from continuous hydrothermal liquefaction of microalgae. *Fuel* 2015;159:197–205. doi:10.1016/j.fuel.2015.06.077.
- [50] Wang S, Dai G, Yang H, Luo Z. Lignocellulosic biomass pyrolysis mechanism: A state-

- of-the-art review. *Prog Energy Combust Sci* 2017;62:33–86. doi:10.1016/J.PECS.2017.05.004.
- [51] Wang G, Dai Y, Yang H, Xiong Q, Wang K, Zhou J, et al. A review of recent advances in biomass pyrolysis. *Energy and Fuels* 2020;34:15557–78. doi:10.1021/acs.energyfuels.0c03107.
- [52] Bridgwater A V. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy* 2012;38:68–94. doi:10.1016/j.biombioe.2011.01.048.
- [53] Brown TR, Thilakaratne R, Brown RC, Hu G. Techno-economic analysis of biomass to transportation fuels and electricity via fast pyrolysis and hydroprocessing. *Fuel* 2013;106:463–9. doi:10.1016/j.fuel.2012.11.029.
- [54] Wright MM, Dugaard DE, Satrio JA, Brown RC. Techno-economic analysis of biomass fast pyrolysis to transportation fuels. *Fuel* 2010;89:S2–10. doi:10.1016/j.fuel.2010.07.029.
- [55] Anex RP, Aden A, Kazi FK, Fortman J, Swanson RM, Wright MM, et al. Techno-economic comparison of biomass-to-transportation fuels via pyrolysis, gasification, and biochemical pathways. *Fuel* 2010;89:S29–35. doi:10.1016/j.fuel.2010.07.015.
- [56] Zhang L, Xu C (Charles), Champagne P. Overview of recent advances in thermo-chemical conversion of biomass. *Energy Convers Manag* 2010;51:969–82. doi:10.1016/j.enconman.2009.11.038.
- [57] Aghbashlo M, Almasi F, Jafari A, Nadian MH, Soltanian S, Lam SS, et al. Describing biomass pyrolysis kinetics using a generic hybrid intelligent model: A critical stage in sustainable waste-oriented biorefineries. *Renew Energy* 2021;170:81–91. doi:10.1016/j.renene.2021.01.111.
- [58] Sun Y, Li C, Zhang S, Li Q, Gholizadeh M, Wang Y, et al. Pyrolysis of soybean residue: Understanding characteristics of the products. *Renew Energy* 2021;174:487–500. doi:10.1016/j.renene.2021.04.063.
- [59] Bridgwater A V., Meier D, Radlein D. An overview of fast pyrolysis of biomass. *Org Geochem* 1999;30:1479–93. doi:10.1016/S0146-6380(99)00120-5.
- [60] Carpenter D, Westover TL, Czernik S, Jablonski W. Biomass feedstocks for renewable

- fuel production: A review of the impacts of feedstock and pretreatment on the yield and product distribution of fast pyrolysis bio-oils and vapors. *Green Chem* 2014;16:384–406. doi:10.1039/c3gc41631c.
- [61] Han Y, Gholizadeh M, Tran CC, Kaliaguine S, Li CZ, Olarte M, et al. Hydrotreatment of pyrolysis bio-oil: A review. *Fuel Process Technol* 2019;195. doi:10.1016/j.fuproc.2019.106140.
- [62] Chen WH, Naveen C, Ghodke PK, Sharma AK, Bobde P. Co-pyrolysis of lignocellulosic biomass with other carbonaceous materials: A review on advance technologies, synergistic effect, and future prospectus. *Fuel* 2023;345:128177. doi:10.1016/j.fuel.2023.128177.
- [63] Ahmed MHM, Batalha N, Mahmudul HMD, Perkins G, Konarova M. A review on advanced catalytic co-pyrolysis of biomass and hydrogen-rich feedstock: Insights into synergistic effect, catalyst development and reaction mechanism. *Bioresour Technol* 2020;310:123457. doi:10.1016/j.biortech.2020.123457.
- [64] Chen W, Chen Y, Yang H, Xia M, Li K, Chen X, et al. Co-pyrolysis of lignocellulosic biomass and microalgae: Products characteristics and interaction effect. *Bioresour Technol* 2017;245:860–8. doi:10.1016/j.biortech.2017.09.022.
- [65] Kawale HD, Kishore N. Comparative study on pyrolysis of Delonix Regia, Pinewood sawdust and their co-feed for plausible bio-fuels production. *Energy* 2020;203:117921. doi:10.1016/j.energy.2020.117921.
- [66] Hua MY, Li BX. Co-pyrolysis characteristics of the sugarcane bagasse and *Enteromorpha prolifera*. *Energy Convers Manag* 2016;120:238–46. doi:10.1016/j.enconman.2016.04.072.
- [67] Chang G, Miao P, Wang H, Wang L, Hu X, Guo Q. A synergistic effect during the co-pyrolysis of *Nannochloropsis* sp. and palm kernel shell for aromatic hydrocarbon production. *Energy Convers Manag* 2018;173:545–54. doi:10.1016/j.enconman.2018.08.003.
- [68] Açıklım K. Evaluation of orange and potato peels as an energy source: a comprehensive study on their pyrolysis characteristics and kinetics. *Biomass Convers Biorefinery* 2022;12:501–14. doi:10.1007/s13399-021-01387-z.

- [69] Emiola-Sadiq T, Zhang L, Dalai AK. Thermal and Kinetic Studies on Biomass Degradation via Thermogravimetric Analysis: A Combination of Model-Fitting and Model-Free Approach. *ACS Omega* 2021;6:22233–47. doi:10.1021/acsomega.1c02937.
- [70] Ahmad MS, Klemeš JJ, Alhumade H, Elkamel A, Mahmood A, Shen B, et al. Thermo-kinetic study to elucidate the bioenergy potential of Maple Leaf Waste (MLW) by pyrolysis, TGA and kinetic modelling. *Fuel* 2021;293. doi:10.1016/j.fuel.2021.120349.
- [71] Annapureddy PKR, Kishore N. Non-isothermal pyrolysis of *Polyalthia longifolia* using thermogravimetric analyzer: Kinetics and thermodynamics . *J Renew Sustain Energy* 2023;15. doi:10.1063/5.0160104.
- [72] Yuan X, He T, Cao H, Yuan Q. Cattle manure pyrolysis process: Kinetic and thermodynamic analysis with isoconversional methods. *Renew Energy* 2017;107:489–96. doi:10.1016/J.RENENE.2017.02.026.
- [73] Galwey AK, Brown ME. Application of the arrhenius equation to solid state kinetics: Can this be justified? *Thermochim Acta* 2002;386:91–8. doi:10.1016/S0040-6031(01)00769-9.
- [74] Psimadas D, Georgoulas P, Valotassiou V, Loudos G. Molecular Nanomedicine Towards Cancer : *J Pharm Sci* 2012;101:2271–80. doi:10.1002/jps.
- [75] Parthasarathy P, Al-Ansari T, Mackey HR, McKay G. Effect of heating rate on the pyrolysis of camel manure. *Biomass Convers Biorefinery* 2023;13:6023–35. doi:10.1007/s13399-021-01531-9.
- [76] Kumar P, Subbarao PMV, Kala LD, Vijay VK. Thermogravimetry and associated characteristics of pearl millet cob and eucalyptus biomass using differential thermal gravimetric analysis for thermochemical gasification. *Therm Sci Eng Prog* 2021;26:101104. doi:10.1016/j.tsep.2021.101104.
- [77] Mishra G, Kumar J, Bhaskar T. Kinetic studies on the pyrolysis of pinewood. *Bioresour Technol* 2015;182:282–8. doi:10.1016/j.biortech.2015.01.087.
- [78] Arenas CN, Navarro MV, Martínez JD. Pyrolysis kinetics of biomass wastes using isoconversional methods and the distributed activation energy model. *Bioresour Technol* 2019;288:121485. doi:10.1016/j.biortech.2019.121485.

- [79] Hidayat S, Bakar MSA, Ahmed A, Iryani DA, Hussain M, Jamil F, et al. Comprehensive kinetic study of *Imperata Cylindrica* pyrolysis via Asym2sig deconvolution and combined kinetics. *J Anal Appl Pyrolysis* 2021;156:105133. doi:10.1016/j.jaap.2021.105133.
- [80] Alves JLF, Da Silva JCG, da Silva Filho VF, Alves RF, Ahmad MS, Ahmad MS, et al. Bioenergy potential of red macroalgae *Gelidium floridanum* by pyrolysis: Evaluation of kinetic triplet and thermodynamics parameters. *Bioresour Technol* 2019;291:121892. doi:10.1016/j.biortech.2019.121892.
- [81] Özsın G, Pütün AE. TGA/MS/FT-IR study for kinetic evaluation and evolved gas analysis of a biomass/PVC co-pyrolysis process. *Energy Convers Manag* 2019;182:143–53. doi:10.1016/j.enconman.2018.12.060.
- [82] Vikraman VK, Boopathi G, Kumar DP, Mythili R, Subramanian P. Non-isothermal pyrolytic kinetics of milk dust powder using thermogravimetric analysis. *Renew Energy* 2021;180:838–49. doi:10.1016/j.renene.2021.08.099.
- [83] Ashraf A, Sattar H, Munir S. Thermal decomposition study and pyrolysis kinetics of coal and agricultural residues under non-isothermal conditions. *Fuel* 2019;235:504–14. doi:10.1016/j.fuel.2018.07.120.
- [84] Ashraf A, Sattar H, Munir S. A comparative applicability study of model-fitting and model-free kinetic analysis approaches to non-isothermal pyrolysis of coal and agricultural residues. *Fuel* 2019;240:326–33. doi:10.1016/j.fuel.2018.11.149.
- [85] Collard FX, Blin J. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. *Renew Sustain Energy Rev* 2014;38:594–608. doi:10.1016/j.rser.2014.06.013.
- [86] Patel A, Agrawal B, Rawal BR. Pyrolysis of biomass for efficient extraction of biofuel. *Energy Sources, Part A Recover Util Environ Eff* 2020;42:1649–61. doi:10.1080/15567036.2019.1604875.
- [87] Hu X, Gholizadeh M. Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialisation stage. *J Energy Chem* 2019;39:109–43. doi:10.1016/j.jechem.2019.01.024.

- [88] Bridgwater A V. Pyrolysis of Solid Biomass: Basics, Processes and Products. *Energy from Org Mater* 2019;1221–50. doi:10.1007/978-1-4939-7813-7_984.
- [89] Şensöz S. Slow pyrolysis of wood barks from *Pinus brutia* Ten . and product compositions 2003;89:307–11. doi:10.1016/S0960-8524(03)00059-2.
- [90] Baghel P, Sakhiya AK, Kaushal P. Influence of temperature on slow pyrolysis of *Prosopis Juliflora*: An experimental and thermodynamic approach. *Renew Energy* 2022;185:538–51. doi:10.1016/j.renene.2021.12.053.
- [91] Ahmed A, Abu Bakar MS, Sukri RS, Hussain M, Farooq A, Moogi S, et al. Sawdust pyrolysis from the furniture industry in an auger pyrolysis reactor system for biochar and bio-oil production. *Energy Convers Manag* 2020;226:113502. doi:10.1016/j.enconman.2020.113502.
- [92] Yorgun S, Yıldız D. Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization. *J Anal Appl Pyrolysis* 2015;114:68–78. doi:10.1016/j.jaap.2015.05.003.
- [93] Kawale HD, Kishore N. Pyrolysis of *Delonix Regia* and Characterization of its Pyrolytic Products: Effect of Pyrolysis Temperature. *J Energy Resour Technol* 2020;142:1–11. doi:10.1115/1.4046226.
- [94] Morali U, Şensöz S. Pyrolysis of hornbeam shell (*Carpinus betulus* L.) in a fixed bed reactor: Characterization of bio-oil and bio-char. *Fuel* 2015;150:672–8. doi:10.1016/j.fuel.2015.02.095.
- [95] Das P, Dinda M, Gosai N, Maiti S. High energy density bio-oil via slow pyrolysis of *Jatropha curcas* shells. *Energy and Fuels* 2015;29:4311–20. doi:10.1021/acs.energyfuels.5b00160.
- [96] Sultana R, Banik U, Nandy PK, Huda MN, Ismail M. Bio-oil production from rubber seed cake via pyrolysis: Process parameter optimization and physicochemical characterization. *Energy Convers Manag X* 2023;20:100429. doi:10.1016/j.ecmx.2023.100429.
- [97] Lachos-Perez D, Martins-Vieira JC, Missau J, Anshu K, Siakpebru OK, Thengane SK, et al. Review on Biomass Pyrolysis with a Focus on Bio-Oil Upgrading Techniques. *Analytica* 2023;4:182–205. doi:10.3390/analytica4020015.

- [98] Zadeh ZE, Abdulkhani A, Aboelazayem O, Saha B. Recent Insights into Lignocellulosic Biomass Pyrolysis: A Critical Review on Pretreatment, Characterization, and Products Upgrading. *Processes* 2020;8:799. doi:10.3390/pr8070799.
- [99] Ucar S, Ozkan AR. Characterization of products from the pyrolysis of rapeseed oil cake. *Bioresour Technol* 2008;99:8771–6. doi:10.1016/j.biortech.2008.04.040.
- [100] Wei Y, Lei H, Wang L, Zhu L, Zhang X, Liu Y, et al. Liquid-liquid extraction of biomass pyrolysis bio-oil. *Energy and Fuels* 2014;28:1207–12. doi:10.1021/ef402490s.
- [101] Ren S, Ye XP, Borole AP, Kim P, Labbé N. Analysis of switchgrass-derived bio-oil and associated aqueous phase generated in a semi-pilot scale auger pyrolyzer. *J Anal Appl Pyrolysis* 2016;119:97–103. doi:10.1016/j.jaap.2016.03.013.
- [102] Li H, Xia S, Ma P. Upgrading fast pyrolysis oil: Solvent-anti-solvent extraction and blending with diesel. *Energy Convers Manag* 2016;110:378–85. doi:10.1016/j.enconman.2015.11.043.
- [103] Kanaujia PK, Naik D V, Tripathi D, Singh R, Poddar MK, Konathala LNSK, et al. Pyrolysis of Jatropha Curcas seed cake followed by optimization of liquid-liquid extraction procedure for the obtained bio-oil. *J Anal Appl Pyrolysis* 2016;118:202–24. doi:10.1016/j.jaap.2016.02.005.
- [104] Das S, Goud V V. RSM-optimised slow pyrolysis of rice husk for bio-oil production and its upgradation. *Energy* 2021;225:120161. doi:10.1016/j.energy.2021.120161.
- [105] Balogun AO, Adeleke AA, Ikubanni PP, Adegoke SO, Alayat AM, McDonald AG. Kinetics modeling, thermodynamics and thermal performance assessments of pyrolytic decomposition of Moringa oleifera husk and Delonix regia pod. *Sci Rep* 2021;11. doi:10.1038/s41598-021-93407-1.
- [106] Chandrasekaran A, Ramachandran S, Subbiah S. Determination of kinetic parameters in the pyrolysis operation and thermal behavior of Prosopis juliflora using thermogravimetric analysis. *Bioresour Technol* 2017;233:413–22. doi:10.1016/j.biortech.2017.02.119.
- [107] Wang X, Wang X, Qin G, Chen M, Wang J. Comparative study on pyrolysis characteristics and kinetics of lignocellulosic biomass and seaweed. *J Therm Anal Calorim* 2018;132:1317–23. doi:10.1007/s10973-018-6987-3.

- [108] Gupta GK, Mondal MK. Kinetics and thermodynamic analysis of maize cob pyrolysis for its bioenergy potential using thermogravimetric analyzer. *J Therm Anal Calorim* 2019;137:1431–41. doi:10.1007/s10973-019-08053-7.
- [109] Ceylan S, Kazan D. Pyrolysis kinetics and thermal characteristics of microalgae *Nannochloropsis oculata* and *Tetraselmis* sp. *Bioresour Technol* 2015;187:1–5. doi:10.1016/j.biortech.2015.03.081.
- [110] Singh S, Patil T, Tekade SP, Gawande MB, Sawarkar AN. Studies on individual pyrolysis and co-pyrolysis of corn cob and polyethylene: Thermal degradation behavior, possible synergism, kinetics, and thermodynamic analysis. *Sci Total Environ* 2021;783:147004. doi:10.1016/J.SCITOTENV.2021.147004.
- [111] Rasool T, Najar I, Srivastava VC, Pandey A. Pyrolysis of almond (*Prunus amygdalus*) shells: Kinetic analysis, modelling, energy assessment and technical feasibility studies. *Bioresour Technol* 2021;337:125466. doi:10.1016/j.biortech.2021.125466.
- [112] Damartzis T, Vamvuka D, Sfakiotakis S, Zabaniotou A. Thermal degradation studies and kinetic modeling of cardoon (*Cynara cardunculus*) pyrolysis using thermogravimetric analysis (TGA). *Bioresour Technol* 2011;102:6230–8. doi:10.1016/J.BIORTECH.2011.02.060.
- [113] Lee BH, Trinh VT, Kim SM, Jeon CH. Pyrolysis of kenaf (*Hibiscus cannabinus* L.) biomass: influence of ashless treatment on kinetics and thermal behavior. *J Therm Anal Calorim* 2022;147:7399–410. doi:10.1007/s10973-021-11036-2.
- [114] Li Y, Yellezuome D, Liu R, Cai J, Gao Y. Investigation of product selectivity and kinetics of poplar sawdust catalytic pyrolysis over bi-metallic Iron-Nickel/ZSM-5 catalyst. *Bioresour Technol* 2022;349:126838. doi:10.1016/j.biortech.2022.126838.
- [115] Rammohan D, Kishore N, Uppaluri RVS. Insights on Kinetic Triplets and Thermodynamic Analysis of Delonix Regia Biomass Pyrolysis. *Bioresour Technol* 2022;127375. doi:10.1016/J.BIORTECH.2022.127375.
- [116] Sharma A, Aravind Kumar A, Mohanty B, Sawarkar AN. Critical insights into pyrolysis and co-pyrolysis of poplar and eucalyptus wood sawdust: Physico-chemical characterization, kinetic triplets, reaction mechanism, and thermodynamic analysis. *Renew Energy* 2023;210:321–34. doi:10.1016/j.renene.2023.04.066.

- [117] Muigai HH, Choudhury BJ, Kalita P, Moholkar VS. Co-pyrolysis of biomass blends: Characterization, kinetic and thermodynamic analysis. *Biomass and Bioenergy* 2020;143:105839. doi:10.1016/j.biombioe.2020.105839.
- [118] Kazawadi D, Ntalikwa J, Kombe G. Co-pyrolysis of cashew nut, coconut shells, and rice husk waste: kinetic and thermodynamic investigations. *Energy Sources, Part A Recover Util Environ Eff* 2022;44:5896–915. doi:10.1080/15567036.2022.2091689.
- [119] Kim JS. Production, separation and applications of phenolic-rich bio-oil - A review. *Bioresour Technol* 2015;178:90–8. doi:10.1016/j.biortech.2014.08.121.
- [120] Oasmaa A, Fonts I, Pelaez-Samaniego MR, Garcia-Perez ME, Garcia-Perez M. Pyrolysis Oil Multiphase Behavior and Phase Stability: A Review. *Energy and Fuels* 2016;30:6179–200. doi:10.1021/acs.energyfuels.6b01287.
- [121] Designation: E871 – 82 Standard Test Method for Moisture Analysis of Particulate Wood Fuels 1 2019. doi:10.1520/E0871-82R19.
- [122] Drews A. Standard Test Method for. *Man Hydrocarb Anal* 6th Ed 2008:545-545–3. doi:10.1520/mnl10913m.
- [123] Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels 1 2019. doi:10.1520/E0872-82R19.
- [124] Eurovector. Smash the Combustion Barrier ! Eurovector Instruments Softw 2010:6. http://www.apolloinstruments.fr/AutoFiles/doc/5679_EuroEA3000%20brochure.pdf, (Accessed 12th November, 2023).
- [125] Krotz L, Galotta W. Elemental Analysis: CHNS determination of organic liquids and fuels by the FlashSmart Elemental Analyzer Author 2019. <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-42346-ea-chns-organic-liquids-fuels-an42346-en.pdf>. (Accessed 18th November, 2023).
- [126] Gopalakrishnan B, Khanna N, Das D. Dark-Fermentative Biohydrogen Production. 2019. doi:10.1016/b978-0-444-64203-5.00004-6.
- [127] Bloom N, Reenen J Van. Laboratory Manual Chemistry Level III. NBER Work Pap 2013:89.
- [128] ASTM. Standard Test Method for Bulk Density of Densified Particulate Biomass Fuels

