

CERTIFICATE

It is certified that the work contained in the thesis titled “**Process Optimization, Characterization, and Energy-Exergy Analysis of Torrefaction and Pyrolysis for Pigeon Pea Stalk and Eucalyptus**” by **Rishikesh Kumar Singh** has been carried out under my supervision and that this work is not submitted elsewhere for any degree.

It is further certified that the student has satisfactorily fulfilled all the requirements of Comprehensive examination, Candidacy, SOTA and Pre-submission seminar for the award of the Ph.D. degree.

Dr. Arnab Sarkar

(Supervisor)

Department of Mechanical Engineering

IIT(BHU) Varanasi

Dr. Jyoti Prasad Chakraborty

(Co-Supervisor)

Department of Chemical Engineering

IIT(BHU) Varanasi

DECLARATION BY THE CANDIDATE

I, **Rishikesh Kumar Singh**, certify that the work embodied in this thesis is my own bona fide work carried out by me under the supervision of **Dr. Arnab Sarkar** and co-supervision of **Dr. Jyoti Prasad Chakraborty** for a period of 5 years from July 2015 to August 2020 at IIT(BHU) Varanasi. The material contained in this thesis has not been submitted for the award of any other degree. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not wilfully copied any others' work, paragraphs, text, data, results etc. reported in journals, books, magazines, reports, dissertations, theses, etc. or available at websites and have not included them in this thesis and have not cited as my own work.

Date:

(Rishikesh Kumar Singh)

Place: Varanasi

Candidate

CERTIFICATE BY THE SUPERVISORS

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

Dr. Arnab Sarkar
(Supervisor)

Dr. Jyoti Prasad Chakraborty
(Co-Supervisor)

Head of the Department

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: **“Process Optimization, Characterization, and Energy-Exergy Analysis of Torrefaction and Pyrolysis for Pigeon Pea Stalk and Eucalyptus”**

Candidate’s Name: **Rishikesh Kumar Singh**

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the Ph.D. degree.

Date: (Rishikesh Kumar Singh)

Place: Varanasi

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for author’s personal use provided that the source and University’s copyright notice are indicated.

ACKNOWLEDGEMENTS

I take this opportunity to express my deep sense of gratitude to my supervisor **Dr. Arnab Sarkar** and co-supervisor **Dr. Jyoti Prasad Chakraborty** for his continuous guidance and whole-hearted cooperation in carrying out this work. His meticulous and valuable review and constructive criticism of the manuscript have greatly improved the quality of work. Sir, for your faith in me and the desire to live up to your expectations, has constantly pushed me to work harder.

My grateful appreciation also goes to **Dr. Jahar Sarkar** and **Professor M.K. Mondal** for serving on my research programme committee (RPC). Thank you all for sparing your valuable time and assisting me throughout my research and completion of this thesis. I wish to extend my sincere thanks to **Prof. A. P. Harsha**, Head, Department of Mechanical Engineering for providing me the necessary resources to enable me to complete this research work. During my stay at IIT (BHU) Varanasi, I have met many people who have made this period of my life memorable and very pleasant. Among them, I would like to sincerely acknowledge the assistance and motivation provided by Prof. P. Ghosh, Dr. R. R. Sahoo, Dr. Laltu Chandra, Dr. S.S. Mondal, Dr. O. P. Singh and Dr. Amitesh Kumar. I want to thank my colleagues at IIT (BHU) Varanasi, especially to Mr. Vivek Kumar, Mr. Sujeeet Yadav, Mr. Devesh Shrivastava and Mr. Satyansh Singh for encouraging me to finish this work. Finally, I would like to thank my parents and family for providing moral and economical support whenever I needed.