- (ASTM E873). ASTM Int 2014;82:2013–4. doi:10.1520/E0873-82R19.3.2.
- [129] Lumay G, Boschini F, Traina K, Bontempi S, Remy JC, Cloots R, et al. Measuring the flowing properties of powders and grains. Powder Technol 2012;224:19–27. doi:10.1016/j.powtec.2012.02.015.
- [130] ASTM. Standard test method for measuring the angle of repose of free-flowing mold powders. ASTM Int 2000:15–6.
- [131] Singh S, Chakraborty JP, Mondal MK. Torrefaction of woody biomass (*Acacia nilotica*): Investigation of fuel and flow properties to study its suitability as a good quality solid fuel. Renew Energy 2020;153:711–24. doi:10.1016/j.renene.2020.02.037.
- [132] Conag AT, Villahermosa JER, Cabatingan LK, Go AW. Energy densification of sugarcane bagasse through torrefaction under minimized oxidative atmosphere. J Environ Chem Eng 2017;5:5411–9. doi:10.1016/j.jece.2017.10.032.
- [133] Perkin Elmer. A Beginner's Guide Introduction. Perkin Elmer 2004:3–19. https://resources.perkinelmer.com/lab-solutions/resources/docs/faq_beginners-guide-to-thermogravimetric-analysis_009380c_01.pdf. (Accessed 21st November, 2023).
- [134] Hoque MK. Ionic conducting oxide materials for clean energy applications: synthesis, structure and conductivity. Chalmers Bibl 2013. doi:10.13140/RG.2.1.2615.9527.
- [135] Nottingham T. Termtanun , Mutsee (2013) Photocatalytic degradation of pesticides using TiO₂ nanoparticles . PhD thesis , University of Nottingham . PHOTOCATALYTIC DEGRADATION OF PESTICIDES USING TIO₂ NANOPARTICLES BY PHILOSOPHY NOVEMBER 2013 2013:239.
- [136] Ahmad A, Ahmad I, Ramzan S, Kiyani MZ, Dubal D, Mubarak NM. Nanomaterial synthesis protocols. Nanomedicine Manuf. Appl., 2021. doi:10.1016/B978-0-12-820773-4.00010-X.
- [137] ZEISS. ZEISS GeminiSEM Family 2015:1–20. <https://www.zeiss.com/microscopy/en/products/sem-fib-sem/sem/sigma.html>. (Accessed 23rd December, 2023).
- [138] Osman AI, Farghali M, Ihara I, Elgarahy AM, Ayyad A, Mehta N, et al. Materials, fuels, upgrading, economy, and life cycle assessment of the pyrolysis of algal and

- lignocellulosic biomass: a review. vol. 21. Springer International Publishing; 2023. doi:10.1007/s10311-023-01573-7.
- [139] Zhang H, Ju S, Jin X, Yuan Y, Wu Y, Nadda AK, et al. A review of sensor applications towards precise control of pyrolysis of solid waste and biomasses. *Renew Sustain Energy Rev* 2022;169:112915. doi:10.1016/j.rser.2022.112915.
- [140] Canché-Escamilla G, Guin-Aguillón L, Duarte-Aranda S, Barahona-Pérez F. Characterization of bio-oil and biochar obtained by pyrolysis at high temperatures from the lignocellulosic biomass of the henequen plant. *J Mater Cycles Waste Manag* 2022;24:751–62. doi:10.1007/s10163-022-01361-5.
- [141] Feng X, Zhuang W-Q, Colletti P, Tang YJ. Metabolic Pathway Determination and Flux Analysis in Nonmodel Microorganisms Through ¹³C-Isotope Labeling. Navid A. *Microb. Syst. Biol. Methods Mol. Biol. (Methods Protoc., 2012, p. 309–30.* doi:10.1007/978-1-61779-827-6_11.
- [142] Bjerrum JT veite. *Metabonomics*. vol. 1277. New York, NY: Springer New York; 2015. doi:10.1007/978-1-4939-2377-9.
- [143] Nanakoudis A. EDX Analysis - SEM - EDS Analysis - Advancing Materials. Thermofisher 2019;1. <https://www.thermofisher.com/in/en/home/global/forms/industrial/edx-analysis-sem.html>. (Accessed 21st December, 2023).
- [144] Poole CF. Gas Chromatography | Detectors. *Encycl Anal Sci* 2016:135–47. doi:10.1016/B978-0-12-409547-2.11719-6.
- [145] marcia l. huber and allan h. harvey. Thermal Conductivity of Gases. *J Fluids Eng* 1954;76:809–16. doi:10.1115/1.4014978.
- [146] Xiao R, Zhang M, Jin B, Huang Y, Zhou H. High-temperature air/steam-blown gasification of coal in a pressurized spout-fluid bed. *Energy and Fuels* 2006;20:715–20. doi:10.1021/ef050233h.
- [147] Hall H. What is Gas Chromatography 2021:2–5. <https://www.ssi.shimadzu.com/service-support/faq/gas-chromatography/what-is-gas-chromatography/index.html#top> (Accessed 2nd January, 2024).

- [148] Yahya S Al, Iqbal T, Omar MM, Ahmad M. Techno-economic analysis of fast pyrolysis of date palm waste for adoption in Saudi Arabia. *Energies* 2021;14. doi:10.3390/en14196048.
- [149] B. Shah J, B. Valaki J. Techno Economic Analysis of Cotton Stalk Biomass Based Bio-Oil Production Using Slow Pyrolysis Process. *J Kejuruter* 2022;34:495–504. doi:10.17576/jkukm-2022-34(3)-16.
- [150] Peters MS, Timmerhaus KD. *PDandEforC Engineers.pdf*. 1991.
- [151] ASCENT INDUSTRIES. Project Report For Pyrolysis of Scrap Tire (A Waste to Energy Project) Products n.d. <https://2.imimg.com/data2/DB/EI/MY-4634954/final.pdf>. (Accessed 7th May, 2024).
- [152] Vyazovkin S. Model-free kinetics. *J Therm Anal Calorim* 2006;83:45–51. doi:10.1007/s10973-005-7044-6.
- [153] Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *J Polym Sci Part C Polym Symp* 1964;6:183–95. doi:10.1002/polc.5070060121.
- [154] Kissinger HE. Reaction Kinetics in Differential Thermal Analysis. *Anal Chem* 1957;29:1702–6. doi:10.1021/ac60131a045.
- [155] Akahira T, Sunose T. Method of determining activation deterioration constant of electrical insulating materials. *Res Rep Chiba Inst Technol* 1971;16.
- [156] Ozawa T. A New Method of Analyzing Thermogravimetric Data. *Bull Chem Soc Jpn* 1965;38:1881–6. doi:10.1246/bcsj.38.1881.
- [157] Flynn JH, Wall LA. A quick, direct method for the determination of activation energy from thermogravimetric data. *J Polym Sci Part B Polym Lett* 1966;4. doi:10.1002/pol.1966.110040504.
- [158] Senum GI, Yang RT. Rational approximations of the integral of the Arrhenius function. *J Therm Anal* 1977;11:445–7. doi:10.1007/BF01903696.
- [159] Miura K, Maki T. A Simple Method for Estimating $f(E)$ and $k_0(E)$ in the Distributed Activation Energy Model. *Energy & Fuels* 1998;12:864–9. doi:10.1021/ef970212q.

- [160] Criado JM, Málek J, Ortega A. Applicability of the master plots in kinetic analysis of non-isothermal data. *Thermochim Acta* 1989;147:377–85. doi:10.1016/0040-6031(89)85192-5.
- [161] Kumari K, Kishore N, Gupta S, Aravind SV, Ahmed G. Effect of varying fraction of polypropylene waste on co-pyrolysis of *Delonix regia* and *Polyalthia longifolia* leaves. *Curr Res Green Sustain Chem* 2022;5:100233. doi:10.1016/j.crgsc.2021.100233.
- [162] Jewiarz M, Mudryk K, Wróbel M, Fraczek J, Dziedzic K. Parameters affecting RDF-based pellet quality. *Energies* 2020;13. doi:10.3390/en13040910.
- [163] Liu Z, Mi B, Jiang Z, Fei B, Cai Z, Liu X. Improved bulk density of bamboo pellets as biomass for energy production. *Renew Energy* 2016;86:1–7. doi:10.1016/j.renene.2015.08.011.
- [164] Akhtar J, Saidina Amin N. A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. *Renew Sustain Energy Rev* 2012;16:5101–9. doi:10.1016/j.rser.2012.05.033.
- [165] Brebu M, Ucar S, Vasile C, Yanik J. Co-pyrolysis of pine cone with synthetic polymers. *Fuel* 2010;89:1911–8. doi:10.1016/j.fuel.2010.01.029.
- [166] Stegen S, Kaparaju P. Effect of temperature on oil quality obtained through pyrolysis of sugarcane bagasse. *Fuel* 2020;276:118112. doi:10.1016/j.fuel.2020.118112.
- [167] Ansari KB, Arora JS, Chew JW, Dauenhauer PJ, Mushrif SH. Effect of Temperature and Transport on the Yield and Composition of Pyrolysis-Derived Bio-Oil from Glucose. *Energy and Fuels* 2018;32:6008–21. doi:10.1021/acs.energyfuels.8b00852.
- [168] Moreira R, dos Reis Orsini R, Vaz JM, Penteado JC, Spinacé E V. Production of Biochar, Bio-Oil and Synthesis Gas from Cashew Nut Shell by Slow Pyrolysis. *Waste and Biomass Valorization* 2017;8:217–24. doi:10.1007/s12649-016-9569-2.
- [169] Gupta S, Kawale HD, Ahmed G, Acharya S, Kishore N. Effect of temperature on catalytic pyrolysis of *Polyalthia Longifolia* leaves solid waste and characterization of their products. *Curr Res Green Sustain Chem* 2021;4:100062. doi:10.1016/j.crgsc.2021.100062.
- [170] Kawale HD, Kishore N. Comprehensive study on thermochemical putrefaction of

- Delonix Regia in non-catalytic, catalytic and hydro-catalytic pyrolysis atmospheres. *Renew Energy* 2021;173:223–36. doi:10.1016/j.renene.2021.03.139.
- [171] Hossain MM, Scott IM, Berruti F, Briens C. A two-dimensional pyrolysis process to concentrate nicotine during tobacco leaf bio-oil production. *Ind Crops Prod* 2018;124:136–41. doi:10.1016/j.indcrop.2018.07.064.
- [172] Mullen CA, Strahan GD, Boateng AA. Characterization of various fast-pyrolysis bio-oils by NMR spectroscopy. *Energy and Fuels* 2009;23:2707–18. doi:10.1021/ef801048b.
- [173] Ateş F, Işıkdağ MA. Influence of temperature and alumina catalyst on pyrolysis of corncob. *Fuel* 2009;88:1991–7. doi:10.1016/j.fuel.2009.03.008.
- [174] Hao N, Ben H, Yoo CG, Adhikari S, Ragauskas AJ. Review of NMR Characterization of Pyrolysis Oils. *Energy and Fuels* 2016;30:6863–80. doi:10.1021/acs.energyfuels.6b01002.
- [175] Merck. NMR Chemical Shifts of Impurities Charts 2022:1–6. <https://www.sigmaaldrich.com/IN/en/technical-documents/technical-article/analytical-chemistry/nuclear-magnetic-resonance/1h-nmr-and-13c-nmr-chemical-shifts-of-impurities-chart>. (Accessed 10th May, 2023).
- [176] Waheed MA, Akogun OA. Quality enhancement of fuel briquette from cornhusk and cassava peel blends for co-firing in coal thermal plant. *Int J Energy Res* 2021;45:1867–78. doi:10.1002/er.5865.
- [177] Ohm TI, Chae JS, Kim JK, Oh SC. Study on the characteristics of biomass for co-combustion in coal power plant. *J Mater Cycles Waste Manag* 2015;17:249–57. doi:10.1007/s10163-014-0334-y.
- [178] Wang Z, Cao J, Wang J. Pyrolytic characteristics of pine wood in a slowly heating and gas sweeping fixed-bed reactor. *J Anal Appl Pyrolysis* 2009;84:179–84. doi:10.1016/j.jaap.2009.02.001.
- [179] Wang G, Fan B, Chen H, Li Y. Understanding the pyrolysis behavior of agriculture, forest and aquatic biomass: Products distribution and characterization. *J Energy Inst* 2020;93:1892–900. doi:10.1016/j.joei.2020.04.004.

- [180] Varma AK, Mondal P. Pyrolysis of sugarcane bagasse in semi batch reactor: Effects of process parameters on product yields and characterization of products. *Ind Crops Prod* 2017;95:704–17. doi:10.1016/j.indcrop.2016.11.039.
- [181] Varma AK, Thakur LS, Shankar R, Mondal P. Pyrolysis of wood sawdust: Effects of process parameters on products yield and characterization of products. *Waste Manag* 2019;89:224–35. doi:10.1016/j.wasman.2019.04.016.
- [182] Taghavi S, Norouzi O, Tavasoli A, Di Maria F, Signoretto M, Menegazzo F, et al. Catalytic conversion of Venice lagoon brown marine algae for producing hydrogen-rich gas and valuable biochemical using algal biochar and Ni/SBA-15 catalyst. *Int J Hydrogen Energy* 2018;43:19918–29. doi:10.1016/j.ijhydene.2018.09.028.
- [183] Yanik J, Stahl R, Troeger N, Sinag A. Pyrolysis of algal biomass. *J Anal Appl Pyrolysis* 2013;103:134–41. doi:10.1016/j.jaap.2012.08.016.
- [184] Jia H, Zhao S, Zhou X, Qu C, Fan D, Wang C. Low-temperature pyrolysis of oily sludge: Roles of Fe/Al-pillared bentonites. *Arch Environ Prot* 2017;43:82–90. doi:10.1515/aep-2017-0027.
- [185] Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007;86:1781–8. doi:10.1016/j.fuel.2006.12.013.
- [186] Sahoo K, Kumar A, Chakraborty JP. A comparative study on valuable products: bio-oil, biochar, non-condensable gases from pyrolysis of agricultural residues. *J Mater Cycles Waste Manag* 2021;23:186–204. doi:10.1007/s10163-020-01114-2.
- [187] Park C, Lee N, Kim J, Lee J. Co-pyrolysis of food waste and wood bark to produce hydrogen with minimizing pollutant emissions. *Environ Pollut* 2021;270:116045. doi:10.1016/j.envpol.2020.116045.
- [188] Ellison CR, Hoff R, Mărculescu C, Boldor D. Investigation of microwave-assisted pyrolysis of biomass with char in a rectangular waveguide applicator with built-in phase-shifting. *Appl Energy* 2020;259. doi:10.1016/j.apenergy.2019.114217.
- [189] Xu S, Cao B, Uzoejinwa BB, Odey EA, Wang S, Shang H, et al. Synergistic effects of catalytic co-pyrolysis of macroalgae with waste plastics. *Process Saf Environ Prot* 2020;137:34–48. doi:10.1016/j.psep.2020.02.001.

- [190] Wang S, Cao B, Feng Y, Sun C, Wang Q, Abomohra AEF, et al. Co-pyrolysis and catalytic co-pyrolysis of Enteromorpha clathrata and rice husk: Toward high-quality products. *J Therm Anal Calorim* 2019;135:2613–23. doi:10.1007/s10973-018-7334-4.
- [191] Czernik S, Bridgwater A V. Overview of applications of biomass fast pyrolysis oil. *Energy and Fuels* 2004;18:590–8. doi:10.1021/ef034067u.
- [192] Price List - Shaikh Petroleum n.d. <https://shaikhpetro.com/price-list/>. <https://shaikhpetro.com/price-list/>. (Accessed on 15th May, 2024).
- [193] Gai C, Dong Y, Zhang T. The kinetic analysis of the pyrolysis of agricultural residue under non-isothermal conditions. *Bioresour Technol* 2013;127:298–305. doi:10.1016/J.BIORTECH.2012.09.089.
- [194] Saha D, Sinha A, Pattanayak S, Roy B. Pyrolysis kinetics and thermodynamic parameters of plastic grocery bag based on thermogravimetric data using iso-conversional methods. *Int J Environ Sci Technol* 2022;19:391–406. doi:10.1007/s13762-020-03106-z.
- [195] Turmanova SC, Genieva SD, Dimitrova AS, Vlaev LT. Non-isothermal degradation kinetics of filled with rice husk ash polypropylene composites. *Express Polym Lett* 2008;2:133–46. doi:10.3144/expresspolymlett.2008.18.
- [196] Varma AK, Lal N, Rathore AK, Katiyar R, Thakur LS, Shankar R, et al. Thermal, kinetic and thermodynamic study for co-pyrolysis of pine needles and styrofoam using thermogravimetric analysis. *Energy* 2021;218:119404. doi:10.1016/j.energy.2020.119404.
- [197] Kaur R, Gera P, Jha MK, Bhaskar T. Pyrolysis kinetics and thermodynamic parameters of castor (*Ricinus communis*) residue using thermogravimetric analysis. *Bioresour Technol* 2018;250:422–8. doi:10.1016/J.BIORTECH.2017.11.077.
- [198] Tao W, Zhang P, Yang X, Li H, Liu Y, Pan B. An integrated study on the pyrolysis mechanism of peanut shell based on the kinetic analysis and solid/gas characterization. *Bioresour Technol* 2021;329:124860. doi:10.1016/J.BIORTECH.2021.124860.
- [199] Li H, Zhou N, Dai L, Cheng Y, Cobb K, Chen P, et al. Effect of lime mud on the reaction kinetics and thermodynamics of biomass pyrolysis. *Bioresour Technol* 2020;310:123475. doi:10.1016/j.biortech.2020.123475.

- [200] Xu Y, Chen B. Investigation of thermodynamic parameters in the pyrolysis conversion of biomass and manure to biochars using thermogravimetric analysis. *Bioresour Technol* 2013;146:485–93. doi:10.1016/J.BIORTECH.2013.07.086.
- [201] Chen J, Wang Y, Lang X, Ren X, Fan S. Evaluation of agricultural residues pyrolysis under non-isothermal conditions: Thermal behaviors, kinetics, and thermodynamics. *Bioresour Technol* 2017;241:340–8. doi:10.1016/j.biortech.2017.05.036.
- [202] Hasan MM, Rasul MG, Ashwath N, Khan MMK, Jahirul MI. Fast pyrolysis of Beauty Leaf Fruit Husk (BLFH) in an auger reactor: Effect of temperature on the yield and physicochemical properties of BLFH oil. *Renew Energy* 2022;194:1098–109. doi:10.1016/j.renene.2022.05.147.
- [203] El Farissi H, Talhaoui A, EL Bachiri A. Influence of pyrolysis process on the production of bio-oil used as alternative green energy from *Pistacia lentiscus* L. *J Anal Appl Pyrolysis* 2022;168:105781. doi:10.1016/j.jaap.2022.105781.
- [204] David E, Kopac J. Pyrolysis of rapeseed oil cake in a fixed bed reactor to produce bio-oil. *J Anal Appl Pyrolysis* 2018;134:495–502. doi:10.1016/j.jaap.2018.07.016.
- [205] Park LKE, Ren S, Yiacoumi S, Ye XP, Borole AP, Tsouris C. Separation of Switchgrass Bio-Oil by Water/Organic Solvent Addition and pH Adjustment. *Energy and Fuels* 2016;30:2164–73. doi:10.1021/acs.energyfuels.5b02537.



Appendices

Appendix A

Table A1 Relevant literature on pyrolysis of lignocellulosic biomass.

Feedstock	Reaction Conditions	Primary results (Yield, calorific value, etc.)	References
<i>Pinus brutia</i>	Fixed bed reactor Temperature: 300-500°C	Maximum calorific value of bio-oil 31.03 MJ/kg at 450°C with a yield of 33.25%.	Şensöz [89]
<i>Prosopis juliflora</i>	Fixed bed reactor Temperature: 300-600°C Atmosphere: Nitrogen	Maximum yield of bio-oil of 38% was found at 500°C and the calorific value was found to be 20.87 MJ/kg.	Baghel et al. [90]
Saw dust (<i>Acacia</i> wood)	Auger reactor Temperature: 400-600°C Atmosphere: Nitrogen	Maximum bio-oil yield of 45.10 wt.% at 500°C while maximum calorific value of 29.871 MJ/kg was achieved at 600°C	Ahmed et al. [91]
Beauty leaf fruit husk	Auger reactor Temperature: 400-550°C Atmosphere: Nitrogen	Maximum bio-oil yield of 45% achieved at 500°C along with a maximum calorific value of 26.8 MJ/kg	Hasan et al. [202]
Paulownia wood (<i>P. tomentosa</i>)	Fixed bed reactor Temperature: 350-600°C Atmosphere: Nitrogen	Maximum yield of 54 wt.% liquid product at 500°C with a calorific value of 28.6 MJ/kg.	Yorgun and Yildiz [92]
Rubber seed cake	Horizontal batch reactor Temperature: 480-520°C Atmosphere: Nitrogen	Maximum bio-oil yield of 59.94% at 500°C with a calorific value of 29.86 MJ/kg.	Sultana et al. [96]
<i>Delonix regia</i>	Fixed bed reactor Temperature: 500-700°C Atmosphere: Nitrogen	Maximum calorific value of 25.70 MJ/kg at a temperature of 700°C and the maximum liquid yield of 38 wt.% at 500°C.	Kawale and Kishore [93]
Cashew nut shell	Fixed bed reactor Atmosphere: Nitrogen and Air	Maximum liquid yield of 40% and calorific value bio-oil was 32 MJ/kg.	Moreira et al. [168]
<i>Pistacia lentiscus</i> L.	Fixed bed reactor Temperature: 300-550°C Atmosphere: Nitrogen	Optimum calorific value of 38.69 MJ/kg with an optimum bio-oil yield of 63.86 wt.% was achieved at 475°C.	El Farissi et al. [203]
<i>Jatropha curcas</i> shells	Fixed bed reactor Temperature: 300-600°C	Maximum bio-oil yield of 31.4 wt.% at 400°C and the calorific value was 30.67 MJ/L.	Das et al. [95]
<i>Carpinus betulus</i> L.	Fixed bed reactor Temperature: 400-600°C Atmosphere: Nitrogen	Maximum bio-oil yield of 24.67% and calorific value bio-oil was 30 MJ/kg was achieved at 550°C.	Morali & Şensöz [94]

Table A2 Relevant literature on fuel phase extraction of bio-oil.