TABLE OF CONTENTS

Contents	Page No.
Certificate	ii-iv
Acknowledgment	v
Table of contents	vi-x
List of figures	xi-xiv
List of tables	xv-xvii
Nomenclature	xviii-xxi
Abstract	xxii-xxiv
1. Introduction	1-12
1.1 Overview	1
1.2 Motivation	1
1.3 Biomass and its Sources	3
1.4 Biomass Pretreatment	5
1.5 Pyrolysis	8
1.6 Contributions	9
1.7 Thesis Structure	11
2. Literature Review	13-30
2.1 Overview	13
2.2 Biomass Distribution and Selection	13

2.3 Torrefaction	18
2.3.1 Influence of operating parameters on torrefaction	19
2.3.2 Impact of torrefaction on product distribution and physicochemical properties	21
2.4 Pyrolysis	23
2.4.1 Influence of operating parameters on pyrolysis	24
2.5 Response Surface Methodology (RSM)	25
2.6 Energy and Exergy analysis	27
2.7 Research Gap	28
3. Torrefaction of pigeon pea stalk and eucalyptus along with their statistical analysis and process optimization using RSM	31-52
3.1 Overview	31
3.2 Materials and Methods	31
3.2.1 Material selection	31
3.2.2 Experimental setup and procedure	32
3.2.3 Experimental design	34
3.3 CCD and statistical analysis	35
3.4 ANOVA analysis	38
3.5 Optimization	43
3.6 3-D plots for individual and interactive influence of operating parameters on responses	45
3.7 Experimental validation of optimum condition	51
3.8 Summary	51

Table of Contents

4. Effect of torrefaction on physicochemical properties of biomass and characterization of torrefaction by-products	53-96
4.1 Overview	53
4.2 Characterization methods	53
4.3 Calculation method opted for estimating kinetic parameters	57
4.4 Effect of operating parameters on the product distribution during the torrefaction of biomass	59
4.5 Effect of torrefaction on HHV and proximate analysis of biomass	62
4.6 Elemental analysis for raw and torrefied biomass	66
4.7 Effect of torrefaction on biomass composition, moisture reabsorption and bulk density	68
4.8 Effect of torrefaction on energy density, compaction, flowability and combustibility of biomass	72
4.9 Effect of torrefaction on FTIR analysis of pigeon pea stalk and eucalyptus	77
4.10 Effect of torrefaction on morphology of pigeon pea stalk and eucalyptus	80
4.11 Thermogravimetric analysis of raw and torrefied biomass	82
4.12 Effect of torrefaction on kinetic parameters for the pyrolysis of raw and torrefied biomass	86
4.13 Characteristics of liquid product (condensable gases) obtained during the torrefaction of biomass	92
4.14 Characteristics of the torgas (NCG) obtained during the torrefaction of biomass	95
4.15 Summary	96
5. Pyrolysis: Optimization and characterization	97-136
5.1 Overview	97
5.2 Materials and Methods	98
5.2.1 Material selection	98

5.2.2 Experimental design and statistical analysis	98
5.2.3 Experimental procedure	99
5.2.4 Characterization methods	99
5.3 CCD and statistical analysis	99
5.4 ANOVA analysis	102
5.5 Influence of operating parameters on bio-oil yield	106
5.6 Optimization and 3-D plots	109
5.7 Experimental validation for optimized process parameters	116
5.8 Product distribution and their characterization	116
5.8.1 Product distribution for the pyrolysis of raw and torrefied biomass	117
5.8.2 Effect of torrefaction on the physicochemical properties of bio-oil	119
5.8.3 Effect of torrefaction on the FTIR analysis of bio-oil	123
5.8.4 Effect of torrefaction on the GC-MS analysis of bio-oil	127
5.8.5 Effect of torrefaction on the properties of bio-char	130
5.8.6 Effect of torrefaction on NCG (pyrolytic gas)	134
5.9 Summary	136
6. Energy and exergy analysis for the torrefaction and pyrolysis of raw and torrefied biomass	137-168
6.1 Overview	137
6.2 Materials and methods	137
6.2.1 Material selection	137
6.2.2 Experimental procedure	138

Table of Contents

6.2.3 Energy analysis	138-142
6.2.4 Exergy analysis	142-146
6.3 Energy and exergy analysis for the torrefaction of pigeon pea stalk and eucalyptus	146
6.3.1 Influence of torrefaction temperature on energy and exergy value of NCG (torgas) and liquid product	146
6.3.2 Influence of torrefaction temperature on energy and exergy value of torrefied biomass	151
6.3.3 Influence of torrefaction temperature on total exergy at inlet, at outlet and its irreversibility	153
6.3.4 Influence of torrefaction temperature on exergy and irreversibility efficiency	154
6.3.5 Energy recovery for torrefaction	155
6.4 Energy and exergy analysis for the pyrolysis of raw and torrefied biomass (pigeon pea stalk and eucalyptus)	157
6.4.1 Influence of pyrolysis temperature on the energy and exergy value of pyrolytic gas and bio-char	157
6.4.2 Influence of pyrolysis temperature on energy and exergy value of bio-oil	162
6.4.3 Influence of pyrolysis temperature on total exergy at inlet, at outlet and its irreversibility	164
6.4 Energy recovery for pyrolysis	165
7. Conclusions and scope for future work	169-174
7.1 Conclusions	169
7.2 Future scope of work	172
References	175-198
List of Publications	199

List of Figures

Fig. No.	Title	Page No.
Fig. 1.1	Different sources of biomass (Adopted from Bar-On et al., 2018)	4
Fig. 1.2	Effect of torrefaction on raw biomass	7
Fig. 2.1	Inefficient and efficient utilization of agricultural residue	14
Fig. 3.1	Pictorial view of the experimental setup	32
Fig. 3.2	Schematic of the experimental setup	32
Fig. 3.3	Experimental verses predicted values for the responses of a) HHV, and b) energy yield of torrefied pigeon pea stalk	35
Fig. 3.4	Experimental verses predicted values for the responses of a) HHV, and b) energy yield of torrefied eucalyptus	36
Fig. 3.5	Response surface 3D plots for the HHV of torrefied pigeon pea stalk showing the effect of (a) temperature and residence time, (b) temperature and heating rate, (c) residence time and heating rate	47
Fig. 3.6	Response surface 3D plots for the HHV of torrefied eucalyptus showing the effect of (a) temperature and residence time, (b) temperature and heating rate, (c) residence time and heating rate	48
Fig. 3.7	Response surface 3D plots for the energy yield of torrefied pigeon pea stalk showing the effect of (a) temperature and residence time, (b) temperature and heating rate, (c) residence time and heating rate	49
Fig. 3.8	Response surface 3D plots for the energy yield of torrefied eucalyptus showing the effect of (a) temperature and residence time, (b) temperature and heating rate, (c) residence time and heating rate	50
Fig. 4.1	Product distribution during the torrefaction of (a) pigeon pea stalk and (b) eucalyptus, at different operating parameters	60

Fig. 4.2	Effect of torrefaction on proximate analysis of pigeon pea stalk and eucalyptus	63
Fig. 4.3	Van Krevelen diagram for raw and torrefied biomass, and Indian coal	68
Fig. 4.4	Moisture reabsorption for raw and torrefied biomass over the period of 168 hrs	70
Fig. 4.5	Effect of torrefaction on HR value and its recommended range for fluidized bed reactor	73
Fig. 4.6	Effect of torrefaction on FR value and its recommended range for co-combustion with coal	74
Fig. 4.7	Effect of torrefaction on CI value and its recommended range for co-combustion with coal	76
Fig. 4.8	Infrared spectra of raw and torrefied pigeon pea stalk	77
Fig. 4.9	Infrared spectra of raw and torrefied eucalyptus	77
Fig. 4.10	SEM images of (a) RPS (2000X), (b) TPSO (2000X), (c) RPS (5000X) and (d) TPSO (5000X)	80
Fig. 4.11	SEM images of (a) REC (2000X), (b) TECO (2000X), (c) REC (5000X) and TECO (5000X)	81
Fig. 4.12	Experimental curves of, (a) TGA, (b) DTG for raw and torrefied pigeon pea stalk	82-83
Fig. 4.13	Experimental curves of, (a) TGA, (b) DTG for raw and torrefied eucalyptus	83-84
Fig. 4.14	Plot obtained by Arrhenius method for hemicellulose present in pigeon pea stalk	88
Fig. 4.15	Plot obtained by Arrhenius method for cellulose present in pigeon pea stalk	88
Fig. 4.16	Plot obtained by Arrhenius method for lignin present in pigeon pea stalk	89
Fig. 4.17	Plot obtained by Arrhenius method for hemicellulose present in	89