Feedstock	Solvent used	Results	References
Bio-oil from Rapeseed oil cake	400-900°C Solvent: diethyl ether	Maximum bio-oil production of 66.80 wt.% achieved at 500°C with a calorific value of 33.17 MJ/kg.	Ucar and Ozkan [99]
Douglas fir pellets pyrolysis oil	Solvent: ether, hexane and chloroform	Chloroform showed the optimum extraction with solvent to water phase ratio of 1:1 with 66.67 wt.% of organics in the solvent phase. Solvent extracted phase had higher concentrations of phenols, guaiacols with low concentrations of alcohols in comparison to raw bio-oil.	Wei et al. [100]
Bio-oil from switch grass	Extraction using: DI water to separate bio-oil aqueous phase and bio-oil organic phase, followed by extraction using ethyl acetate and chloroform	High portion (60 wt.%) of chemicals was transferred to aqueous phase which have the possibility to be enhanced to hydrocarbon fuels. Maximum organic extraction of 70 wt.% was achieved from aqueous phase was found using diethyl acetate at 2:1 ratio of solvent to aqueous phase.	Ren et al. [101]
Rapeseed oil cake	Temperature: 600°C Solvent: diethyl ether	Maximum fuel phase recovery of 36.2% was achieved at 450°C, while maximum calorific value of 33.13 MJ/kg was found at 500°C.	David & Kopac [204]
<i>Jatropha</i> <i>Curcas</i> seed cake oil	Solvent: benzene, ethyl acetate, chloroform, carbon tetrachloride, DCM, iso-octane, diethyl ether, hexane, xylene and cyclohexane	Ethyl acetate and DCM showed optimum recoveries 3.79 and 3.63 wt.% of different functional groups. Separation of bio-oil phase and solvents occurred on the basis of polarity.	Kanaujia et al. [103]
Switchgrass	Temperature: 500°C Solvent: (hexadecane + octane) and sodium hydroxide	Extracted bio-oil phase contained 37% less oxygen content than the raw bio-oil, while the calorific value of extracted bio-oil phase increased by 100% than the raw bio-oil.	Park et al. [205]
Rice husk	Temperature: 300-600°C Solvent: hexane, ethyl acetate and acetone	Ethyl acetate recovered the maximum bio-oil yield of 35.5% and the calorific value was found to be 14.56 MJ/kg. Solvent extraction of bio-oil improved quality of bio-oil in terms of water content by lowering it to 25.8% from 55%. Optimum extraction was obtained at 10:10:3 (volume ratio) of oil:dichloromethane:water.	Das & Goud [104]
Rice straw pyrolysis oil	Extraction using: DCM as solvent and water as anti-solvent	46.62 wt.% of the flowable organic phase could be separated from the pyrolysis oil. Organic phase obtained had significant constituents of phenols, with low contents of sugars and water as compared to raw bio-oil.	Li et al. [102]
<i>Delonix regia</i>	Temperature: 600°C Solvent: dichloromethane and n-hexane	Extraction of the fuel phase using n-hexane improved the physical property in terms of density and calorific value was found to be 23% higher than that extracted by DCM.	Aravind et al. [40]

Table A3 Relevant literature on kinetics and thermodynamics of pyrolysis of lignocellulosic biomass.

Feedstock	Operating conditions			Critical findings		References
	Temperature range (°C)	Purge gas (ml/min)	Heating rate (°C/min)	Activation energy (kJ/mol)	Thermodynamics properties ΔH (kJ/mol), ΔG (kJ/mol), ΔS (kJ/mol·K)	
<i>Delonix regia</i> pods	29 – 900	Nitrogen, 30	5, 10, 20 and 50	196 -277, 194-234 and 194-236 using DFM, OFW and STK 204.0, 203.2 and 219.3	ΔH : 214 using DFM ΔG : 143 using DFM ΔS : 0.116 using DFM	Balogun et al.[105]
<i>Prosopis juliflora</i>	30-600	Argon, 60	2, 5, 10,15, 20 and 25	using KAS, OFW and DFM 201-364, 292-	-	Chandrasekaran et al. [106]
<i>Moringa oleifera</i> husk	29 – 900	Nitrogen, 30	5, 10, 20 and 50	296 and 199-200 using DFM, OFW and STK	ΔH : 233 using DFM ΔG : 135 using DFM ΔS : 0.152 using DFM	Balogun et al.[105]
<i>Gracilaria lemaneiformis</i>	25-700	Nitrogen, 30	10, 20, 30, 50 and 80	153.79 using OFW	-	Wang et al. [107]
Maize cob	25 – 900	Nitrogen, 60	5, 10 and 20	197.63, 186.06, 185.39 and 185.80 using DFM, OFW, KAS and STK	ΔH : 192.83 and 180.58 using DFM and KAS ΔG : 176.49 and 176.76 using DFM and KAS ΔS : 0.027 and 0.006 using DFM and KAS	G. K. Gupta & Mondal [108]
<i>Tetraselmis sp.</i>	25-800	Nitrogen, 80	5. 10 and 20	334 using DAEM	-	Ceylan & Kazan [109]
Corncob	25 – 900	Nitrogen, 50	10, 20 and 30	240, 238, 241 and 248 using KAS, OFW, STK and DFM	ΔH : 236 and 243 using STK and DFM ΔG : 181 and 181 using STK and DFM ΔS : -0.137 and -0.162 using STK and DFM	Singh et al. [110]

					ΔH : 147.76, 149.71 and 149.70 using KAS, OFW and STK ΔG : 180.55, 181.73 and 181.81 using KAS, OFW and STK ΔS : -0.054, -0.052 and -0.052 using KAS, OFW and STK	
Almond shells	30 – 1000	Nitrogen, 200	10, 25 and 50	153.0, 152.02 and 152.73 using KAS, OFW and STK		Rasool et al. [111]
Cardoon stems	25-850	Nitrogen, 60	5, 10, 20 and 30	224.51 and 229.70 using KAS and OFW	-	Damartzis et al. [112]
<i>Hibiscus cannabinus L.</i>	25-900	Nitrogen, 100	5, 10, 20, 30, 40 and 50	180.51 using DAEM	ΔH : 175.65 using DAEM ΔG : 172.96 using DAEM ΔS : 0.443 using DAEM	Lee et al. [113]
Poplar sawdust	25 – 900	Nitrogen, 100	5, 10, 20 and 40	159, 157, 159, 157 using DFM, STK, OFW and KAS	ΔH : 140.7-230.6 ΔG : 162.0-164.5	Li et al. [114]
<i>Nannochloropsis oculata</i>	25-800	Nitrogen, 80	5, 10 and 20	152.20 by DAEM	-	Ceylan & Kazan [109]
<i>Delonix regia</i>	25 – 1000	Nitrogen, 40	5, 10, 20, 35 and 55	202, 206, 205, 206 and 206 using DFM, KAS, OFW, STK and DAEM	ΔH : 197.14 and 204.7 using DFM and DAEM ΔG : 181.52 and 181.01 using DFM and DAEM	Rammohan et al. [115]

Appendix B

B.1 DETAILED CALCULATIONS FOR ECONOMIC ANALYSIS

Cost of pyrolysis unit batch type (5 tons/day capacity) = INR 76,70,000

Cost of pyrolysis unit batch type (10 tons/day capacity)

$$= 76,70,000 \times \left(\frac{10}{5}\right)^{0.6} = \text{INR } 1,16,25,546$$

Total cost of pyrolysis unit = Cost of pyrolysis unit batch type (10 tons/day capacity) + Freight charges (@5% of cost of the plant+5% tax on freight charges)

$$= 1,16,25,546 + 6,10,341 = \text{INR } 1,22,35,887$$

B1.1 Initial cost of setting up the pyrolysis plant

Initial cost of setting up the pyrolysis plant = cost of pyrolysis unit + cost of shredder + cost of biomass dryer + cost of additional storage tank + cost of backhoe loader + cost of DG set + cost of transformer + cost of installation + cost of shed and civil work + cost of miscellaneous equipment

$$= 1,22,35,887 + 12,00,000 + 3,00,000 + 3,50,000 + 25,00,000 + 6,26,000 + 13,50,000 + 3,00,000 + 25,00,000 + 3,00,000 = \text{INR } 2,16,61,887$$

B1.2 Operating cost

Fixed cost

- Depreciation cost (@11.25% of initial cost of investment per annum)
 $= 0.1125 \times 2,16,61,887 = \text{INR } 24,36,962$
- Interest on investment (@10% of initial cost of investment per annum)
 $= 0.1 \times 2,16,61,887 = \text{INR } 21,66,189$
- Land rent (INR 1,00,000 per annum)
 $= \text{INR } 1,00,000$
- Insurance (@2% of initial cost of investment per annum)
 $= 0.02 \times 2,16,61,887 = \text{INR } 4,33,238$

Total fixed cost = depreciation cost + interest on investment + land rent + insurance

$$= 24,36,962 + 21,66,189 + 1,00,000 + 4,33,238 = \text{INR } 51,36,389$$

Variable cost

- Repair and maintenance cost (@2% of initial cost of investment per annum)
 $= 0.02 \times 2,16,61,887 = \text{INR } 4,33,238$
- Labor cost (01 highly skilled @ INR 697.05 per person per day, 02 skilled @ INR 542.12 per person per day and 09 highly skilled @ INR 433.72 per person per day)
 $= [(1 \times 697.05) + (2 \times 542.12) + (9 \times 433.72)] \times 312 = \text{INR } 17,73,648$
- Biomass waste purchasing and transportation cost (@INR 5 per kg)
 $= 5 \times 10000 \times 312 = \text{INR } 1,56,00,000$
- Cost of electricity for preprocessing and fuelwood for initial investment (@INR 1,70,000 per annum)
 $= \text{INR } 1,70,000$
- Packaging and marketing (@INR 40,000 per annum)
 $= \text{INR } 40,000$
- Acetone for cleaning (20 litres per day @INR 45 per litre)
 $= 20 \times 45 \times 312 = \text{INR } 2,80,800$
- n-hexane for extraction of fuel phase of bio-oil (@INR 58 per litre):
 - For single-feed pyrolysis of EI biomass
 $= 0.26873 \times 0.1 \times 58 \times 10000 \times 312 = \text{INR } 48,62,938$
 - For single-feed pyrolysis of AI biomass
 $= 0.27286 \times 0.1 \times 58 \times 10000 \times 312 = \text{INR } 49,37,675$
 - For co-feed pyrolysis of EI and AI biomass at 1:1 co-feed ratio
 $= 0.31437 \times 0.1 \times 58 \times 10000 \times 312 = \text{INR } 56,88,840$

Total variable cost for single-feed pyrolysis of EI biomass

$$= 4,33,238 + 17,73,648 + 1,56,00,000 + 1,70,000 + 40,000 + 2,80,800 + 48,62,938 \\ = \text{INR } 2,31,60,624$$

Total variable cost for single-feed pyrolysis of AI biomass

$$= 4,33,238 + 17,73,648 + 1,56,00,000 + 1,70,000 + 40,000 + 2,80,800 + 49,37,675 \\ = \text{INR } 2,32,35,361$$

Total variable cost for co-feed pyrolysis of EI and AI biomass at 1:1 co-feed ratio
 = 433238 + 17,73,648 + 1,56,00,000 + 1,70,000 + 40,000 + 2,80,800 + 56,88,840
 = INR 2,39,86,526

Total operating cost = fixed cost + variable cost

- Total operating cost for single-feed pyrolysis of EI biomass
 = 51,36,389 + 2,31,60,624 = INR 2,82,97,013
- Total operating cost for single-feed pyrolysis of AI biomass
 = 51,36,389 + 2,32,35,361 = INR 2,83,71,750
- Total operating cost for co-feed pyrolysis of EI and AI biomass at 1:1 co-feed ratio
 = 51,36,389 + 2,39,86,526 = INR 2,91,22,915

B1.3 Yield of pyrolysis products

Yield of pyrolysis products obtained from single-feed pyrolysis of EI biomass:

- Yield of fuel phase
 wt.% of bio-oil yield: 26.873%
 vol.% of fuel phase: 16.719% = 0.16719
 vol.% of non-fuel phase: 83.595% = 0.83595
 Density of fuel phase: $\rho_{\text{fuel}} = 0.912 \text{ g/mL}$
 Density of non-fuel phase: $\rho_{\text{non-fuel}} = 0.998 \text{ g/mL}$
 Assuming we have 1 mL of the bio-oil mixture
 Volume of fuel phase: $V_{\text{fuel}} = 0.16719 \text{ mL}$
 Volume of non-fuel phase: $V_{\text{non-fuel}} = 0.83595 \text{ mL}$
 Mass of fuel phase: $m_{\text{fuel}} = V_{\text{fuel}} \times \rho_{\text{fuel}}$
 = $0.16719 \text{ mL} \times 0.912 \text{ g/mL} = 0.15247728 \text{ g}$
 Mass of non-fuel phase: $m_{\text{non-fuel}} = V_{\text{non-fuel}} \times \rho_{\text{non-fuel}}$
 = $0.83595 \text{ mL} \times 0.998 \text{ g/mL} = 0.8342781 \text{ g}$
 Total mass = $m_{\text{fuel}} + m_{\text{non-fuel}}$
 = $0.15247728 \text{ g} + 0.8342781 \text{ g} = 0.98675538 \text{ g}$
 wt.% of fuel phase
 = $\left(\frac{m_{\text{fuel}}}{\text{Total mass}} \right) \times 100 = \left(\frac{0.15247728}{0.98675538} \right) \times 100 = 15.452\%$

wt.% of non-fuel phase

$$= \left(\frac{m_{\text{non-fuel}}}{\text{Total mass}} \right) \times 100 = \left(\frac{0.8342781}{0.98675538} \right) \times 100 = 84.547\%$$

Yield of fuel phase per annum

$$= \left(\frac{0.15452 \times 0.26873 \times 10000 \times 312}{0.912} \right) = 142056 \text{ L}$$

➤ Yield of biochar

wt.% of biochar yield: 42.870%

Yield of biochar per annum

$$= 0.42870 \times 10000 \times 312 = 1337544 \text{ kg}$$

➤ Yield of non-condensable gases

wt.% of non-condensable gases yield: 30.257%

Densities of the gases:

Hydrogen (H_2): $d_{\text{H}_2} = 0.0887 \text{ kg/m}^3$

Methane (CH_4): $d_{\text{CH}_4} = 0.7057 \text{ kg/m}^3$

Carbon monoxide (CO): $d_{\text{CO}} = 1.2321 \text{ kg/m}^3$

Carbon dioxide (CO_2): $d_{\text{CO}_2} = 1.9359 \text{ kg/m}^3$

Volume percentages (in decimal form):

Hydrogen: $v_{\text{H}_2} = 16.822\% = 0.16822$

Methane: $v_{\text{CH}_4} = 23.183\% = 0.23183$

Carbon monoxide: $v_{\text{CO}} = 24.664\% = 0.24664$

Carbon dioxide: $v_{\text{CO}_2} = 35.329\% = 0.35329$

Weighted average density of the gas mixture:

$$d_{\text{avg}} = (0.16822 \times 0.0887) + (0.23183 \times 0.7057) + (0.24664 \times 1.2321) + (0.35329 \times 1.9359) = 1.167 \text{ kg/m}^3$$

Yield of non-condensable gases per annum

$$= \left(\frac{0.30257 \times 10000 \times 312}{1.167} \right) = 808928 \text{ m}^3$$

Yield of pyrolysis products obtained from single-feed pyrolysis of AI biomass:

➤ Yield of fuel phase

wt.% of bio-oil yield: 27.286%

vol.% of fuel phase: 13.685% = 0.13685

vol.% of non-fuel phase: 83.089% = 0.83089

Density of fuel phase: $\rho_{\text{fuel}} = 0.870 \text{ g/mL}$

Density of non-fuel phase: $\rho_{\text{non-fuel}} = 1.004 \text{ g/mL}$

Assuming we have 1 mL of the bio-oil mixture

Volume of fuel phase: $V_{\text{fuel}} = 0.13685 \text{ mL}$

Volume of non-fuel phase: $V_{\text{non-fuel}} = 0.83089 \text{ mL}$

Mass of fuel phase: $m_{\text{fuel}} = V_{\text{fuel}} \times \rho_{\text{fuel}}$

$$= 0.13685 \text{ mL} \times 0.870 \text{ g/mL} = 0.119059 \text{ g}$$

Mass of non-fuel phase: $m_{\text{non-fuel}} = V_{\text{non-fuel}} \times \rho_{\text{non-fuel}}$

$$= 0.83089 \text{ mL} \times 1.004 \text{ g/mL} = 0.834213 \text{ g}$$

Total mass = $m_{\text{fuel}} + m_{\text{non-fuel}}$

$$= 0.119059 \text{ g} + 0.834213 \text{ g} = 0.953272 \text{ g}$$

wt.% of fuel phase

$$= \left(\frac{m_{\text{fuel}}}{\text{Total mass}} \right) \times 100 = \left(\frac{0.119059}{0.953272} \right) \times 100 = 12.489\%$$

wt.% of non-fuel phase

$$= \left(\frac{m_{\text{non-fuel}}}{\text{Total mass}} \right) \times 100 = \left(\frac{0.834213}{0.953272} \right) \times 100 = 87.510\%$$

Yield of fuel phase obtained per annum

$$= \left(\frac{0.12489 \times 0.27286 \times 10000 \times 312}{0.870} \right) = 122209 \text{ L}$$

➤ Yield of biochar

wt.% of biochar yield: 41.050%

Yield of biochar per annum

$$= 0.41053 \times 10000 \times 312 = 1280854 \text{ kg}$$

➤ Yield of non-condensable gases

wt.% of non-condensable gases yield: 31.662%

Densities of the gases:

Hydrogen (H_2): $d_{\text{H}_2} = 0.0887 \text{ kg/m}^3$

Methane (CH_4): $d_{\text{CH}_4} = 0.7057 \text{ kg/m}^3$

Carbon monoxide (CO): $d_{\text{CO}} = 1.2321 \text{ kg/m}^3$

Carbon dioxide (CO_2): $d_{\text{CO}_2} = 1.9359 \text{ kg/m}^3$

Volume percentages (in decimal form):

Hydrogen: $v_{H_2} = 15.874\% = 0.15874$

Methane: $v_{CH_4} = 23.849\% = 0.23849$

Carbon monoxide: $v_{CO} = 26.656\% = 0.26656$

Carbon dioxide: $v_{CO_2} = 33.620\% = 0.33620$

Weighted average density of the gas mixture:

$$d_{\text{avg}} = (0.15874 \times 0.0887) + (0.23849 \times 0.7057) + (0.26656 \times 1.2321) + (0.33620 \times 1.9359) = 1.161 \text{ kg/m}^3$$

Yield of non-condensable gases per annum

$$= \left(\frac{0.31662 \times 10000 \times 312}{1.161} \right) = 850865 \text{ m}^3$$

Yield of pyrolysis products obtained from co-feed pyrolysis of EI and AI biomass at 1:1 co-feed ratio:

➤ Yield of fuel phase

wt.% of bio-oil yield: 31.437%

vol.% of fuel phase: 16.698% = 0.16698

vol.% of non-fuel phase: 82.560% = 0.82560

Density of fuel phase: $\rho_{\text{fuel}} = 0.820 \text{ g/mL}$

Density of non-fuel phase: $\rho_{\text{non-fuel}} = 1.005 \text{ g/mL}$

Assuming we have 1 mL of the bio-oil mixture

Volume of fuel phase: $V_{\text{fuel}} = 0.16698 \text{ mL}$

Volume of non-fuel phase: $V_{\text{non-fuel}} = 0.82560 \text{ mL}$

Mass of fuel phase: $m_{\text{fuel}} = V_{\text{fuel}} \times \rho_{\text{fuel}}$

$$= 0.16698 \text{ mL} \times 0.820 \text{ g/mL} = 0.136923 \text{ g}$$

Mass of non-fuel phase: $m_{\text{non-fuel}} = V_{\text{non-fuel}} \times \rho_{\text{non-fuel}}$

$$= 0.82560 \text{ mL} \times 1.005 \text{ g/mL} = 0.829728 \text{ g}$$

Total mass = $m_{\text{fuel}} + m_{\text{non-fuel}}$

$$= 0.136923 \text{ g} + 0.829728 \text{ g} = 0.966651 \text{ g}$$

wt.% of fuel phase

$$= \left(\frac{m_{\text{fuel}}}{\text{Total mass}} \right) \times 100 = \left(\frac{0.136923}{0.966651} \right) \times 100 = 14.165\%$$

wt.% of non-fuel phase

$$= \left(\frac{m_{\text{non-fuel}}}{\text{Total mass}} \right) \times 100 = \left(\frac{0.829728}{0.966651} \right) \times 100 = 85.835\%$$

Yield of fuel phase obtained per annum

$$= \left(\frac{0.14165 \times 0.31437 \times 10000 \times 312}{0.820} \right) = 169433 \text{ L}$$

➤ Yield of biochar

wt.% of biochar yield: 41.662%

Yield of biochar per annum

$$= 0.41662 \times 10000 \times 312 = 1299854 \text{ kg}$$

➤ Yield of non-condensable gases

wt.% of non-condensable gases yield: 26.901%

Densities of the gases:

Hydrogen (H₂): $d_{H_2} = 0.0887 \text{ kg/m}^3$

Methane (CH₄): $d_{CH_4} = 0.7057 \text{ kg/m}^3$

Carbon monoxide (CO): $d_{CO} = 1.2321 \text{ kg/m}^3$

Carbon dioxide (CO₂): $d_{CO_2} = 1.9359 \text{ kg/m}^3$

Volume percentages (in decimal form):

Hydrogen: $v_{H_2} = 7.452\% = 0.07452$

Methane: $v_{CH_4} = 21.332\% = 0.21332$

Carbon monoxide: $v_{CO} = 34.257\% = 0.34257$

Carbon dioxide: $v_{CO_2} = 36.969\% = 0.36969$

Weighted average density of the gas mixture:

$$d_{\text{avg}} = (0.07452 \times 0.0887) + (0.21332 \times 0.7057) + (0.34257 \times 1.2321) + (0.36969 \times 1.9359) = 1.295 \text{ kg/m}^3$$

Yield of non-condensable gases per annum

$$= \left(\frac{0.26901 \times 10000 \times 312}{1.295} \right) = 648117 \text{ m}^3$$

B1.4 Revenue generated by selling pyrolysis products per annum

➤ For single-feed pyrolysis of EI biomass

Revenue generated from fuel phase

$$= 142056 \times 50 = \text{INR } 71,02,800$$

Revenue generated from biochar

$$= 1337544 \times 20 = \text{INR } 2,67,50,880$$

Total revenue generated by selling fuel phase of bio-oil and biochar

$$= 71,02,800 + 2,67,50,880 = \text{INR } 3,38,53,680$$

- For single-feed pyrolysis of AI biomass

Revenue generated from fuel phase

$$= 122209 \times 50 = \text{INR } 61,10,450$$

Revenue generated from biochar

$$= 1280854 \times 20 = \text{INR } 2,56,17,080$$

Total revenue generated by selling fuel phase of bio-oil and biochar

$$= 61,10,450 + 2,56,17,080 = \text{INR } 3,17,27,530$$

- For co-feed pyrolysis of EI and AI biomass at 1:1 co-feed ratio

Revenue generated from fuel phase

$$= 169433 \times 50 = \text{INR } 84,71,650$$

Revenue generated from biochar

$$= 1299854 \times 20 = \text{INR } 2,59,97,080$$

Total revenue generated by selling fuel phase of bio-oil and biochar

$$= 84,71,650 + 2,59,97,080 = \text{INR } 3,44,68,730$$

B1.5 Total revenue saved by using non-condensable gases for heating reactor

- For single-feed pyrolysis of EI biomass

Calorific value of non-condensable gases = 14.486 MJ/Nm^3

Energy generated by combusting the non-condensable gases = 11718124 MJ

Total quantity of fuelwood saved

$$= \left(\frac{11718124}{18} \right) = 651007 \text{ kg}$$

Total revenue saved by using non-condensable gases for heating reactor

$$= 651007 \times 5 = \text{INR } 32,55,034$$

- For single-feed pyrolysis of AI biomass

Calorific value of non-condensable gases = 14.882 MJ/Nm^3

Energy generated by combusting the non-condensable gases = 12662575 MJ

Total quantity of fuelwood saved

$$= \left(\frac{12662575}{18} \right) = 703476 \text{ kg}$$

Total revenue saved by using non-condensable gases for heating reactor

$$= 703476 \times 5 = \text{INR } 35,17,382$$

- For co-feed pyrolysis of EI and AI biomass at co-feed ratio of 1:1

Calorific value of non-condensable gases = 13.761 MJ/Nm³

Energy generated by combusting the non-condensable gases = 8918735 MJ

Total quantity of fuelwood saved

$$= \left(\frac{8918735}{18} \right) = 495485 \text{ kg}$$

Total revenue saved by using non-condensable gases for heating reactor

$$= 495485 \times 5 = \text{INR } 24,77,426$$

B1.6 Minimum fuel selling price

- Minimum fuel selling price of fuel phase obtained from EI biomass

$$= \frac{28297013 - 26750880}{142056} = \text{INR } 10.88$$

- Minimum fuel selling price of fuel phase obtained from AI biomass

$$= \frac{28371750 - 25617080}{122209} = \text{INR } 22.54$$

- Minimum fuel selling price of fuel phase obtained from co-feed pyrolysis of EI and AI biomass at 1:1 co-feed ratio

$$= \frac{29122915 - 25997080}{169433} = \text{INR } 18.45$$

B1.7 Break-even point

- Break-even point for the single-feed pyrolysis project considering EI biomass as feedstock

$$= \frac{21661887}{33853680 - 28297013} = 3.90 \text{ years}$$

- Break-even point for the single-feed pyrolysis project considering AI biomass as feedstock

$$= \frac{21661887}{31727530 - 28371750} = 6.46 \text{ years}$$

- Break-even point for the co-feed pyrolysis project considering EI and AI biomass as feedstock at co-feed ratio of 1:1

$$= \frac{21661887}{34468730 - 29122915} = 4.05 \text{ years}$$

B1.8 Net present value

The net present value for the single-feed and co-feed pyrolysis project are calculated using the following formula:

$$= \sum_{t=0}^T \frac{C}{(1+r)^t}$$

Where, t indicates time period of the project, C indicates annual cash flow and r indicates the discount rate

Initial cost of setting up the pyrolysis plant = INR 2,16,61,887

Discount rate = 10%

Time period of project = 15 years

Salvage value = INR 21,66,189

- For single-feed pyrolysis of EI biomass
Annual cash flow = INR 55,56,667
Net present value = INR +2,11,21,132
- For single-feed pyrolysis of AI biomass
Annual cash flow = INR 33,55,780
Net present value = INR +43,81,010
- For co-feed pyrolysis of EI and AI biomass at co-feed ratio of 1:1
Annual cash flow = INR 53,45,815
Net present value = +1,95,17,375

B1.9 Internal rate of return

The internal rate of return for the single-feed and co-feed pyrolysis project are calculated using the following formula:

$$\sum_{t=0}^T \frac{C}{(1+IRR)^t} = 0$$

Where IRR indicates the internal rate of return

- For single-feed pyrolysis of EI biomass
Annual cash flow = INR 55,56,667
Internal rate of return = 24.83%
- For single-feed pyrolysis of AI biomass
Annual cash flow = INR 33,55,780
Internal rate of return = 13.33%
- For co-feed pyrolysis of EI and AI biomass at co-feed ratio of 1:1
Annual cash flow = INR 53,45,815
Internal rate of return = 23.98%



Appendix C

Table C1 Kinetic data of iso-conversional plots of EI biomass pyrolysis.

Heating rate (°C/min)	Conversion (α)	1/T (K ⁻¹)	DFM $\ln[\beta d\alpha/dT]$	KAS $\ln[\beta/T^2]$	OFW $\ln(\beta)$	STK $\ln[\beta/T^{1.92}]$	DAEM $\ln[\beta/T^2]$
10	0.1	0.00189	-3.204	-10.240	2.303	-9.739	-10.240
20	0.1	0.00185	-2.620	-9.585	2.996	-9.081	-9.585
30	0.1	0.00184	-2.224	-9.198	3.401	-8.694	-9.198
40	0.1	0.00182	-2.008	-8.926	3.689	-8.422	-8.926
10	0.2	0.00182	-2.870	-10.318	2.303	-9.813	-10.318
20	0.2	0.00178	-2.188	-9.665	2.996	-9.158	-9.665
30	0.2	0.00176	-1.790	-9.281	3.401	-8.774	-9.281
40	0.2	0.00175	-1.598	-9.008	3.689	-8.500	-9.008
10	0.3	0.00177	-2.585	-10.372	2.303	-9.865	-10.372
20	0.3	0.00173	-1.935	-9.721	2.996	-9.212	-9.721
30	0.3	0.00171	-1.548	-9.336	3.401	-8.827	-9.336
40	0.3	0.00170	-1.329	-9.064	3.689	-8.553	-9.064
10	0.4	0.00173	-2.311	-10.414	2.303	-9.905	-10.414
20	0.4	0.00169	-1.615	-9.765	2.996	-9.255	-9.765
30	0.4	0.00168	-1.252	-9.377	3.401	-8.866	-9.377
40	0.4	0.00166	-0.935	-9.107	3.689	-8.595	-9.107
10	0.5	0.00171	-2.087	-10.445	2.303	-9.935	-10.445
20	0.5	0.00167	-1.384	-9.796	2.996	-9.284	-9.796
30	0.5	0.00165	-0.992	-9.410	3.401	-8.898	-9.410
40	0.5	0.00164	-0.715	-9.137	3.689	-8.624	-9.137
10	0.6	0.00168	-2.028	-10.472	2.303	-9.961	-10.472
20	0.6	0.00165	-1.322	-9.819	2.996	-9.306	-9.819
30	0.6	0.00163	-0.925	-9.433	3.401	-8.920	-9.433
40	0.6	0.00162	-0.599	-9.160	3.689	-8.646	-9.160
10	0.7	0.00166	-2.339	-10.499	2.303	-9.987	-10.499
20	0.7	0.00163	-1.681	-9.848	2.996	-9.335	-9.848
30	0.7	0.00161	-1.266	-9.463	3.401	-8.948	-9.463
40	0.7	0.00160	-0.877	-9.186	3.689	-8.671	-9.186
10	0.8	0.00160	-3.775	-10.571	2.303	-10.056	-10.571
20	0.8	0.00157	-2.615	-9.912	2.996	-9.396	-9.912
30	0.8	0.00156	-2.635	-9.523	3.401	-9.006	-9.523
40	0.8	0.00156	-2.198	-9.233	3.689	-8.716	-9.233

Table C2 Kinetic data of iso-conversional plots of AI biomass pyrolysis.

Heating rate (°C/min)	Conversion (α)	1/T (K ⁻¹)	DFM $\ln[\beta d\alpha/dT]$	KAS $\ln[\beta/T^2]$	OFW $\ln(\beta)$	STK $\ln[\beta/T^{1.92}]$	DAEM $\ln[\beta/T^2]$
10	0.1	0.00186	-3.059	-10.274	2.303	-9.771	-10.274
20	0.1	0.00182	-2.497	-9.617	2.996	-9.112	-9.617
30	0.1	0.00181	-2.107	-9.224	3.401	-8.719	-9.224
40	0.1	0.00180	-1.782	-8.950	3.689	-8.444	-8.950
10	0.2	0.00179	-2.879	-10.344	2.303	-9.838	-10.344
20	0.2	0.00176	-2.187	-9.688	2.996	-9.181	-9.688
30	0.2	0.00175	-1.783	-9.298	3.401	-8.790	-9.298
40	0.2	0.00174	-1.510	-9.024	3.689	-8.516	-9.024
10	0.3	0.00174	-2.681	-10.400	2.303	-9.892	-10.400
20	0.3	0.00171	-1.999	-9.744	2.996	-9.234	-9.744
30	0.3	0.00170	-1.629	-9.354	3.401	-8.843	-9.354
40	0.3	0.00169	-1.298	-9.082	3.689	-8.572	-9.082
10	0.4	0.00171	-2.416	-10.445	2.303	-9.935	-10.445
20	0.4	0.00168	-1.748	-9.788	2.996	-9.277	-9.788
30	0.4	0.00166	-1.400	-9.401	3.401	-8.888	-9.401
40	0.4	0.00165	-1.074	-9.129	3.689	-8.616	-9.129
10	0.5	0.00168	-2.155	-10.479	2.303	-9.968	-10.479
20	0.5	0.00164	-1.490	-9.825	2.996	-9.312	-9.825
30	0.5	0.00163	-1.152	-9.437	3.401	-8.923	-9.437
40	0.5	0.00162	-0.917	-9.165	3.689	-8.651	-9.165
10	0.6	0.00165	-2.071	-10.506	2.303	-9.993	-10.506
20	0.6	0.00162	-1.365	-9.851	2.996	-9.337	-9.851
30	0.6	0.00161	-1.041	-9.466	3.401	-8.951	-9.466
40	0.6	0.00159	-0.826	-9.194	3.689	-8.679	-9.194
10	0.7	0.00163	-2.222	-10.532	2.303	-10.019	-10.532
20	0.7	0.00160	-1.471	-9.877	2.996	-9.362	-9.877
30	0.7	0.00158	-1.166	-9.495	3.401	-8.979	-9.495
40	0.7	0.00157	-0.888	-9.222	3.689	-8.706	-9.222
10	0.8	0.00160	-3.306	-10.574	2.303	-10.059	-10.574
20	0.8	0.00157	-2.164	-9.911	2.996	-9.395	-9.911
30	0.8	0.00156	-1.830	-9.529	3.401	-9.012	-9.529
40	0.8	0.00154	-1.396	-9.257	3.689	-8.739	-9.257

Table C3 Activation energy (kJ/mol), pre-exponential factor (min⁻¹) and R² values of EI biomass pyrolysis.

Conversion (α)	DFM			KAS			OFW			STK			DAEM		
	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²
0.1	151.183	3.717×10^{13}	0.996	164.329	1.218×10^{15}	0.999	164.781	6.662×10^{12}	0.999	164.556	9.901×10^{14}	0.999	164.329	1.156×10^{16}	0.999
0.2	157.719	6.690×10^{13}	0.998	159.546	1.957×10^{14}	0.999	160.580	1.226×10^{12}	0.999	159.791	1.600×10^{14}	0.999	159.546	8.770×10^{14}	0.999
0.3	155.813	2.670×10^{13}	0.999	160.400	1.404×10^{14}	0.997	161.636	9.178×10^{11}	0.998	160.655	1.150×10^{14}	0.998	160.400	3.937×10^{14}	0.997
0.4	169.203	3.305×10^{14}	0.996	162.059	1.348×10^{14}	0.993	163.409	8.996×10^{11}	0.994	162.321	1.105×10^{14}	0.993	162.059	2.638×10^{14}	0.993
0.5	173.043	6.361×10^{14}	0.997	164.613	1.807×10^{14}	0.995	165.981	1.205×10^{12}	0.995	164.878	1.481×10^{14}	0.995	164.613	2.607×10^{14}	0.995
0.6	191.861	2.354×10^{16}	0.997	177.474	2.164×10^{15}	0.998	178.331	1.278×10^{13}	0.998	177.735	1.765×10^{15}	0.998	177.474	2.362×10^{15}	0.998
0.7	194.618	2.308×10^{16}	0.971	178.723	2.188×10^{15}	0.989	179.644	1.308×10^{13}	0.990	178.987	1.786×10^{15}	0.989	178.723	1.817×10^{15}	0.989
0.8	284.856	8.304×10^{22}	0.888	247.744	6.393×10^{20}	0.919	245.581	2.144×10^{18}	0.925	247.966	5.092×10^{20}	0.920	247.744	3.972×10^{20}	0.919
Avg.	184.787	1.038×10^{22}	0.980	176.861	7.991×10^{19}	0.986	177.493	2.680×10^{17}	0.987	177.111	6.366×10^{19}	0.986	176.861	4.965×10^{19}	0.986

Table C4 Activation energy (kJ/mol), pre-exponential factor (min⁻¹) and R² values of AI biomass pyrolysis.

Conversion (α)	DFM			KAS			OFW			STK			DAEM		
	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²
0.1	185.754	5.267×10^{16}	0.977	195.611	7.980×10^{17}	0.989	194.650	3.195×10^{15}	0.990	195.818	6.404×10^{17}	0.989	195.611	7.574×10^{18}	0.989
0.2	193.435	9.254×10^{16}	0.994	185.911	4.162×10^{16}	0.993	185.741	1.974×10^{14}	0.994	186.139	3.364×10^{16}	0.993	185.911	1.865×10^{17}	0.993
0.3	196.603	7.856×10^{16}	0.997	189.411	4.411×10^{16}	0.995	189.331	2.134×10^{14}	0.995	189.647	3.568×10^{16}	0.995	189.411	1.237×10^{17}	0.995
0.4	188.891	9.943×10^{15}	0.999	187.724	1.769×10^{16}	0.999	187.941	9.108×10^{13}	0.999	187.970	1.435×10^{16}	0.999	187.724	3.464×10^{16}	0.999
0.5	174.678	4.641×10^{14}	0.999	184.723	6.475×10^{15}	0.997	185.252	3.558×10^{13}	0.997	184.979	5.266×10^{15}	0.997	184.723	9.342×10^{15}	0.997
0.6	172.379	2.556×10^{14}	0.997	180.473	2.152×10^{15}	1.000	181.346	1.271×10^{13}	1.000	180.738	1.755×10^{15}	1.000	180.473	2.348×10^{15}	1.000
0.7	178.024	5.724×10^{14}	0.994	176.346	7.548×10^{14}	1.000	177.556	4.792×10^{12}	1.000	176.620	6.175×10^{14}	1.000	176.346	6.269×10^{14}	1.000
0.8	283.318	9.424×10^{22}	0.969	200.703	5.947×10^{16}	0.997	200.910	3.047×10^{14}	0.997	200.965	4.822×10^{16}	0.997	200.703	3.695×10^{16}	0.997
Avg.	196.635	1.178×10^{22}	0.991	187.613	1.213×10^{17}	0.996	187.841	5.068×10^{14}	0.996	187.859	9.749×10^{16}	0.996	187.613	9.961×10^{17}	0.996

Table C5 Enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI biomass pyrolysis.

DFM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	146.286	170.800	-0.042	146.195	170.809	-0.041	146.186	169.093	-0.038	146.103	170.697	-0.040
0.2	152.822	170.593	-0.030	152.730	170.598	-0.030	152.722	168.882	-0.027	152.639	170.482	-0.029
0.3	150.916	170.653	-0.034	150.824	170.659	-0.033	150.816	168.942	-0.030	150.733	170.544	-0.032
0.4	164.306	170.249	-0.010	164.215	170.248	-0.010	164.207	168.530	-0.007	164.123	170.125	-0.010
0.5	168.146	170.139	-0.003	168.055	170.136	-0.003	168.047	168.418	-0.001	167.964	170.011	-0.003
0.6	186.964	169.634	0.029	186.872	169.621	0.029	186.864	167.903	0.032	186.781	169.486	0.028
0.7	189.722	169.564	0.034	189.630	169.550	0.033	189.622	167.831	0.036	189.539	169.414	0.033
0.8	279.959	167.698	0.191	279.868	167.649	0.187	279.860	165.928	0.190	279.776	167.479	0.184
Avg.	179.890	169.916	0.017	179.799	169.909	0.016	179.790	168.191	0.019	179.707	169.780	0.016

KAS												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	159.432	170.392	-0.019	159.341	170.394	-0.018	159.332	168.677	-0.016	159.249	170.273	-0.018
0.2	154.649	170.537	-0.027	154.558	170.541	-0.027	154.550	168.824	-0.024	154.466	170.423	-0.026
0.3	155.504	170.511	-0.025	155.412	170.514	-0.025	155.404	168.797	-0.022	155.321	170.396	-0.025
0.4	157.162	170.460	-0.023	157.071	170.463	-0.022	157.062	168.746	-0.019	156.979	170.344	-0.022
0.5	159.716	170.384	-0.018	159.624	170.385	-0.018	159.616	168.668	-0.015	159.533	170.264	-0.018
0.6	172.577	170.015	0.004	172.486	170.010	0.004	172.478	168.292	0.007	172.395	169.882	0.004
0.7	173.826	169.981	0.007	173.734	169.975	0.006	173.726	168.257	0.009	173.643	169.847	0.006
0.8	242.847	168.382	0.126	242.755	168.346	0.124	242.747	166.625	0.127	242.664	168.188	0.122
Avg.	171.964	170.083	0.003	171.873	170.078	0.003	171.864	168.361	0.006	171.781	169.952	0.003

OFW												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	159.884	170.512	-0.018	159.792	170.380	-0.018	159.784	168.663	-0.015	159.701	170.259	-0.017
0.2	155.683	170.741	-0.025	155.591	170.509	-0.025	155.583	168.792	-0.022	155.500	170.390	-0.024
0.3	156.739	170.683	-0.023	156.648	170.476	-0.023	156.639	168.759	-0.020	156.556	170.357	-0.023
0.4	158.512	170.586	-0.020	158.420	170.422	-0.020	158.412	168.705	-0.017	158.329	170.302	-0.020
0.5	161.084	170.447	-0.016	160.992	170.344	-0.016	160.984	168.627	-0.013	160.901	170.222	-0.015
0.6	173.434	169.794	0.006	173.342	169.986	0.006	173.334	168.268	0.008	173.251	169.858	0.006
0.7	174.747	169.726	0.008	174.656	169.949	0.008	174.647	168.231	0.011	174.564	169.821	0.008
0.8	240.684	166.591	0.123	240.593	168.389	0.120	240.584	166.669	0.123	240.501	168.232	0.118
Avg.	172.596	169.885	0.004	172.504	170.057	0.004	172.496	168.339	0.007	172.413	169.930	0.004

STK												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	159.659	170.385	-0.018	159.459	170.387	-0.018	159.559	168.670	-0.015	159.476	170.266	-0.018
0.2	154.894	170.529	-0.027	154.695	170.533	-0.026	154.794	168.816	-0.023	154.711	170.415	-0.026
0.3	155.758	170.503	-0.025	155.558	170.506	-0.025	155.658	168.790	-0.022	155.575	170.388	-0.024
0.4	157.424	170.452	-0.022	157.224	170.455	-0.022	157.324	168.738	-0.019	157.241	170.336	-0.021
0.5	159.981	170.376	-0.018	159.782	170.377	-0.018	159.882	168.660	-0.015	159.798	170.256	-0.017
0.6	172.838	170.008	0.005	172.638	170.002	0.004	172.738	168.285	0.007	172.655	169.875	0.005
0.7	174.090	169.974	0.007	173.891	169.967	0.007	173.990	168.250	0.010	173.907	169.839	0.007
0.8	243.069	168.377	0.127	242.869	168.341	0.124	242.969	166.621	0.127	242.886	168.183	0.122
Avg.	172.214	170.076	0.004	172.014	170.071	0.003	172.114	168.354	0.006	172.031	169.945	0.003

DAEM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	159.432	170.392	-0.019	159.341	170.394	-0.018	159.332	168.677	-0.016	159.249	170.273	-0.018
0.2	154.649	170.537	-0.027	154.558	170.541	-0.027	154.550	168.824	-0.024	154.466	170.423	-0.026
0.3	155.504	170.511	-0.025	155.412	170.514	-0.025	155.404	168.797	-0.022	155.321	170.396	-0.025
0.4	157.162	170.460	-0.023	157.071	170.463	-0.022	157.062	168.746	-0.019	156.979	170.344	-0.022
0.5	159.716	170.384	-0.018	159.624	170.385	-0.018	159.616	168.668	-0.015	159.533	170.264	-0.018
0.6	172.577	170.015	0.004	172.486	170.010	0.004	172.478	168.292	0.007	172.395	169.882	0.004
0.7	173.826	169.981	0.007	173.734	169.975	0.006	173.726	168.257	0.009	173.643	169.847	0.006
0.8	242.847	168.382	0.126	242.755	168.346	0.124	242.747	166.625	0.127	242.664	168.188	0.122
Avg.	171.964	170.083	0.003	171.873	170.078	0.003	171.864	168.361	0.006	171.781	169.952	0.003

Table C6 Enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for AI biomass pyrolysis.