List of Figures

	eucalyptus	
Fig. 4.18	Plot obtained by Arrhenius method for cellulose present in eucalyptus	90
Fig. 4.19	Plot obtained by Arrhenius method for lignin present in eucalyptus	90
Fig. 4.20	Relative yield (%) of compound groups present in the liquid product	94
Fig. 4.21	Composition variation of torgas (N ₂ free basis) with severity of torrefaction	95
Fig. 5.1	Comparison of experimental and predicted values of the responses for bio-oil yield of (a) torrefied pigeon pea stalk and (b) torrefied eucalyptus	100
Fig. 5.2	3-D plots for the combined effect of (a) temperature and residence time, (b) temperature and heating rate, (c) temperature and nitrogen sweeping rate, (d) residence time and heating rate, (e) residence time and nitrogen sweeping rate, and (f) heating rate and nitrogen sweeping rate, on bio-oil yield of torrefied pigeon pea stalk	111-112
Fig. 5.3	3-D plots for the combined effect of (a) temperature and residence time, (b) temperature and heating rate, (c) temperature and nitrogen sweeping rate, (d) residence time and heating rate, (e) residence time and nitrogen sweeping rate, and (f) heating rate and nitrogen sweeping rate, on bio-oil yield of torrefied eucalyptus	112-113
Fig. 5.4	Product distribution for the pyrolysis of raw and torrefied biomass	118
Fig. 5.5	Effect of torrefaction on the FTIR spectra of the bio-oil from pigeon pea stalk	101
Fig. 5.6	Effect of torrefaction on the FTIR spectra of the bio-oil from eucalyptus	124
Fig. 5.7	Effect of torrefaction on the Relative yield (%) of various compound derivatives of present in the bio-oil	128
Fig. 5.8	FTIR spectra of bio-char from the pyrolysis of raw and torrefied pigeon pea stalk	133

Fig. 5.9	FTIR spectra of bio-char from the pyrolysis of raw and torrefied eucalyptus	133
Fig. 5.10	Comparison of pyrolytic gas (NCG) evolving from the pyrolysis of raw and torrefied biomass	134
Fig. 6.1	Energy and exergy flows for both torrefaction and pyrolysis system	139
Fig. 6.2	Variation in chemical energy of torgas (NCG) components with temperature	147
Fig. 6.3	Variation in chemical energy of torgas (NCG) components with temperature	148
Fig. 6.4	Total energy and exergy variation of torgas with temperature	149
Fig. 6.5	Influence of temperature on total exergy of torrefaction products	150
Fig. 6.6	Influence of temperature on total irreversibilities, total exergy in and out during torrefaction process	153
Fig. 6.7	Effect of temperature on exergy efficiency and irreversibility of torrefaction products	154
Fig. 6.8	Chemical energy of the components for the pyrolytic gas during the pyrolysis of raw and torrefied pigeon pea stalk	159
Fig. 6.9	Chemical energy of the components for the pyrolytic gas during the pyrolysis of raw and torrefied eucalyptus	159
Fig. 6.10	Physical energy of the components for the pyrolytic gas during the pyrolysis of raw and torrefied pigeon pea stalk	160
Fig. 6.11	Physical energy of the components for the pyrolytic gas during the pyrolysis of raw and torrefied eucalyptus	160
Fig. 6.12	Effect of pyrolysis temperature on the exergy of its products	163
Fig. 6.13	Impact of pyrolysis temperature on total exergy in and out along with total irreversibilities of the pyrolysis system	164