DFM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	180.757	173.554	0.012	180.657	173.789	0.011	180.641	167.770	0.021	180.566	173.588	0.011
0.2	188.438	173.351	0.025	188.338	173.582	0.024	188.321	167.384	0.034	188.247	173.378	0.024
0.3	191.606	173.270	0.030	191.506	173.499	0.029	191.490	167.227	0.039	191.415	173.293	0.029
0.4	183.894	173.470	0.017	183.795	173.703	0.016	183.778	167.611	0.026	183.703	173.501	0.016
0.5	169.681	173.861	-0.007	169.581	174.102	-0.007	169.565	168.342	0.002	169.490	173.907	-0.007
0.6	167.383	173.927	-0.011	167.283	174.169	-0.011	167.266	168.463	-0.002	167.191	173.976	-0.011
0.7	173.027	173.766	-0.001	172.927	174.005	-0.002	172.911	168.167	0.008	172.836	173.808	-0.002
0.8	278.321	171.444	0.175	278.221	171.637	0.174	278.205	163.339	0.187	278.130	171.398	0.171
Avg.	191.638	173.330	0.030	191.539	173.561	0.029	191.522	167.288	0.039	191.447	173.356	0.029

KAS												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	190.615	173.295	0.029	190.515	173.525	0.028	190.498	172.068	0.030	190.423	173.320	0.027
0.2	180.914	173.549	0.012	180.814	173.784	0.011	180.798	172.328	0.014	180.723	173.584	0.011
0.3	184.414	173.456	0.018	184.314	173.689	0.017	184.298	172.233	0.020	184.223	173.487	0.017
0.4	182.727	173.501	0.015	182.628	173.735	0.015	182.611	172.278	0.017	182.536	173.533	0.014
0.5	179.727	173.581	0.010	179.627	173.817	0.009	179.610	172.361	0.012	179.535	173.617	0.009
0.6	175.476	173.698	0.003	175.377	173.936	0.002	175.360	172.480	0.005	175.285	173.738	0.002
0.7	171.349	173.813	-0.004	171.250	174.053	-0.005	171.233	172.598	-0.002	171.158	173.858	-0.004
0.8	195.706	173.167	0.038	195.606	173.394	0.036	195.590	171.937	0.038	195.515	173.186	0.036
Avg.	182.616	173.508	0.015	182.516	173.742	0.014	182.500	172.285	0.017	182.425	173.540	0.014

OFW												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	189.653	173.320	0.027	189.554	173.550	0.026	189.537	172.093	0.028	189.462	173.345	0.026
0.2	180.745	173.554	0.012	180.645	173.789	0.011	180.628	172.333	0.013	180.554	173.588	0.011
0.3	184.334	173.458	0.018	184.234	173.691	0.017	184.217	172.235	0.019	184.143	173.489	0.017
0.4	182.944	173.495	0.016	182.844	173.729	0.015	182.828	172.273	0.017	182.753	173.527	0.015
0.5	180.255	173.567	0.011	180.156	173.802	0.010	180.139	172.346	0.013	180.064	173.602	0.010
0.6	176.349	173.674	0.004	176.249	173.911	0.004	176.232	172.455	0.006	176.158	173.713	0.004
0.7	172.560	173.779	-0.002	172.460	174.019	-0.003	172.443	172.563	0.000	172.368	173.822	-0.002
0.8	195.914	173.162	0.038	195.814	173.389	0.037	195.797	171.931	0.039	195.722	173.181	0.036
Avg.	182.844	173.501	0.016	182.744	173.735	0.015	182.728	172.279	0.017	182.653	173.533	0.015

STK												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	190.821	173.290	0.029	190.722	173.520	0.028	190.705	172.063	0.030	190.630	173.314	0.028
0.2	181.142	173.543	0.013	181.042	173.778	0.012	181.025	172.322	0.014	180.951	173.577	0.012
0.3	184.650	173.450	0.019	184.550	173.683	0.018	184.534	172.226	0.020	184.459	173.480	0.018
0.4	182.974	173.494	0.016	182.874	173.728	0.015	182.857	172.272	0.017	182.782	173.526	0.015
0.5	179.982	173.575	0.011	179.882	173.810	0.010	179.866	172.354	0.012	179.791	173.610	0.010
0.6	175.741	173.690	0.003	175.641	173.928	0.003	175.625	172.472	0.005	175.550	173.730	0.003
0.7	171.623	173.806	-0.004	171.523	174.046	-0.004	171.506	172.590	-0.002	171.432	173.850	-0.004
0.8	195.968	173.160	0.038	195.869	173.387	0.037	195.852	171.930	0.039	195.777	173.180	0.036
Avg.	182.863	173.501	0.016	182.763	173.735	0.015	182.746	172.279	0.017	182.671	173.533	0.015

DAEM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	190.615	173.295	0.029	190.515	173.525	0.028	190.498	172.068	0.030	190.423	173.320	0.027
0.2	180.914	173.549	0.012	180.814	173.784	0.011	180.798	172.328	0.014	180.723	173.584	0.011
0.3	184.414	173.456	0.018	184.314	173.689	0.017	184.298	172.233	0.020	184.223	173.487	0.017
0.4	182.727	173.501	0.015	182.628	173.735	0.015	182.611	172.278	0.017	182.536	173.533	0.014
0.5	179.727	173.581	0.010	179.627	173.817	0.009	179.610	172.361	0.012	179.535	173.617	0.009
0.6	175.476	173.698	0.003	175.377	173.936	0.002	175.360	172.480	0.005	175.285	173.738	0.002
0.7	171.349	173.813	-0.004	171.250	174.053	-0.005	171.233	172.598	-0.002	171.158	173.858	-0.004
0.8	195.706	173.167	0.038	195.606	173.394	0.036	195.590	171.937	0.038	195.515	173.186	0.036
Avg.	182.616	173.508	0.015	182.516	173.742	0.014	182.500	172.285	0.017	182.425	173.540	0.014

Table C7 Kinetic data of iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:4.

Heating rate (°C/min)	Conversion (α)	1/T (K ⁻¹)	DFM $\ln[\beta d\alpha/dT]$	KAS $\ln[\beta/T^2]$	OFW $\ln(\beta)$	STK $\ln[\beta/T^{1.92}]$	DAEM $\ln[\beta/T^2]$
10	0.1	0.00185	-3.147	-10.278	2.303	-9.775	-10.278
20	0.1	0.00182	-2.470	-9.624	2.996	-9.120	-9.624
30	0.1	0.00180	-2.098	-9.238	3.401	-8.732	-9.238
40	0.1	0.00179	-1.905	-8.964	3.689	-8.458	-8.964
10	0.2	0.00179	-2.811	-10.344	2.303	-9.838	-10.344
20	0.2	0.00176	-2.139	-9.692	2.996	-9.185	-9.692
30	0.2	0.00174	-1.732	-9.309	3.401	-8.800	-9.309
40	0.2	0.00172	-1.505	-9.038	3.689	-8.529	-9.038
10	0.3	0.00174	-2.672	-10.401	2.303	-9.892	-10.401
20	0.3	0.00171	-1.947	-9.748	2.996	-9.238	-9.748
30	0.3	0.00169	-1.614	-9.363	3.401	-8.853	-9.363
40	0.3	0.00168	-1.371	-9.092	3.689	-8.581	-9.092
10	0.4	0.00171	-2.458	-10.445	2.303	-9.935	-10.445
20	0.4	0.00167	-1.766	-9.795	2.996	-9.283	-9.795
30	0.4	0.00165	-1.424	-9.410	3.401	-8.898	-9.410
40	0.4	0.00164	-1.151	-9.139	3.689	-8.626	-9.139
10	0.5	0.00167	-2.250	-10.483	2.303	-9.971	-10.483
20	0.5	0.00164	-1.556	-9.828	2.996	-9.315	-9.828
30	0.5	0.00162	-1.208	-9.446	3.401	-8.932	-9.446
40	0.5	0.00161	-1.018	-9.175	3.689	-8.660	-9.175
10	0.6	0.00165	-2.177	-10.512	2.303	-10.000	-10.512
20	0.6	0.00162	-1.477	-9.857	2.996	-9.343	-9.857
30	0.6	0.00160	-1.078	-9.478	3.401	-8.963	-9.478
40	0.6	0.00158	-0.827	-9.206	3.689	-8.691	-9.206
10	0.7	0.00162	-2.193	-10.542	2.303	-10.028	-10.542
20	0.7	0.00159	-1.490	-9.886	2.996	-9.371	-9.886
30	0.7	0.00158	-0.988	-9.504	3.401	-8.988	-9.504
40	0.7	0.00156	-0.790	-9.235	3.689	-8.718	-9.235
10	0.8	0.00160	-2.403	-10.571	2.303	-10.056	-10.571
20	0.8	0.00157	-1.664	-9.915	2.996	-9.398	-9.915
30	0.8	0.00155	-1.212	-9.532	3.401	-9.015	-9.532
40	0.8	0.00154	-0.960	-9.263	3.689	-8.745	-9.263

Table C8 Kinetic data of iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:3.

Heating rate (°C/min)	Conversion (α)	1/T (K ⁻¹)	DFM $\ln[\beta d\alpha/dT]$	KAS $\ln[\beta/T^2]$	OFW $\ln(\beta)$	STK $\ln[\beta/T^{1.92}]$	DAEM $\ln[\beta/T^2]$
10	0.1	0.00185	-3.107	-10.282	2.303	-9.779	-10.282
20	0.1	0.00182	-2.481	-9.617	2.996	-9.113	-9.617
30	0.1	0.00180	-2.086	-9.237	3.401	-8.732	-9.237
40	0.1	0.00179	-1.821	-8.963	3.689	-8.457	-8.963
10	0.2	0.00179	-2.802	-10.348	2.303	-9.842	-10.348
20	0.2	0.00176	-2.145	-9.689	2.996	-9.181	-9.689
30	0.2	0.00174	-1.737	-9.308	3.401	-8.800	-9.308
40	0.2	0.00173	-1.452	-9.034	3.689	-8.525	-9.034
10	0.3	0.00174	-2.639	-10.404	2.303	-9.896	-10.404
20	0.3	0.00171	-2.005	-9.741	2.996	-9.232	-9.741
30	0.3	0.00169	-1.592	-9.363	3.401	-8.852	-9.363
40	0.3	0.00168	-1.384	-9.088	3.689	-8.577	-9.088
10	0.4	0.00170	-2.436	-10.449	2.303	-9.939	-10.449
20	0.4	0.00167	-1.785	-9.788	2.996	-9.277	-9.788
30	0.4	0.00165	-1.412	-9.410	3.401	-8.897	-9.410
40	0.4	0.00164	-1.125	-9.135	3.689	-8.622	-9.135
10	0.5	0.00167	-2.222	-10.483	2.303	-9.971	-10.483
20	0.5	0.00164	-1.567	-9.825	2.996	-9.312	-9.825
30	0.5	0.00162	-1.196	-9.446	3.401	-8.932	-9.446
40	0.5	0.00161	-0.836	-9.171	3.689	-8.656	-9.171
10	0.6	0.00165	-2.147	-10.512	2.303	-10.000	-10.512
20	0.6	0.00162	-1.470	-9.854	2.996	-9.340	-9.854
30	0.6	0.00160	-0.966	-9.475	3.401	-8.960	-9.475
40	0.6	0.00159	-0.724	-9.199	3.689	-8.684	-9.199
10	0.7	0.00162	-2.215	-10.542	2.303	-10.028	-10.542
20	0.7	0.00160	-1.501	-9.883	2.996	-9.368	-9.883
30	0.7	0.00158	-1.090	-9.503	3.401	-8.987	-9.503
40	0.7	0.00157	-0.864	-9.228	3.689	-8.711	-9.228
10	0.8	0.00160	-2.460	-10.574	2.303	-10.059	-10.574
20	0.8	0.00157	-1.698	-9.912	2.996	-9.396	-9.912
30	0.8	0.00155	-1.247	-9.532	3.401	-9.014	-9.532
40	0.8	0.00154	-1.057	-9.259	3.689	-8.741	-9.259

Table C9 Kinetic data of iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:2.

Heating rate (°C/min)	Conversion (α)	1/T (K ⁻¹)	DFM $\ln[\beta d\alpha/dT]$	KAS $\ln[\beta/T^2]$	OFW $\ln(\beta)$	STK $\ln[\beta/T^{1.92}]$	DAEM $\ln[\beta/T^2]$
10	0.1	0.00185	-3.139	-10.278	2.303	-9.775	-10.278
20	0.1	0.00182	-2.478	-9.621	2.996	-9.116	-9.621
30	0.1	0.00181	-2.112	-9.231	3.401	-8.725	-9.231
40	0.1	0.00180	-1.834	-8.956	3.689	-8.451	-8.956
10	0.2	0.00179	-2.835	-10.343	2.303	-9.838	-10.343
20	0.2	0.00176	-2.133	-9.692	2.996	-9.185	-9.692
30	0.2	0.00174	-1.744	-9.302	3.401	-8.793	-9.302
40	0.2	0.00173	-1.518	-9.027	3.689	-8.518	-9.027
10	0.3	0.00174	-2.638	-10.400	2.303	-9.892	-10.400
20	0.3	0.00171	-1.961	-9.744	2.996	-9.235	-9.744
30	0.3	0.00170	-1.578	-9.357	3.401	-8.846	-9.357
40	0.3	0.00169	-1.385	-9.082	3.689	-8.571	-9.082
10	0.4	0.00171	-2.393	-10.442	2.303	-9.932	-10.442
20	0.4	0.00167	-1.737	-9.788	2.996	-9.277	-9.788
30	0.4	0.00166	-1.313	-9.400	3.401	-8.888	-9.400
40	0.4	0.00165	-1.085	-9.128	3.689	-8.616	-9.128
10	0.5	0.00168	-2.171	-10.475	2.303	-9.964	-10.475
20	0.5	0.00165	-1.508	-9.821	2.996	-9.309	-9.821
30	0.5	0.00163	-1.139	-9.436	3.401	-8.923	-9.436
40	0.5	0.00162	-0.823	-9.164	3.689	-8.650	-9.164
10	0.6	0.00165	-2.121	-10.505	2.303	-9.993	-10.505
20	0.6	0.00162	-1.408	-9.851	2.996	-9.337	-9.851
30	0.6	0.00161	-1.045	-9.466	3.401	-8.951	-9.466
40	0.6	0.00159	-0.739	-9.193	3.689	-8.678	-9.193
10	0.7	0.00163	-2.248	-10.532	2.303	-10.018	-10.532
20	0.7	0.00160	-1.507	-9.877	2.996	-9.362	-9.877
30	0.7	0.00158	-1.166	-9.494	3.401	-8.979	-9.494
40	0.7	0.00157	-0.860	-9.222	3.689	-8.705	-9.222
10	0.8	0.00160	-2.496	-10.567	2.303	-10.053	-10.567
20	0.8	0.00158	-1.744	-9.908	2.996	-9.392	-9.908
30	0.8	0.00156	-1.377	-9.526	3.401	-9.009	-9.526
40	0.8	0.00155	-1.105	-9.250	3.689	-8.732	-9.250

Table C10 Kinetic data of iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 1:1.

Heating rate (°C/min)	Conversion (α)	1/T (K ⁻¹)	DFM $\ln[\beta d\alpha/dT]$	KAS $\ln[\beta/T^2]$	OFW $\ln(\beta)$	STK $\ln[\beta/T^{1.92}]$	DAEM $\ln[\beta/T^2]$
10	0.1	0.00186	-3.174	-10.270	2.303	-9.767	-10.270
20	0.1	0.00183	-2.511	-9.614	2.996	-9.109	-9.614
30	0.1	0.00181	-2.124	-9.231	3.401	-8.726	-9.231
40	0.1	0.00179	-1.805	-8.962	3.689	-8.456	-8.962
10	0.2	0.00180	-2.836	-10.340	2.303	-9.834	-10.340
20	0.2	0.00176	-2.124	-9.686	2.996	-9.178	-9.686
30	0.2	0.00174	-1.745	-9.302	3.401	-8.794	-9.302
40	0.2	0.00173	-1.466	-9.032	3.689	-8.523	-9.032
10	0.3	0.00175	-2.622	-10.393	2.303	-9.885	-10.393
20	0.3	0.00172	-1.961	-9.738	2.996	-9.229	-9.738
30	0.3	0.00170	-1.540	-9.357	3.401	-8.847	-9.357
40	0.3	0.00168	-1.222	-9.086	3.689	-8.575	-9.086
10	0.4	0.00171	-2.376	-10.438	2.303	-9.928	-10.438
20	0.4	0.00168	-1.725	-9.782	2.996	-9.271	-9.782
30	0.4	0.00166	-1.323	-9.401	3.401	-8.889	-9.401
40	0.4	0.00165	-1.054	-9.130	3.689	-8.617	-9.130
10	0.5	0.00168	-2.148	-10.472	2.303	-9.961	-10.472
20	0.5	0.00165	-1.493	-9.815	2.996	-9.303	-9.815
30	0.5	0.00163	-1.085	-9.434	3.401	-8.920	-9.434
40	0.5	0.00162	-0.774	-9.162	3.689	-8.648	-9.162
10	0.6	0.00166	-2.087	-10.499	2.303	-9.987	-10.499
20	0.6	0.00163	-1.405	-9.845	2.996	-9.331	-9.845
30	0.6	0.00161	-0.973	-9.459	3.401	-8.945	-9.459
40	0.6	0.00160	-0.744	-9.191	3.689	-8.676	-9.191
10	0.7	0.00164	-2.295	-10.528	2.303	-10.015	-10.528
20	0.7	0.00161	-1.517	-9.871	2.996	-9.356	-9.871
30	0.7	0.00159	-1.060	-9.485	3.401	-8.970	-9.485
40	0.7	0.00158	-0.808	-9.217	3.689	-8.701	-9.217
10	0.8	0.00161	-2.554	-10.561	2.303	-10.046	-10.561
20	0.8	0.00158	-1.807	-9.906	2.996	-9.390	-9.906
30	0.8	0.00157	-1.409	-9.517	3.401	-9.000	-9.517
40	0.8	0.00155	-1.149	-9.248	3.689	-8.731	-9.248

Table C11 Kinetic data of iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 2:1.

Heating rate (°C/min)	Conversion (α)	1/T (K ⁻¹)	DFM $\ln[\beta d\alpha/dT]$	KAS $\ln[\beta/T^2]$	OFW $\ln(\beta)$	STK $\ln[\beta/T^{1.92}]$	DAEM $\ln[\beta/T^2]$
10	0.1	0.00186	-3.131	-10.271	2.303	-9.768	-10.271
20	0.1	0.00185	-2.447	-9.584	2.996	-9.081	-9.584
30	0.1	0.00181	-2.120	-9.223	3.401	-8.718	-9.223
40	0.1	0.00180	-1.790	-8.950	3.689	-8.445	-8.950
10	0.2	0.00180	-2.763	-10.341	2.303	-9.835	-10.341
20	0.2	0.00179	-1.998	-9.654	2.996	-9.148	-9.654
30	0.2	0.00175	-1.719	-9.294	3.401	-8.786	-9.294
40	0.2	0.00174	-1.501	-9.021	3.689	-8.512	-9.021
10	0.3	0.00175	-2.586	-10.394	2.303	-9.886	-10.394
20	0.3	0.00175	-1.815	-9.700	2.996	-9.192	-9.700
30	0.3	0.00170	-1.422	-9.349	3.401	-8.839	-9.349
40	0.3	0.00169	-1.248	-9.076	3.689	-8.565	-9.076
10	0.4	0.00171	-2.343	-10.435	2.303	-9.926	-10.435
20	0.4	0.00171	-1.650	-9.741	2.996	-9.232	-9.741
30	0.4	0.00167	-1.339	-9.390	3.401	-8.878	-9.390
40	0.4	0.00165	-1.051	-9.119	3.689	-8.607	-9.119
10	0.5	0.00169	-2.088	-10.466	2.303	-9.955	-10.466
20	0.5	0.00169	-1.539	-9.772	2.996	-9.261	-9.772
30	0.5	0.00164	-1.086	-9.426	3.401	-8.913	-9.426
40	0.5	0.00163	-0.785	-9.155	3.689	-8.642	-9.155
10	0.6	0.00167	-2.011	-10.493	2.303	-9.981	-10.493
20	0.6	0.00166	-1.556	-9.805	2.996	-9.293	-9.805
30	0.6	0.00162	-0.969	-9.452	3.401	-8.938	-9.452
40	0.6	0.00160	-0.769	-9.181	3.689	-8.666	-9.181
10	0.7	0.00165	-2.160	-10.516	2.303	-10.003	-10.516
20	0.7	0.00163	-1.752	-9.838	2.996	-9.325	-9.838
30	0.7	0.00160	-0.946	-9.478	3.401	-8.963	-9.478
40	0.7	0.00158	-0.723	-9.210	3.689	-8.694	-9.210
10	0.8	0.00162	-2.656	-10.552	2.303	-10.038	-10.552
20	0.8	0.00160	-2.209	-9.880	2.996	-9.365	-9.880
30	0.8	0.00157	-1.457	-9.509	3.401	-8.993	-9.509
40	0.8	0.00156	-1.161	-9.238	3.689	-8.721	-9.238

Table C12 Kinetic data of iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 3:1.

Heating rate (°C/min)	Conversion (α)	1/T (K ⁻¹)	DFM $\ln[\beta d\alpha/dT]$	KAS $\ln[\beta/T^2]$	OFW $\ln(\beta)$	STK $\ln[\beta/T^{1.92}]$	DAEM $\ln[\beta/T^2]$
10	0.1	0.00187	-3.154	-10.262	2.303	-9.760	-10.262
20	0.1	0.00185	-2.500	-9.592	2.996	-9.089	-9.592
30	0.1	0.00183	-2.102	-9.208	3.401	-8.703	-9.208
40	0.1	0.00181	-1.849	-8.935	3.689	-8.430	-8.935
10	0.2	0.00180	-2.785	-10.332	2.303	-9.827	-10.332
20	0.2	0.00178	-2.104	-9.661	2.996	-9.155	-9.661
30	0.2	0.00177	-1.687	-9.276	3.401	-8.769	-9.276
40	0.2	0.00175	-1.437	-9.010	3.689	-8.502	-9.010
10	0.3	0.00176	-2.563	-10.382	2.303	-9.875	-10.382
20	0.3	0.00174	-1.872	-9.714	2.996	-9.206	-9.714
30	0.3	0.00172	-1.518	-9.328	3.401	-8.819	-9.328
40	0.3	0.00170	-1.212	-9.062	3.689	-8.552	-9.062
10	0.4	0.00172	-2.308	-10.424	2.303	-9.915	-10.424
20	0.4	0.00170	-1.684	-9.755	2.996	-9.245	-9.755
30	0.4	0.00168	-1.339	-9.373	3.401	-8.862	-9.373
40	0.4	0.00167	-1.045	-9.106	3.689	-8.594	-9.106
10	0.5	0.00170	-2.062	-10.455	2.303	-9.944	-10.455
20	0.5	0.00167	-1.499	-9.789	2.996	-9.278	-9.789
30	0.5	0.00166	-1.134	-9.406	3.401	-8.894	-9.406
40	0.5	0.00164	-0.886	-9.139	3.689	-8.626	-9.139
10	0.6	0.00167	-2.004	-10.482	2.303	-9.970	-10.482
20	0.6	0.00165	-1.410	-9.816	2.996	-9.303	-9.816
30	0.6	0.00163	-0.989	-9.436	3.401	-8.922	-9.436
40	0.6	0.00161	-0.609	-9.168	3.689	-8.654	-9.168
10	0.7	0.00165	-2.158	-10.508	2.303	-9.996	-10.508
20	0.7	0.00163	-1.535	-9.845	2.996	-9.332	-9.845
30	0.7	0.00161	-1.032	-9.462	3.401	-8.947	-9.462
40	0.7	0.00159	-0.645	-9.194	3.689	-8.678	-9.194
10	0.8	0.00163	-2.746	-10.541	2.303	-10.027	-10.541
20	0.8	0.00160	-1.991	-9.881	2.996	-9.366	-9.881
30	0.8	0.00158	-1.463	-9.494	3.401	-8.978	-9.494
40	0.8	0.00157	-1.089	-9.222	3.689	-8.706	-9.222

Table C13 Kinetic data of iso-conversional plots of EI and AI biomass pyrolysis at co-feed ratio of 4:1.

Heating rate (°C/min)	Conversion (α)	1/T (K ⁻¹)	DFM $\ln[\beta d\alpha/dT]$	KAS $\ln[\beta/T^2]$	OFW $\ln(\beta)$	STK $\ln[\beta/T^{1.92}]$	DAEM $\ln[\beta/T^2]$
10	0.1	0.00187	-3.193	-10.260	2.303	-9.757	-10.260
20	0.1	0.00184	-2.532	-9.599	2.996	-9.095	-9.599
30	0.1	0.00183	-2.008	-9.209	3.401	-8.704	-9.209
40	0.1	0.00181	-1.854	-8.935	3.689	-8.430	-8.935
10	0.2	0.00180	-2.825	-10.333	2.303	-9.828	-10.333
20	0.2	0.00177	-2.145	-9.675	2.996	-9.168	-9.675
30	0.2	0.00177	-1.514	-9.273	3.401	-8.766	-9.273
40	0.2	0.00175	-1.328	-9.003	3.689	-8.495	-9.003
10	0.3	0.00176	-2.578	-10.386	2.303	-9.879	-10.386
20	0.3	0.00173	-1.944	-9.727	2.996	-9.218	-9.727
30	0.3	0.00173	-1.316	-9.315	3.401	-8.807	-9.315
40	0.3	0.00171	-1.097	-9.051	3.689	-8.542	-9.051
10	0.4	0.00172	-2.310	-10.428	2.303	-9.919	-10.428
20	0.4	0.00169	-1.669	-9.772	2.996	-9.261	-9.772
30	0.4	0.00170	-1.179	-9.353	3.401	-8.843	-9.353
40	0.4	0.00168	-1.030	-9.092	3.689	-8.581	-9.092
10	0.5	0.00169	-2.085	-10.459	2.303	-9.948	-10.459
20	0.5	0.00166	-1.438	-9.802	2.996	-9.290	-9.802
30	0.5	0.00167	-1.091	-9.383	3.401	-8.872	-9.383
40	0.5	0.00165	-0.796	-9.125	3.689	-8.613	-9.125
10	0.6	0.00167	-1.971	-10.482	2.303	-9.971	-10.482
20	0.6	0.00164	-1.295	-9.828	2.996	-9.315	-9.828
30	0.6	0.00165	-1.099	-9.413	3.401	-8.901	-9.413
40	0.6	0.00163	-0.687	-9.155	3.689	-8.641	-9.155
10	0.7	0.00165	-2.157	-10.509	2.303	-9.997	-10.509
20	0.7	0.00162	-1.418	-9.854	2.996	-9.340	-9.854
30	0.7	0.00163	-1.258	-9.443	3.401	-8.929	-9.443
40	0.7	0.00160	-0.800	-9.180	3.689	-8.666	-9.180
10	0.8	0.00162	-2.817	-10.545	2.303	-10.031	-10.545
20	0.8	0.00160	-1.945	-9.883	2.996	-9.368	-9.883
30	0.8	0.00159	-1.913	-9.488	3.401	-8.972	-9.488
40	0.8	0.00158	-1.125	-9.209	3.689	-8.693	-9.209

Table C14 Activation energy (kJ/mol), pre-exponential factor (min⁻¹) and R² values of EI and AI biomass pyrolysis at co-feed ratio of 1:4.

Conversion (α)	DFM			KAS			OFW			STK			DAEM		
	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²
0.1	159.312	1.281×10^{14}	0.998	165.698	7.885×10^{14}	0.997	166.245	4.404×10^{12}	0.997	165.931	6.417×10^{14}	0.997	165.698	7.484×10^{15}	0.997
0.2	155.907	3.067×10^{13}	0.998	154.211	3.740×10^{13}	0.999	155.629	2.571×10^{11}	0.999	154.466	3.070×10^{13}	0.999	154.211	1.676×10^{14}	0.999
0.3	162.770	6.755×10^{13}	0.998	163.294	1.589×10^{14}	0.999	164.519	1.031×10^{12}	0.999	163.551	1.301×10^{14}	0.999	163.294	4.454×10^{14}	0.999
0.4	162.720	4.441×10^{13}	1.000	163.150	9.793×10^{13}	0.998	164.595	6.655×10^{11}	0.998	163.417	8.036×10^{13}	0.998	163.150	1.917×10^{14}	0.998
0.5	161.091	2.639×10^{13}	0.995	168.798	2.269×10^{14}	1.000	170.142	1.496×10^{12}	1.000	169.068	1.860×10^{14}	1.000	168.798	3.274×10^{14}	1.000
0.6	172.397	2.047×10^{14}	0.998	165.657	9.338×10^{13}	0.999	167.306	6.581×10^{11}	0.999	165.936	7.674×10^{13}	0.999	165.657	1.019×10^{14}	0.999
0.7	190.637	5.743×10^{15}	0.991	173.475	3.562×10^{14}	0.999	174.882	2.360×10^{12}	0.999	173.754	2.920×10^{14}	0.999	173.475	2.959×10^{14}	0.999
0.8	199.036	2.065×10^{16}	0.996	178.641	7.903×10^{14}	0.999	179.936	5.085×10^{12}	0.999	178.921	6.470×10^{14}	0.999	178.641	4.911×10^{14}	0.999
Avg.	170.484	3.362×10^{15}	0.997	166.616	3.187×10^{14}	0.999	167.907	1.995×10^{12}	0.999	166.880	2.606×10^{14}	0.999	166.616	1.188×10^{15}	0.999

Table C15 Activation energy (kJ/mol), pre-exponential factor (min⁻¹) and R² values of EI and AI biomass pyrolysis at co-feed ratio of 1:3.

Conversion (α)	DFM			KAS			OFW			STK			DAEM		
	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²
0.1	170.497	1.552×10^{15}	0.994	173.980	5.167×10^{15}	0.991	174.131	2.631×10^{13}	0.992	174.206	4.188×10^{15}	0.991	173.980	4.904×10^{16}	0.991
0.2	173.469	1.286×10^{15}	0.999	168.623	8.715×10^{14}	0.998	169.335	5.037×10^{12}	0.998	168.865	7.102×10^{14}	0.998	168.623	3.906×10^{15}	0.998
0.3	171.217	3.935×10^{14}	0.994	176.157	2.487×10^{15}	0.991	176.755	1.394×10^{13}	0.992	176.405	2.024×10^{15}	0.991	176.157	6.973×10^{15}	0.991
0.4	175.313	5.785×10^{14}	0.994	176.291	1.526×10^{15}	0.995	177.095	8.926×10^{12}	0.995	176.548	1.244×10^{15}	0.995	176.291	2.987×10^{15}	0.995
0.5	181.168	1.499×10^{15}	0.990	174.531	7.504×10^{14}	0.997	175.587	4.630×10^{12}	0.997	174.796	6.132×10^{14}	0.997	174.531	1.083×10^{15}	0.997
0.6	199.192	4.200×10^{16}	1.000	179.886	1.704×10^{15}	0.997	180.821	1.020×10^{13}	0.997	180.152	1.391×10^{15}	0.997	179.886	1.859×10^{15}	0.997
0.7	193.247	9.415×10^{15}	0.997	185.321	3.845×10^{15}	0.997	186.132	2.234×10^{13}	0.997	185.589	3.134×10^{15}	0.997	185.321	3.194×10^{15}	0.997
0.8	210.576	1.752×10^{17}	0.986	193.275	1.374×10^{16}	0.994	193.854	7.587×10^{13}	0.995	193.544	1.118×10^{16}	0.994	193.275	8.538×10^{15}	0.994
Avg.	184.335	2.899×10^{16}	0.994	178.508	3.761×10^{15}	0.995	179.214	2.091×10^{13}	0.995	178.763	3.060×10^{15}	0.995	178.508	9.697×10^{15}	0.995

Table C16 Activation energy (kJ/mol), pre-exponential factor (min⁻¹) and R² values of EI and AI biomass pyrolysis at co-feed ratio of 1:2.

Conversion (α)	DFM			KAS			OFW			STK			DAEM		
	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²
0.1	183.123	2.587×10^{16}	0.997	185.939	8.132×10^{16}	0.995	185.475	3.613×10^{14}	0.996	186.154	6.554×10^{16}	0.995	185.939	7.718×10^{17}	0.995
0.2	178.677	4.025×10^{15}	0.993	176.268	4.895×10^{15}	0.986	176.576	2.579×10^{13}	0.987	176.503	3.974×10^{15}	0.986	176.268	2.194×10^{16}	0.986
0.3	181.168	3.281×10^{15}	0.998	187.207	2.737×10^{16}	0.996	187.234	1.354×10^{14}	0.997	187.445	2.216×10^{16}	0.996	187.207	7.673×10^{16}	0.996
0.4	180.339	1.867×10^{15}	0.994	178.871	2.902×10^{15}	0.996	179.511	1.638×10^{13}	0.997	179.124	2.363×10^{15}	0.996	178.871	5.681×10^{15}	0.996
0.5	179.236	1.203×10^{15}	0.998	176.053	1.153×10^{15}	0.999	176.998	6.942×10^{12}	0.999	176.315	9.411×10^{14}	0.999	176.053	1.663×10^{15}	0.999
0.6	189.826	7.663×10^{15}	1.000	181.473	2.640×10^{15}	0.999	182.295	1.542×10^{13}	0.999	181.737	2.152×10^{15}	0.999	181.473	2.881×10^{15}	0.999
0.7	186.113	2.695×10^{15}	0.997	177.331	9.208×10^{14}	1.000	178.491	5.780×10^{12}	1.000	177.604	7.530×10^{14}	1.000	177.331	7.648×10^{14}	1.000
0.8	209.616	1.552×10^{17}	0.996	198.529	4.303×10^{16}	0.998	198.809	2.237×10^{14}	0.998	198.792	3.491×10^{16}	0.998	198.529	2.674×10^{16}	0.998
Avg.	186.012	2.522×10^{16}	0.997	182.709	2.053×10^{16}	0.996	183.173	9.883×10^{13}	0.997	182.959	1.660×10^{16}	0.996	182.709	1.135×10^{17}	0.996

Table C17 Activation energy (kJ/mol), pre-exponential factor (min⁻¹) and R² values of EI and AI biomass pyrolysis at co-feed ratio of 1:1.

Conversion (α)	DFM			KAS			OFW			STK			DAEM		
	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²
0.1	160.721	1.974×10^{14}	1.000	154.728	7.613×10^{13}	0.999	155.792	4.835×10^{11}	0.999	154.969	6.229×10^{13}	0.999	154.728	7.226×10^{14}	0.999
0.2	165.580	2.621×10^{14}	0.999	158.313	1.011×10^{14}	1.000	159.507	6.573×10^{11}	1.000	158.563	8.281×10^{13}	1.000	158.313	4.532×10^{14}	1.000
0.3	169.395	3.193×10^{14}	1.000	158.598	6.696×10^{13}	1.000	160.024	4.572×10^{11}	1.000	158.858	5.496×10^{13}	1.000	158.598	1.877×10^{14}	1.000
0.4	168.159	1.687×10^{14}	1.000	165.978	2.086×10^{14}	1.000	167.248	1.361×10^{12}	1.000	166.241	1.709×10^{14}	1.000	165.978	4.083×10^{14}	1.000
0.5	179.500	1.400×10^{15}	1.000	171.769	5.145×10^{14}	0.999	172.914	3.243×10^{12}	1.000	172.034	4.208×10^{14}	1.000	171.769	7.422×10^{14}	0.999
0.6	178.152	8.854×10^{14}	0.994	171.556	3.963×10^{14}	0.998	172.843	2.572×10^{12}	0.998	171.827	3.245×10^{14}	0.998	171.556	4.325×10^{14}	0.998
0.7	211.255	3.909×10^{17}	0.992	184.645	4.365×10^{15}	0.997	185.425	2.522×10^{13}	0.997	184.911	3.557×10^{15}	0.997	184.645	3.625×10^{15}	0.997
0.8	205.700	7.768×10^{16}	0.994	191.554	1.222×10^{16}	0.995	192.151	6.777×10^{13}	0.996	191.821	9.939×10^{15}	0.995	191.554	7.591×10^{15}	0.995
Avg.	179.808	5.898×10^{16}	0.997	169.643	2.243×10^{15}	0.998	170.738	1.272×10^{13}	0.999	169.903	1.826×10^{15}	0.998	169.643	1.770×10^{15}	0.998

Table C18 Activation energy (kJ/mol), pre-exponential factor (min⁻¹) and R² values of EI and AI biomass pyrolysis at co-feed ratio of 2:1.

Conversion (α)	DFM			KAS			OFW			STK			DAEM		
	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²
0.1	146.723	1.154×10^{13}	0.822	146.657	1.515×10^{13}	0.824	148.095	1.062×10^{11}	0.841	146.903	1.245×10^{13}	0.824	146.657	1.438×10^{14}	0.824
0.2	135.614	5.827×10^{11}	0.747	147.134	1.089×10^{13}	0.819	148.856	8.124×10^{10}	0.836	147.392	8.973×10^{12}	0.819	147.134	4.881×10^{13}	0.819
0.3	134.232	2.980×10^{11}	0.708	131.268	2.448×10^{11}	0.738	134.006	2.395×10^{09}	0.764	131.549	2.040×10^{11}	0.739	131.268	6.862×10^{11}	0.738
0.4	127.944	6.480×10^{10}	0.727	132.534	2.501×10^{11}	0.741	135.406	2.503×10^{09}	0.767	132.823	2.086×10^{11}	0.742	132.534	4.896×10^{11}	0.741
0.5	131.021	1.167×10^{11}	0.832	123.184	3.020×10^{10}	0.738	126.672	3.594×10^{08}	0.767	123.487	2.538×10^{10}	0.739	123.184	4.357×10^{10}	0.738
0.6	148.461	3.294×10^{12}	0.927	138.867	6.812×10^{11}	0.805	141.719	6.608×10^{09}	0.826	139.162	5.674×10^{11}	0.806	138.867	7.434×10^{11}	0.805
0.7	184.325	2.907×10^{15}	0.988	146.560	2.814×10^{12}	0.888	149.167	2.524×10^{10}	0.901	146.855	2.336×10^{12}	0.889	146.560	2.337×10^{12}	0.888
0.8	218.556	1.011×10^{18}	0.999	177.038	9.066×10^{14}	0.949	178.309	5.818×10^{12}	0.954	177.316	7.421×10^{14}	0.949	177.038	5.633×10^{14}	0.949
Avg.	153.359	1.267×10^{17}	0.844	142.906	1.171×10^{14}	0.813	145.279	7.554×10^{11}	0.832	143.186	9.585×10^{13}	0.813	142.906	9.502×10^{13}	0.813

Table C19 Activation energy (kJ/mol), pre-exponential factor (min⁻¹) and R² values of EI and AI biomass pyrolysis at co-feed ratio of 3:1.

Conversion (α)	DFM			KAS			OFW			STK			DAEM		
	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²
0.1	197.329	9.225×10^{17}	0.985	199.500	2.805×10^{18}	0.985	198.297	1.068×10^{16}	0.986	199.701	2.246×10^{18}	0.985	199.500	2.662×10^{19}	0.985
0.2	195.906	2.515×10^{17}	0.959	191.056	1.895×10^{17}	0.962	190.584	8.429×10^{14}	0.965	191.277	1.527×10^{17}	0.962	191.056	8.493×10^{17}	0.962
0.3	195.038	1.020×10^{17}	0.977	192.283	1.319×10^{17}	0.975	191.980	6.089×10^{14}	0.977	192.513	1.065×10^{17}	0.975	192.283	3.699×10^{17}	0.975
0.4	179.194	2.432×10^{15}	0.979	188.271	3.355×10^{16}	0.973	188.362	1.682×10^{14}	0.975	188.512	2.718×10^{16}	0.973	188.271	6.569×10^{16}	0.973
0.5	167.142	1.758×10^{14}	0.989	186.373	1.600×10^{16}	0.983	186.706	8.437×10^{13}	0.985	186.622	1.299×10^{16}	0.983	186.373	2.308×10^{16}	0.983
0.6	191.304	1.883×10^{16}	0.997	180.723	3.875×10^{15}	0.980	181.468	2.231×10^{13}	0.982	180.983	3.158×10^{15}	0.980	180.723	4.229×10^{15}	0.980
0.7	217.492	2.285×10^{18}	0.999	188.677	1.513×10^{16}	0.990	189.156	8.214×10^{13}	0.991	188.935	1.230×10^{16}	0.990	188.677	1.257×10^{16}	0.990
0.8	257.526	2.337×10^{21}	0.998	205.170	2.803×10^{17}	0.999	204.988	1.331×10^{15}	0.999	205.421	2.266×10^{17}	0.999	205.170	1.742×10^{17}	0.999
Avg.	200.116	2.926×10^{20}	0.986	191.507	4.344×10^{17}	0.981	191.443	1.727×10^{15}	0.983	191.746	3.484×10^{17}	0.981	191.507	3.515×10^{18}	0.981

Table C20 Activation energy (kJ/mol), pre-exponential factor (min⁻¹) and R² values of EI and AI biomass pyrolysis at co-feed ratio of 4:1.

Conversion (α)	DFM			KAS			OFW			STK			DAEM		
	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²	E_α	k_o	R ²
0.1	204.413	4.340×10^{18}	0.982	195.654	1.147×10^{18}	0.998	194.628	4.526×10^{15}	0.998	195.858	9.202×10^{17}	0.998	195.654	1.089×10^{19}	0.998
0.2	255.982	9.609×10^{22}	0.899	224.434	2.705×10^{20}	0.952	222.302	8.735×10^{17}	0.955	224.627	2.151×10^{20}	0.952	224.434	1.212×10^{21}	0.952
0.3	260.818	9.944×10^{22}	0.751	239.245	3.002×10^{21}	0.831	236.619	8.996×10^{18}	0.842	239.437	2.380×10^{21}	0.831	239.245	8.416×10^{21}	0.831
0.4	215.403	4.370×10^{18}	0.662	227.121	1.196×10^{20}	0.722	225.281	4.135×10^{17}	0.738	227.331	9.540×10^{19}	0.722	227.121	2.342×10^{20}	0.722
0.5	216.773	4.253×10^{18}	0.763	222.143	2.767×10^{19}	0.726	220.698	1.031×10^{17}	0.743	222.363	2.214×10^{19}	0.727	222.143	3.992×10^{19}	0.726
0.6	210.810	9.876×10^{17}	0.906	214.118	3.815×10^{18}	0.800	213.191	1.567×10^{16}	0.814	214.349	3.064×10^{18}	0.800	214.118	4.163×10^{18}	0.800
0.7	233.716	5.731×10^{19}	0.952	226.557	3.326×10^{19}	0.847	225.144	1.254×10^{17}	0.858	226.784	2.662×10^{19}	0.848	226.557	2.763×10^{19}	0.847
0.8	310.439	5.766×10^{25}	0.903	271.003	1.229×10^{23}	0.979	267.567	3.367×10^{20}	0.981	271.201	9.705×10^{22}	0.979	271.003	7.634×10^{22}	0.979
Avg.	238.544	7.232×10^{24}	0.852	227.534	1.579×10^{22}	0.857	225.679	4.340×10^{19}	0.866	227.744	1.247×10^{22}	0.857	227.534	1.079×10^{22}	0.857

Table C21 Enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI and AI biomass pyrolysis at co-feed ratio of 1:4.