List of Tables

Table No.	Title	Page No.
Table 1.1	Types of pyrolysis with operating parameters and favourable products (Basu, 2013; Bertero and Sedran, 2015)	9
Table 2.1	Properties of feedstock from various agricultural residue and woody biomass	17-18
Table 2.2	Process optimization for torrefaction and pyrolysis using RSM	26
Table 3.1	Experimental responses for the torrefaction process of pigeon pea stalk	37
Table 3.2	Experimental responses for the torrefaction process of eucalyptus	38
Table 3.3	ANOVA for the responses of the reduced quadratic models for the torrefaction of pigeon pea stalk	39
Table 3.4	ANOVA for the responses of the reduced quadratic models for the torrefaction of eucalyptus	40
Table 3.5	Optimization condition (constraints)	44
Table 3.6	HHV and energy yield at optimized condition and corresponding experimental values	44
Table 4.1	Variation of proximate analysis, HHV and bulk density of torrefied biomass with the severity of torrefaction	62
Table 4.2	Elemental analysis for raw and torrefied biomass	63
Table 4.3	Effect of torrefaction on the fiber analysis of pigeon pea stalk and eucalyptus	69
Table 4.4	Energy density, compactibility, flowability and combustion indices for raw and torrefied biomass (pigeon pea stalk and eucalyptus)	72

Table 4.5	Position vibration, in cm^{-1} , of the most representative peaks found in the infrared analysis of raw and torrefied biomass (pigeon pea stalk and eucalyptus)	79
Table 4.6	Kinetic parameters for the pseudo-components of raw and torrefied pigeon pea stalk	91
Table 4.7	Kinetic parameters for the pseudo-components of raw and torrefied eucalyptus	92
Table 4.8	HHV and water content of the liquid product obtained during torrefaction	94
Table 5.1	Experimental matrix with responses for the pyrolysis of torrefied pigeon pea stalk	101
Table 5.2	Experimental matrix with responses for the pyrolysis of torrefied eucalyptus	102
Table 5.3	ANOVA of reduced quadratic model for pyrolysis of torrefied pigeon	103
Table 5.4	ANOVA of reduced quadratic model for pyrolysis of torrefied eucalyptus	103
Table 5.5	Constraints provided during process optimization	109
Table 5.6	Optimum operating conditions with predicted and experimental values	110
Table 5.7	Properties of bio-oil obtained from raw and torrefied biomass (pigeon pea stalk and eucalyptus)	120
Table 5.8	Position vibration, in cm^{-1} , of the most representative peaks found during infrared analysis for bio-oil	125
Table 5.9	HHV, elemental and proximate analysis of bio-char from the pyrolysis of raw and torrefied biomass (pigeon pea stalk and eucalyptus)	132
Table 6.1	Standard specific enthalpy, entropy, HHV and standard chemical exergy of NCG (Liu et al., 2014; Wang et al., 2016)	140
Table 6.2	Value of the coefficients for the constant pressure specific heat of NCG (Peters et al., 2014)	143

Table 6.3	Total energy and exergy of raw biomass and torrefaction products	149
Table 6.4	The value of β associated with exergy calculation	151
Table 6.5	Energy recovery in products of biomass torrefaction	156
Table 6.6	Total energy and exergy of raw biomass, torrefied biomass and their pyrolysis products	161
Table 6.7	Energy recovery in the pyrolysis products form raw and torrefied biomass	166