DFM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	154.240	177.158	-0.038	154.140	177.360	-0.037	154.066	178.026	-0.038	154.016	178.345	-0.038
0.2	150.836	177.267	-0.043	150.736	177.472	-0.043	150.661	178.139	-0.044	150.611	178.460	-0.044
0.3	157.699	177.049	-0.032	157.599	177.249	-0.032	157.524	177.913	-0.032	157.474	178.231	-0.033
0.4	157.648	177.050	-0.032	157.549	177.251	-0.032	157.474	177.915	-0.032	157.424	178.233	-0.033
0.5	156.019	177.101	-0.035	155.919	177.303	-0.034	155.845	177.967	-0.035	155.795	178.286	-0.035
0.6	167.326	176.757	-0.015	167.226	176.952	-0.016	167.151	177.611	-0.017	167.101	177.927	-0.017
0.7	185.566	176.247	0.015	185.466	176.432	0.015	185.391	177.084	0.013	185.341	177.395	0.012
0.8	193.964	176.028	0.029	193.864	176.209	0.028	193.789	176.858	0.027	193.740	177.166	0.026
Avg.	165.412	176.832	-0.019	165.313	177.029	-0.019	165.238	177.689	-0.020	165.188	178.005	-0.020

KAS												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	160.627	176.958	-0.027	160.527	177.157	-0.027	160.452	177.819	-0.028	160.402	178.137	-0.028
0.2	149.140	177.323	-0.046	149.040	177.529	-0.046	148.965	178.196	-0.046	148.915	178.518	-0.046
0.3	158.222	177.032	-0.031	158.122	177.233	-0.031	158.048	177.896	-0.031	157.998	178.214	-0.032
0.4	158.079	177.037	-0.031	157.979	177.237	-0.031	157.904	177.901	-0.032	157.854	178.219	-0.032
0.5	163.726	176.864	-0.022	163.627	177.061	-0.022	163.552	177.722	-0.022	163.502	178.039	-0.023
0.6	160.586	176.959	-0.027	160.486	177.158	-0.027	160.411	177.821	-0.028	160.361	178.138	-0.028
0.7	168.404	176.726	-0.014	168.304	176.920	-0.014	168.229	177.579	-0.015	168.179	177.894	-0.015
0.8	173.569	176.577	-0.005	173.469	176.768	-0.005	173.394	177.425	-0.006	173.345	177.739	-0.007
Avg.	161.544	176.934	-0.025	161.444	177.133	-0.025	161.369	177.795	-0.026	161.320	178.112	-0.026

OFW												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	161.173	176.819	-0.026	161.074	177.140	-0.026	160.999	177.802	-0.027	160.949	178.120	-0.027
0.2	150.558	177.028	-0.044	150.458	177.481	-0.043	150.383	178.148	-0.044	150.333	178.469	-0.044
0.3	159.447	176.851	-0.029	159.348	177.194	-0.029	159.273	177.857	-0.029	159.223	178.175	-0.030
0.4	159.523	176.850	-0.029	159.423	177.192	-0.029	159.349	177.854	-0.029	159.299	178.172	-0.030
0.5	165.070	176.747	-0.019	164.970	177.020	-0.019	164.895	177.681	-0.020	164.846	177.997	-0.021
0.6	162.234	176.799	-0.024	162.135	177.107	-0.024	162.060	177.769	-0.025	162.010	178.086	-0.025
0.7	169.810	176.664	-0.011	169.711	176.878	-0.012	169.636	177.536	-0.013	169.586	177.851	-0.013
0.8	174.864	176.579	-0.003	174.765	176.731	-0.003	174.690	177.387	-0.004	174.640	177.700	-0.005
Avg.	162.835	176.792	-0.023	162.735	177.093	-0.023	162.661	177.754	-0.024	162.611	178.071	-0.024

STK												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	160.859	176.951	-0.026	160.834	177.150	-0.026	160.684	177.812	-0.027	160.635	178.130	-0.027
0.2	149.394	177.314	-0.046	149.369	177.520	-0.045	149.219	178.188	-0.046	149.170	178.509	-0.046
0.3	158.480	177.024	-0.030	158.455	177.225	-0.030	158.305	177.888	-0.031	158.255	178.206	-0.031
0.4	158.345	177.028	-0.031	158.320	177.229	-0.030	158.171	177.892	-0.031	158.121	178.210	-0.032
0.5	163.996	176.856	-0.021	163.971	177.053	-0.021	163.822	177.714	-0.022	163.772	178.030	-0.022
0.6	160.864	176.951	-0.026	160.839	177.150	-0.026	160.690	177.812	-0.027	160.640	178.129	-0.027
0.7	168.682	176.717	-0.013	168.657	176.912	-0.013	168.508	177.570	-0.014	168.458	177.886	-0.015
0.8	173.849	176.569	-0.004	173.824	176.760	-0.005	173.675	177.417	-0.006	173.625	177.730	-0.006
Avg.	161.809	176.926	-0.025	161.784	177.125	-0.025	161.634	177.787	-0.026	161.584	178.104	-0.026

DAEM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	160.627	176.958	-0.027	160.527	177.157	-0.027	160.452	177.819	-0.028	160.402	178.137	-0.028
0.2	149.140	177.323	-0.046	149.040	177.529	-0.046	148.965	178.196	-0.046	148.915	178.518	-0.046
0.3	158.222	177.032	-0.031	158.122	177.233	-0.031	158.048	177.896	-0.031	157.998	178.214	-0.032
0.4	158.079	177.037	-0.031	157.979	177.237	-0.031	157.904	177.901	-0.032	157.854	178.219	-0.032
0.5	163.726	176.864	-0.022	163.627	177.061	-0.022	163.552	177.722	-0.022	163.502	178.039	-0.023
0.6	160.586	176.959	-0.027	160.486	177.158	-0.027	160.411	177.821	-0.028	160.361	178.138	-0.028
0.7	168.404	176.726	-0.014	168.304	176.920	-0.014	168.229	177.579	-0.015	168.179	177.894	-0.015
0.8	173.569	176.577	-0.005	173.469	176.768	-0.005	173.394	177.425	-0.006	173.345	177.739	-0.007
Avg.	161.544	176.934	-0.025	161.444	177.133	-0.025	161.369	177.795	-0.026	161.320	178.112	-0.026

Table C22 Enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI and AI biomass pyrolysis at co-feed ratio of 1:3.

DFM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	165.450	175.869	-0.017	165.342	176.390	-0.018	165.267	177.057	-0.019	165.251	176.160	-0.017
0.2	168.423	175.782	-0.012	168.315	176.301	-0.013	168.240	176.966	-0.014	168.223	176.070	-0.012
0.3	166.170	175.848	-0.016	166.062	176.369	-0.017	165.987	177.035	-0.018	165.971	176.138	-0.016
0.4	170.266	175.729	-0.009	170.158	176.247	-0.010	170.083	176.911	-0.011	170.066	176.014	-0.009
0.5	176.122	175.563	0.001	176.014	176.078	0.000	175.939	176.739	-0.001	175.922	175.842	0.000
0.6	194.146	175.084	0.031	194.038	175.589	0.030	193.963	176.243	0.028	193.946	175.344	0.029
0.7	188.200	175.237	0.021	188.092	175.745	0.020	188.017	176.402	0.018	188.001	175.503	0.020
0.8	205.530	174.804	0.051	205.421	175.302	0.049	205.347	175.953	0.047	205.330	175.053	0.048
Avg.	179.288	175.489	0.006	179.180	176.003	0.005	179.105	176.663	0.004	179.089	175.766	0.005

KAS												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	168.933	175.767	-0.011	168.825	176.286	-0.012	168.750	176.951	-0.013	168.734	176.054	-0.012
0.2	163.576	175.925	-0.020	163.468	176.447	-0.021	163.393	177.115	-0.022	163.376	176.218	-0.020
0.3	171.111	175.704	-0.008	171.003	176.222	-0.008	170.928	176.886	-0.009	170.911	175.989	-0.008
0.4	171.245	175.701	-0.007	171.137	176.218	-0.008	171.062	176.882	-0.009	171.045	175.985	-0.008
0.5	169.485	175.751	-0.010	169.377	176.270	-0.011	169.302	176.934	-0.012	169.285	176.038	-0.011
0.6	174.839	175.599	-0.001	174.731	176.114	-0.002	174.656	176.776	-0.003	174.640	175.879	-0.002
0.7	180.274	175.448	0.008	180.166	175.961	0.007	180.091	176.621	0.006	180.075	175.723	0.007
0.8	188.228	175.236	0.021	188.120	175.744	0.020	188.046	176.401	0.019	188.029	175.503	0.020
Avg.	173.461	175.641	-0.004	173.353	176.158	-0.005	173.278	176.821	-0.006	173.262	175.924	-0.004

OFW												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	169.085	175.752	-0.011	168.977	176.282	-0.012	168.902	176.946	-0.013	168.885	176.050	-0.011
0.2	164.289	175.860	-0.019	164.181	176.426	-0.020	164.106	177.092	-0.021	164.089	176.196	-0.019
0.3	171.709	175.694	-0.007	171.601	176.205	-0.007	171.526	176.868	-0.008	171.509	175.971	-0.007
0.4	172.049	175.687	-0.006	171.941	176.195	-0.007	171.866	176.858	-0.008	171.849	175.961	-0.007
0.5	170.540	175.720	-0.009	170.432	176.239	-0.009	170.357	176.903	-0.010	170.340	176.006	-0.009
0.6	175.774	175.607	0.000	175.666	176.087	-0.001	175.591	176.749	-0.002	175.574	175.852	0.000
0.7	181.085	175.497	0.009	180.977	175.938	0.008	180.902	176.598	0.007	180.885	175.700	0.008
0.8	188.807	175.344	0.022	188.699	175.729	0.021	188.624	176.385	0.019	188.608	175.487	0.021
Avg.	174.167	175.645	-0.002	174.059	176.138	-0.003	173.984	176.800	-0.004	173.968	175.903	-0.003

STK method												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	169.159	175.761	-0.011	169.109	176.280	-0.012	168.976	176.944	-0.013	168.960	176.048	-0.011
0.2	163.819	175.918	-0.020	163.769	176.440	-0.020	163.636	177.107	-0.021	163.619	176.211	-0.020
0.3	171.358	175.697	-0.007	171.308	176.215	-0.008	171.175	176.879	-0.009	171.159	175.982	-0.008
0.4	171.501	175.693	-0.007	171.451	176.211	-0.008	171.318	176.874	-0.009	171.302	175.977	-0.007
0.5	169.749	175.744	-0.010	169.700	176.262	-0.011	169.566	176.926	-0.012	169.550	176.030	-0.010
0.6	175.106	175.591	-0.001	175.056	176.107	-0.002	174.923	176.769	-0.003	174.906	175.871	-0.002
0.7	180.543	175.441	0.008	180.493	175.953	0.007	180.360	176.613	0.006	180.343	175.715	0.007
0.8	188.497	175.229	0.022	188.447	175.737	0.021	188.314	176.394	0.019	188.297	175.495	0.020
Avg.	173.717	175.634	-0.003	173.667	176.151	-0.004	173.534	176.813	-0.005	173.517	175.916	-0.004

DAEM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	168.933	175.767	-0.011	168.825	176.286	-0.012	168.750	176.951	-0.013	168.734	176.054	-0.012
0.2	163.576	175.925	-0.020	163.468	176.447	-0.021	163.393	177.115	-0.022	163.376	176.218	-0.020
0.3	171.111	175.704	-0.008	171.003	176.222	-0.008	170.928	176.886	-0.009	170.911	175.989	-0.008
0.4	171.245	175.701	-0.007	171.137	176.218	-0.008	171.062	176.882	-0.009	171.045	175.985	-0.008
0.5	169.485	175.751	-0.010	169.377	176.270	-0.011	169.302	176.934	-0.012	169.285	176.038	-0.011
0.6	174.839	175.599	-0.001	174.731	176.114	-0.002	174.656	176.776	-0.003	174.640	175.879	-0.002
0.7	180.274	175.448	0.008	180.166	175.961	0.007	180.091	176.621	0.006	180.075	175.723	0.007
0.8	188.228	175.236	0.021	188.120	175.744	0.020	188.046	176.401	0.019	188.029	175.503	0.020
Avg.	173.461	175.641	-0.004	173.353	176.158	-0.005	173.278	176.821	-0.006	173.262	175.924	-0.004

Table C23 Enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI and AI biomass pyrolysis at co-feed ratio of 1:2.

DFM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	178.110	174.253	0.006	178.001	174.787	0.005	177.952	174.543	0.005	177.893	175.179	0.004
0.2	173.663	174.376	-0.001	173.555	174.913	-0.002	173.505	174.670	-0.002	173.447	175.307	-0.003
0.3	176.154	174.306	0.003	176.046	174.842	0.002	175.996	174.599	0.002	175.938	175.235	0.001
0.4	175.325	174.329	0.002	175.217	174.866	0.001	175.167	174.622	0.001	175.109	175.259	0.000
0.5	174.223	174.360	0.000	174.115	174.897	-0.001	174.065	174.654	-0.001	174.007	175.291	-0.002
0.6	184.812	174.072	0.018	184.704	174.603	0.016	184.655	174.357	0.017	184.596	174.991	0.015
0.7	181.099	174.171	0.011	180.991	174.704	0.010	180.941	174.459	0.010	180.883	175.094	0.009
0.8	204.602	173.575	0.051	204.494	174.095	0.049	204.444	173.844	0.049	204.386	174.472	0.048
Avg.	180.999	174.180	0.011	180.891	174.713	0.010	180.841	174.469	0.010	180.783	175.103	0.009
KAS												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	180.926	174.176	0.011	180.818	174.709	0.010	180.768	174.464	0.010	180.710	175.099	0.009
0.2	171.254	174.444	-0.005	171.146	174.983	-0.006	171.096	174.741	-0.006	171.038	175.378	-0.007
0.3	182.194	174.142	0.013	182.086	174.674	0.012	182.036	174.429	0.012	181.978	175.063	0.011
0.4	173.857	174.370	-0.001	173.749	174.907	-0.002	173.699	174.665	-0.002	173.641	175.302	-0.003
0.5	171.039	174.450	-0.006	170.931	174.989	-0.007	170.882	174.747	-0.006	170.823	175.385	-0.007
0.6	176.460	174.298	0.004	176.352	174.833	0.002	176.302	174.590	0.003	176.244	175.226	0.002
0.7	172.318	174.414	-0.003	172.210	174.952	-0.004	172.160	174.709	-0.004	172.102	175.347	-0.005
0.8	193.516	173.848	0.033	193.408	174.373	0.031	193.358	174.125	0.031	193.300	174.756	0.029
Avg.	177.696	174.268	0.006	177.587	174.803	0.005	177.538	174.559	0.005	177.479	175.194	0.004

OFW												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	180.462	174.189	0.010	180.353	174.722	0.009	180.304	174.477	0.009	180.245	175.112	0.008
0.2	171.563	174.435	-0.005	171.455	174.974	-0.006	171.405	174.731	-0.005	171.346	175.369	-0.006
0.3	182.220	174.141	0.013	182.112	174.673	0.012	182.063	174.428	0.012	182.004	175.063	0.011
0.4	174.497	174.353	0.000	174.389	174.889	-0.001	174.339	174.646	0.000	174.281	175.283	-0.002
0.5	171.984	174.423	-0.004	171.876	174.961	-0.005	171.826	174.719	-0.005	171.768	175.357	-0.006
0.6	177.281	174.275	0.005	177.173	174.810	0.004	177.123	174.567	0.004	177.065	175.202	0.003
0.7	173.478	174.381	-0.001	173.370	174.918	-0.003	173.320	174.676	-0.002	173.262	175.313	-0.003
0.8	193.796	173.841	0.033	193.687	174.366	0.031	193.638	174.118	0.031	193.579	174.749	0.030
Avg.	178.160	174.255	0.006	178.052	174.789	0.005	178.002	174.545	0.006	177.944	175.181	0.004

STK												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	181.141	174.170	0.012	181.058	174.703	0.010	180.983	174.458	0.010	180.925	175.093	0.009
0.2	171.490	174.437	-0.005	171.407	174.976	-0.006	171.332	174.734	-0.005	171.274	175.371	-0.007
0.3	182.431	174.136	0.014	182.348	174.668	0.012	182.273	174.423	0.013	182.215	175.057	0.011
0.4	174.110	174.363	0.000	174.027	174.900	-0.001	173.952	174.657	-0.001	173.894	175.294	-0.002
0.5	171.302	174.443	-0.005	171.218	174.981	-0.006	171.144	174.739	-0.006	171.085	175.377	-0.007
0.6	176.724	174.291	0.004	176.641	174.826	0.003	176.566	174.583	0.003	176.508	175.218	0.002
0.7	172.591	174.406	-0.003	172.507	174.944	-0.004	172.433	174.701	-0.004	172.374	175.339	-0.005
0.8	193.778	173.841	0.033	193.695	174.367	0.031	193.620	174.119	0.031	193.562	174.749	0.030
Avg.	177.946	174.261	0.006	177.863	174.796	0.005	177.788	174.552	0.005	177.730	175.187	0.004

DAEM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	180.926	174.176	0.011	180.818	174.709	0.010	180.768	174.464	0.010	180.710	175.099	0.009
0.2	171.254	174.444	-0.005	171.146	174.983	-0.006	171.096	174.741	-0.006	171.038	175.378	-0.007
0.3	182.194	174.142	0.013	182.086	174.674	0.012	182.036	174.429	0.012	181.978	175.063	0.011
0.4	173.857	174.370	-0.001	173.749	174.907	-0.002	173.699	174.665	-0.002	173.641	175.302	-0.003
0.5	171.039	174.450	-0.006	170.931	174.989	-0.007	170.882	174.747	-0.006	170.823	175.385	-0.007
0.6	176.460	174.298	0.004	176.352	174.833	0.002	176.302	174.590	0.003	176.244	175.226	0.002
0.7	172.318	174.414	-0.003	172.210	174.952	-0.004	172.160	174.709	-0.004	172.102	175.347	-0.005
0.8	193.516	173.848	0.033	193.408	174.373	0.031	193.358	174.125	0.031	193.300	174.756	0.029
Avg.	177.696	174.268	0.006	177.587	174.803	0.005	177.538	174.559	0.005	177.479	175.194	0.004

Table C24 Enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI and AI biomass pyrolysis at co-feed ratio of 1:1.

DFM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	155.733	173.962	-0.030	155.625	174.526	-0.031	155.567	174.605	-0.031	155.500	175.557	-0.032
0.2	160.591	173.813	-0.022	160.483	174.375	-0.023	160.425	174.451	-0.023	160.358	175.401	-0.024
0.3	164.407	173.700	-0.015	164.299	174.258	-0.016	164.240	174.334	-0.016	164.174	175.282	-0.018
0.4	163.171	173.736	-0.018	163.063	174.296	-0.018	163.004	174.372	-0.018	162.938	175.320	-0.020
0.5	174.512	173.411	0.002	174.404	173.963	0.001	174.346	174.035	0.001	174.279	174.980	-0.001
0.6	173.163	173.448	0.000	173.055	174.002	-0.002	172.997	174.074	-0.002	172.930	175.019	-0.003
0.7	206.266	172.598	0.056	206.158	173.133	0.054	206.100	173.196	0.053	206.034	174.129	0.051
0.8	200.712	172.731	0.047	200.604	173.269	0.045	200.545	173.333	0.044	200.479	174.268	0.042
Avg.	174.819	173.425	0.002	174.711	173.978	0.001	174.653	174.050	0.001	174.587	174.994	-0.001

KAS												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	149.740	174.152	-0.041	149.632	174.720	-0.041	149.574	174.801	-0.041	149.507	175.755	-0.042
0.2	153.324	174.037	-0.035	153.216	174.603	-0.035	153.158	174.683	-0.035	153.092	175.635	-0.036
0.3	153.609	174.028	-0.034	153.501	174.594	-0.034	153.443	174.673	-0.034	153.376	175.626	-0.035
0.4	160.990	173.801	-0.021	160.882	174.362	-0.022	160.823	174.439	-0.022	160.757	175.388	-0.023
0.5	166.781	173.630	-0.011	166.673	174.187	-0.012	166.615	174.262	-0.012	166.548	175.209	-0.014
0.6	166.568	173.637	-0.012	166.460	174.194	-0.013	166.402	174.269	-0.013	166.335	175.216	-0.014
0.7	179.656	173.270	0.011	179.548	173.819	0.009	179.490	173.890	0.009	179.423	174.832	0.007
0.8	186.565	173.087	0.022	186.457	173.632	0.021	186.399	173.700	0.020	186.332	174.640	0.019
Avg.	164.654	173.705	-0.015	164.546	174.264	-0.016	164.488	174.339	-0.016	164.421	175.288	-0.017

OFW												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	150.803	174.209	-0.039	150.695	174.685	-0.039	150.637	174.765	-0.039	150.571	175.719	-0.040
0.2	154.519	174.072	-0.032	154.411	174.565	-0.033	154.353	174.644	-0.033	154.286	175.596	-0.034
0.3	155.036	174.053	-0.032	154.928	174.548	-0.032	154.870	174.627	-0.032	154.803	175.579	-0.033
0.4	162.260	173.796	-0.019	162.152	174.323	-0.020	162.093	174.400	-0.020	162.027	175.349	-0.021
0.5	167.925	173.601	-0.009	167.817	174.154	-0.010	167.759	174.228	-0.010	167.692	175.175	-0.012
0.6	167.855	173.603	-0.010	167.747	174.156	-0.010	167.688	174.230	-0.011	167.622	175.177	-0.012
0.7	180.437	173.188	0.012	180.329	173.798	0.011	180.271	173.868	0.010	180.204	174.810	0.009
0.8	187.163	172.976	0.024	187.055	173.616	0.022	186.996	173.684	0.021	186.930	174.624	0.020
Avg.	165.750	173.687	-0.013	165.642	174.231	-0.014	165.583	174.306	-0.014	165.517	175.254	-0.016

STK												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	149.980	174.144	-0.040	149.872	174.712	-0.041	149.814	174.793	-0.040	149.747	175.747	-0.041
0.2	153.574	174.029	-0.034	153.466	174.595	-0.034	153.408	174.674	-0.034	153.342	175.627	-0.035
0.3	153.869	174.020	-0.034	153.761	174.586	-0.034	153.703	174.665	-0.034	153.637	175.617	-0.035
0.4	161.253	173.794	-0.021	161.145	174.354	-0.022	161.086	174.431	-0.022	161.020	175.380	-0.023
0.5	167.046	173.623	-0.011	166.938	174.180	-0.012	166.880	174.254	-0.012	166.813	175.201	-0.013
0.6	166.839	173.629	-0.011	166.731	174.186	-0.012	166.672	174.260	-0.012	166.606	175.208	-0.014
0.7	179.922	173.263	0.011	179.814	173.812	0.010	179.756	173.882	0.009	179.689	174.825	0.008
0.8	186.832	173.080	0.023	186.724	173.625	0.021	186.666	173.693	0.021	186.599	174.633	0.019
Avg.	164.914	173.698	-0.015	164.806	174.256	-0.015	164.748	174.332	-0.015	164.682	175.280	-0.017

DAEM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	149.740	174.152	-0.041	149.632	174.720	-0.041	149.574	174.801	-0.041	149.507	175.755	-0.042
0.2	153.324	174.037	-0.035	153.216	174.603	-0.035	153.158	174.683	-0.035	153.092	175.635	-0.036
0.3	153.609	174.028	-0.034	153.501	174.594	-0.034	153.443	174.673	-0.034	153.376	175.626	-0.035
0.4	160.990	173.801	-0.021	160.882	174.362	-0.022	160.823	174.439	-0.022	160.757	175.388	-0.023
0.5	166.781	173.630	-0.011	166.673	174.187	-0.012	166.615	174.262	-0.012	166.548	175.209	-0.014
0.6	166.568	173.637	-0.012	166.460	174.194	-0.013	166.402	174.269	-0.013	166.335	175.216	-0.014
0.7	179.656	173.270	0.011	179.548	173.819	0.009	179.490	173.890	0.009	179.423	174.832	0.007
0.8	186.565	173.087	0.022	186.457	173.632	0.021	186.399	173.700	0.020	186.332	174.640	0.019
Avg.	164.654	173.705	-0.015	164.546	174.264	-0.016	164.488	174.339	-0.016	164.421	175.288	-0.017

Table C25 Enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI and AI biomass pyrolysis at co-feed ratio of 2:1.

DFM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	141.751	173.785	-0.054	141.768	169.720	-0.047	141.585	174.460	-0.053	141.527	175.117	-0.054
0.2	130.642	174.177	-0.073	130.658	170.110	-0.066	130.475	174.865	-0.072	130.417	175.526	-0.072
0.3	129.260	174.228	-0.075	129.277	170.161	-0.069	129.094	174.917	-0.074	129.036	175.579	-0.074
0.4	122.972	174.466	-0.086	122.989	170.398	-0.080	122.806	175.164	-0.085	122.748	175.828	-0.085
0.5	126.049	174.348	-0.081	126.066	170.281	-0.074	125.883	175.042	-0.080	125.825	175.705	-0.080
0.6	143.489	173.727	-0.051	143.506	169.661	-0.044	143.323	174.399	-0.050	143.265	175.056	-0.051
0.7	179.353	172.651	0.011	179.370	168.589	0.018	179.187	173.288	0.010	179.129	173.931	0.008
0.8	213.584	171.804	0.070	213.601	167.745	0.077	213.418	172.412	0.066	213.360	173.046	0.065
Avg.	148.388	173.648	-0.042	148.404	169.583	-0.036	148.221	174.318	-0.042	148.163	174.973	-0.043
KAS												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	141.686	173.788	-0.054	141.702	169.722	-0.047	141.519	174.462	-0.053	141.461	175.119	-0.054
0.2	142.162	173.771	-0.053	142.179	169.706	-0.046	141.996	174.446	-0.053	141.938	175.102	-0.053
0.3	126.296	174.339	-0.080	126.313	170.271	-0.074	126.130	175.032	-0.079	126.072	175.695	-0.079
0.4	127.563	174.291	-0.078	127.579	170.224	-0.072	127.396	174.983	-0.077	127.338	175.645	-0.077
0.5	118.213	174.655	-0.094	118.229	170.586	-0.088	118.046	175.358	-0.093	117.988	176.025	-0.093
0.6	133.895	174.059	-0.067	133.912	169.992	-0.061	133.729	174.743	-0.066	133.671	175.403	-0.067
0.7	141.589	173.791	-0.054	141.605	169.725	-0.047	141.422	174.466	-0.053	141.364	175.123	-0.054
0.8	172.067	172.852	-0.001	172.083	168.789	0.006	171.900	173.495	-0.003	171.842	174.141	-0.004
Avg.	137.934	173.943	-0.060	137.950	169.877	-0.054	137.767	174.623	-0.060	137.709	175.282	-0.060

OFW												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	143.123	173.954	-0.051	143.140	169.674	-0.045	142.957	174.412	-0.051	142.899	175.068	-0.051
0.2	143.884	173.921	-0.050	143.901	169.648	-0.043	143.718	174.386	-0.050	143.660	175.042	-0.050
0.3	129.034	174.573	-0.076	129.050	170.169	-0.069	128.868	174.926	-0.075	128.809	175.588	-0.075
0.4	130.435	174.509	-0.073	130.451	170.117	-0.067	130.268	174.872	-0.072	130.210	175.534	-0.073
0.5	121.700	174.916	-0.088	121.717	170.448	-0.082	121.534	175.215	-0.087	121.476	175.880	-0.087
0.6	136.747	174.227	-0.062	136.764	169.892	-0.056	136.581	174.638	-0.062	136.523	175.297	-0.062
0.7	144.195	173.908	-0.049	144.212	169.638	-0.043	144.029	174.375	-0.049	143.971	175.031	-0.050
0.8	173.338	172.770	0.001	173.354	168.754	0.008	173.171	173.458	0.000	173.113	174.104	-0.002
Avg.	140.307	174.097	-0.056	140.324	169.792	-0.049	140.141	174.535	-0.056	140.083	175.193	-0.056

STK												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	141.931	173.779	-0.053	141.807	169.714	-0.047	141.765	174.454	-0.053	141.707	175.110	-0.053
0.2	142.421	173.763	-0.052	142.296	169.697	-0.046	142.254	174.437	-0.052	142.196	175.093	-0.053
0.3	126.577	174.328	-0.080	126.452	170.261	-0.074	126.411	175.021	-0.079	126.352	175.684	-0.079
0.4	127.851	174.280	-0.078	127.726	170.213	-0.071	127.684	174.971	-0.077	127.626	175.634	-0.077
0.5	118.515	174.643	-0.094	118.390	170.574	-0.088	118.349	175.346	-0.092	118.290	176.013	-0.092
0.6	134.190	174.048	-0.067	134.066	169.982	-0.060	134.024	174.732	-0.066	133.966	175.392	-0.066
0.7	141.883	173.781	-0.053	141.759	169.715	-0.047	141.717	174.455	-0.053	141.659	175.112	-0.054
0.8	172.344	172.844	-0.001	172.219	168.781	0.006	172.177	173.487	-0.002	172.119	174.133	-0.003
Avg.	138.214	173.933	-0.060	138.089	169.867	-0.053	138.048	174.613	-0.059	137.990	175.271	-0.060

DAEM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	141.686	173.788	-0.054	141.702	169.722	-0.047	141.519	174.462	-0.053	141.461	175.119	-0.054
0.2	142.162	173.771	-0.053	142.179	169.706	-0.046	141.996	174.446	-0.053	141.938	175.102	-0.053
0.3	126.296	174.339	-0.080	126.313	170.271	-0.074	126.130	175.032	-0.079	126.072	175.695	-0.079
0.4	127.563	174.291	-0.078	127.579	170.224	-0.072	127.396	174.983	-0.077	127.338	175.645	-0.077
0.5	118.213	174.655	-0.094	118.229	170.586	-0.088	118.046	175.358	-0.093	117.988	176.025	-0.093
0.6	133.895	174.059	-0.067	133.912	169.992	-0.061	133.729	174.743	-0.066	133.671	175.403	-0.067
0.7	141.589	173.791	-0.054	141.605	169.725	-0.047	141.422	174.466	-0.053	141.364	175.123	-0.054
0.8	172.067	172.852	-0.001	172.083	168.789	0.006	171.900	173.495	-0.003	171.842	174.141	-0.004
Avg.	137.934	173.943	-0.060	137.950	169.877	-0.054	137.767	174.623	-0.060	137.709	175.282	-0.060

Table C26 Enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI and AI biomass pyrolysis at co-feed ratio of 3:1.

DFM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	192.374	171.686	0.035	192.291	171.326	0.035	192.224	171.719	0.033	192.166	172.367	0.032
0.2	190.950	171.722	0.032	190.867	171.362	0.032	190.801	171.756	0.031	190.743	172.404	0.030
0.3	190.083	171.744	0.031	190.000	171.385	0.031	189.934	171.778	0.030	189.875	172.427	0.028
0.4	174.238	172.164	0.003	174.155	171.812	0.004	174.089	172.211	0.003	174.031	172.864	0.002
0.5	162.187	172.509	-0.017	162.104	172.162	-0.017	162.037	172.566	-0.017	161.979	173.224	-0.018
0.6	186.349	171.840	0.024	186.266	171.482	0.024	186.200	171.877	0.023	186.141	172.527	0.022
0.7	212.537	171.204	0.069	212.454	170.836	0.069	212.387	171.222	0.067	212.329	171.864	0.065
0.8	252.571	170.367	0.138	252.487	169.984	0.136	252.421	170.359	0.134	252.363	170.992	0.131
Avg.	195.161	171.654	0.039	195.078	171.294	0.039	195.011	171.686	0.038	194.953	172.334	0.036

KAS												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	194.545	171.632	0.038	194.462	171.271	0.038	194.395	171.663	0.037	194.337	172.310	0.035
0.2	186.101	171.846	0.024	186.018	171.489	0.024	185.951	171.884	0.023	185.893	172.533	0.022
0.3	187.328	171.814	0.026	187.245	171.456	0.026	187.179	171.851	0.025	187.120	172.500	0.024
0.4	183.316	171.919	0.019	183.232	171.563	0.019	183.166	171.959	0.018	183.108	172.609	0.017
0.5	181.418	171.969	0.016	181.335	171.614	0.016	181.268	172.010	0.015	181.210	172.662	0.014
0.6	175.768	172.122	0.006	175.685	171.769	0.006	175.618	172.167	0.006	175.560	172.820	0.004
0.7	183.721	171.908	0.020	183.638	171.552	0.020	183.572	171.948	0.019	183.514	172.598	0.018
0.8	200.215	171.493	0.048	200.132	171.130	0.048	200.065	171.520	0.046	200.007	172.165	0.045
Avg.	186.551	171.838	0.025	186.468	171.480	0.025	186.402	171.875	0.024	186.344	172.525	0.022

OFW												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	193.342	171.349	0.036	193.259	171.301	0.036	193.192	171.694	0.035	193.134	172.341	0.033
0.2	185.629	171.638	0.023	185.546	171.501	0.023	185.480	171.896	0.022	185.421	172.546	0.021
0.3	187.024	171.585	0.026	186.941	171.464	0.026	186.875	171.859	0.024	186.817	172.509	0.023
0.4	183.406	171.723	0.019	183.323	171.560	0.019	183.257	171.956	0.018	183.199	172.607	0.017
0.5	181.751	171.787	0.017	181.668	171.605	0.017	181.601	172.001	0.016	181.543	172.652	0.014
0.6	176.513	171.991	0.007	176.430	171.748	0.008	176.363	172.146	0.007	176.305	172.799	0.006
0.7	184.201	171.693	0.021	184.118	171.539	0.021	184.051	171.935	0.020	183.993	172.585	0.018
0.8	200.033	171.104	0.048	199.950	171.134	0.048	199.884	171.524	0.046	199.825	172.170	0.045
Avg.	186.487	171.609	0.025	186.404	171.482	0.025	186.338	171.876	0.024	186.280	172.526	0.022

STK												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	194.746	171.627	0.039	194.605	171.266	0.039	194.597	171.658	0.037	194.538	172.305	0.036
0.2	186.322	171.840	0.024	186.181	171.483	0.024	186.173	171.878	0.023	186.114	172.527	0.022
0.3	187.558	171.808	0.026	187.417	171.450	0.026	187.409	171.845	0.025	187.350	172.494	0.024
0.4	183.557	171.913	0.020	183.416	171.556	0.020	183.407	171.952	0.019	183.349	172.603	0.017
0.5	181.667	171.962	0.016	181.526	171.607	0.016	181.518	172.003	0.015	181.459	172.655	0.014
0.6	176.027	172.114	0.007	175.886	171.762	0.007	175.878	172.160	0.006	175.820	172.813	0.005
0.7	183.980	171.901	0.020	183.839	171.545	0.020	183.830	171.941	0.019	183.772	172.591	0.018
0.8	200.466	171.487	0.049	200.325	171.123	0.048	200.317	171.513	0.047	200.258	172.159	0.045
Avg.	186.791	171.832	0.025	186.649	171.474	0.025	186.641	171.869	0.024	186.583	172.518	0.023

DAEM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	194.545	171.632	0.038	194.462	171.271	0.038	194.395	171.663	0.037	194.337	172.310	0.035
0.2	186.101	171.846	0.024	186.018	171.489	0.024	185.951	171.884	0.023	185.893	172.533	0.022
0.3	187.328	171.814	0.026	187.245	171.456	0.026	187.179	171.851	0.025	187.120	172.500	0.024
0.4	183.316	171.919	0.019	183.232	171.563	0.019	183.166	171.959	0.018	183.108	172.609	0.017
0.5	181.418	171.969	0.016	181.335	171.614	0.016	181.268	172.010	0.015	181.210	172.662	0.014
0.6	175.768	172.122	0.006	175.685	171.769	0.006	175.618	172.167	0.006	175.560	172.820	0.004
0.7	183.721	171.908	0.020	183.638	171.552	0.020	183.572	171.948	0.019	183.514	172.598	0.018
0.8	200.215	171.493	0.048	200.132	171.130	0.048	200.065	171.520	0.046	200.007	172.165	0.045
Avg.	186.551	171.838	0.025	186.468	171.480	0.025	186.402	171.875	0.024	186.344	172.525	0.022

Table C27 Enthalpy change (kJ/mol), Gibbs free energy change (kJ/mol) and entropy change (kJ/mol·K) for EI and AI biomass pyrolysis at co-feed ratio of 4:1.

DFM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	199.449	171.824	0.046	199.349	172.070	0.045	199.432	166.978	0.054	199.283	170.976	0.046
0.2	251.019	170.707	0.135	250.919	170.931	0.131	251.002	165.858	0.142	250.853	169.822	0.131
0.3	255.854	170.614	0.143	255.754	170.837	0.139	255.838	165.765	0.150	255.688	169.726	0.139
0.4	210.439	171.564	0.065	210.340	171.805	0.063	210.423	166.718	0.073	210.273	170.707	0.064
0.5	211.810	171.533	0.067	211.710	171.773	0.066	211.793	166.686	0.075	211.644	170.675	0.066
0.6	205.847	171.671	0.057	205.747	171.914	0.056	205.830	166.825	0.065	205.680	170.818	0.057
0.7	228.753	171.159	0.096	228.653	171.392	0.094	228.736	166.311	0.104	228.587	170.289	0.094
0.8	305.476	169.750	0.227	305.376	169.955	0.222	305.459	164.897	0.235	305.310	168.833	0.221
Avg.	233.581	171.103	0.105	233.481	171.335	0.102	233.564	166.255	0.112	233.415	170.231	0.102
KAS												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	190.690	172.041	0.031	190.591	172.292	0.030	190.674	167.196	0.039	190.524	171.201	0.031
0.2	219.470	171.360	0.081	219.370	171.597	0.078	219.454	166.513	0.088	219.304	170.497	0.079
0.3	234.282	171.043	0.106	234.182	171.274	0.103	234.265	166.195	0.114	234.116	170.169	0.104
0.4	222.158	171.301	0.085	222.058	171.537	0.083	222.141	166.454	0.093	221.991	170.436	0.084
0.5	217.180	171.411	0.077	217.080	171.649	0.075	217.163	166.564	0.084	217.013	170.549	0.075
0.6	209.154	171.594	0.063	209.055	171.836	0.061	209.138	166.747	0.071	208.988	170.738	0.062
0.7	221.593	171.313	0.084	221.494	171.550	0.082	221.577	166.466	0.092	221.427	170.448	0.083
0.8	266.040	170.424	0.160	265.940	170.643	0.156	266.023	165.574	0.168	265.873	169.529	0.156
Avg.	222.571	171.311	0.086	222.471	171.547	0.084	222.554	166.464	0.094	222.405	170.446	0.084

OFW												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	189.665	171.841	0.030	189.565	172.319	0.028	189.648	167.223	0.037	189.498	171.228	0.030
0.2	217.338	170.896	0.077	217.238	171.646	0.075	217.321	166.561	0.085	217.172	170.546	0.076
0.3	231.656	170.439	0.102	231.556	171.330	0.099	231.639	166.250	0.109	231.489	170.225	0.099
0.4	220.318	170.799	0.082	220.218	171.578	0.080	220.301	166.494	0.090	220.152	170.477	0.081
0.5	215.735	170.948	0.074	215.635	171.682	0.072	215.718	166.597	0.082	215.569	170.583	0.073
0.6	208.227	171.197	0.061	208.128	171.858	0.060	208.211	166.769	0.069	208.061	170.760	0.060
0.7	220.180	170.804	0.082	220.081	171.581	0.080	220.164	166.497	0.090	220.014	170.480	0.080
0.8	262.604	169.512	0.154	262.504	170.707	0.151	262.587	165.638	0.162	262.438	169.595	0.150
Avg.	220.715	170.805	0.083	220.616	171.588	0.081	220.699	166.503	0.090	220.549	170.487	0.081

STK												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	190.894	172.036	0.032	190.761	172.287	0.030	190.878	167.191	0.040	190.728	171.195	0.032
0.2	219.664	171.356	0.081	219.531	171.593	0.079	219.647	166.509	0.089	219.498	170.492	0.079
0.3	234.474	171.039	0.106	234.341	171.270	0.104	234.457	166.191	0.114	234.307	170.165	0.104
0.4	222.367	171.297	0.086	222.234	171.532	0.083	222.351	166.449	0.093	222.201	170.431	0.084
0.5	217.400	171.406	0.077	217.266	171.644	0.075	217.383	166.559	0.085	217.233	170.544	0.076
0.6	209.386	171.588	0.063	209.253	171.830	0.061	209.369	166.742	0.071	209.220	170.733	0.062
0.7	221.820	171.309	0.085	221.687	171.545	0.082	221.804	166.461	0.092	221.654	170.443	0.083
0.8	266.238	170.421	0.160	266.105	170.639	0.157	266.221	165.570	0.168	266.071	169.526	0.156
Avg.	222.780	171.306	0.086	222.647	171.543	0.084	222.764	166.459	0.094	222.614	170.441	0.085

DAEM												
Conversion (α)	Heating rate, 10°C/min			Heating rate, 20°C/min			Heating rate, 30°C/min			Heating rate, 40°C/min		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	190.690	172.041	0.031	190.591	172.292	0.030	190.674	167.196	0.039	190.524	171.201	0.031
0.2	219.470	171.360	0.081	219.370	171.597	0.078	219.454	166.513	0.088	219.304	170.497	0.079
0.3	234.282	171.043	0.106	234.182	171.274	0.103	234.265	166.195	0.114	234.116	170.169	0.104
0.4	222.158	171.301	0.085	222.058	171.537	0.083	222.141	166.454	0.093	221.991	170.436	0.084
0.5	217.180	171.411	0.077	217.080	171.649	0.075	217.163	166.564	0.084	217.013	170.549	0.075
0.6	209.154	171.594	0.063	209.055	171.836	0.061	209.138	166.747	0.071	208.988	170.738	0.062
0.7	221.593	171.313	0.084	221.494	171.550	0.082	221.577	166.466	0.092	221.427	170.448	0.083
0.8	266.040	170.424	0.160	265.940	170.643	0.156	266.023	165.574	0.168	265.873	169.529	0.156
Avg.	222.571	171.311	0.086	222.471	171.547	0.084	222.554	166.464	0.094	222.405	170.446	0.084