NOMENCLATURE

RSM	Response surface methodology
HHV	Higher heating value (MJ/kg)
X₁	Torrefaction temperature (°C)
X₂	Residence time (min)
X₃	Heating rate (°C/min)
X₄	Nitrogen sweeping rate (ml/min)
RPS	Raw pigeon pea stalk
REC	Raw eucalyptus
TPS-X₁-X₂-X₃	Torrefaction of pigeon pea stalk at temperature X (°C), residence time X ₂ (minutes) and heating rate X ₃ (°C/min)
TEC-X₁-X₂-X₃	Torrefaction of eucalyptus at temperature X (°C), residence time X ₂ (minutes) and heating rate X ₃ (°C/min)
TPSO	Torrefaction of pigeon pea stalk at the optimum condition obtained using RSM
TECO	Torrefaction of eucalyptus at the optimum condition obtained using RSM
PRPS-X₁-X₂-X₃-X₄	Pyrolysis of raw biomass at temperature X (°C), residence time X ₂ (minutes), heating rate X ₃ (°C/min), and X ₄ (ml/min)
PREC-X₁-X₂-X₃-X₄	Pyrolysis of raw eucalyptus at temperature X (°C), residence time X ₂

	(minutes), heating rate X_3 ($^{\circ}\text{C}/\text{min}$), and X_4 (ml/min)
PTPS-X_1-X_2-X_3-X_4	Pyrolysis of torrefied pigeon pea stalk (TPSO) at temperature X ($^{\circ}\text{C}$), residence time X_2 (minutes), heating rate X_3 ($^{\circ}\text{C}/\text{min}$), and X_4 (ml/min)
PTPS-X_1-X_2-X_3-X_4	Pyrolysis of torrefied eucalyptus (TECO) at temperature X ($^{\circ}\text{C}$), residence time X_2 (minutes), heating rate X_3 ($^{\circ}\text{C}/\text{min}$), and X_4 (ml/min)
PTPSO	Pyrolysis of torrefied pigeon pea stalk (TPSO) at the optimum pyrolysis condition
PTECO	Pyrolysis of torrefied eucalyptus (TECO) at the optimum pyrolysis condition
PRPSO	Pyrolysis of raw pigeon pea stalk at the same optimum pyrolysis condition obtained for the pyrolysis of torrefied pigeon pea stalk
PRECO	Pyrolysis of raw eucalyptus at the same optimum pyrolysis condition obtained for the pyrolysis of torrefied eucalyptus
CCD	Central composite design
ANOVA	Analysis of variance
P-value	Probability value
F-value	The Fischer test value
m	Mass (kg)
LOF	Lack of fit
Y	Yield
ASTM	American standard of testing of materials
FR	Fuel ratio

Nomenclature

ASH	Ash Content, wt%
FC	Fixed Carbon, wt%
VM	Volatile Material, wt%
M	Moisture Content, wt%
ASTM	American standard of testing of materials
NCG	Non- Condensable Gas (wt%)
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscope
DTG	Derivative thermogravimetric
GC/MS	Gas chromatograph-mass spectrometry
TCD	Thermal conductivity detector
MFC	Mass flow controller
KBR	Potassium Bromide
Ex	Exergy, kJ/kg raw biomass
En	Energy, kJ/kg raw biomass
n_i	Number of moles of ith species, kmol/kg raw biomass
M	Mass, kg
T	Temperature
P	Pressure, Pa
h	Specific enthalpy, kJ/kmol
s	Specific entropy, kJ/kmol-K

ex	Standard specific exergy, kJ/kmol
C_p	Constant pressure specific heat capacity, kJ/kmol-K

Greek letters

Correlation factor

Exergy efficiency

Superscripts

std	Standard condition
solid	Related to torrefied biomass
liquid	Related to liquid obtained during torrefaction

Subscripts

o	Ambient condition
PHY	Physical
CHE	Chemical
KE	Kinetic
PE	Potential
irreversibility	Related to irreversibility
electricity	Related to electrical energy or exergy of furnace

Abstract

In the present study, two different types of biomass materials (agricultural residue like pigeon pea stalk and commercial farm wood such as eucalyptus) have been used for the possible generalization of torrefaction and pyrolysis of torrefied biomass on other different biomass materials for the enhancement of bio-fuel properties through pre-treatment process. The research work mainly focuses on torrefaction of these biomass materials and thereafter pyrolysis leading to the drastic improvement bio-fuel properties in sharp contrast to the pyrolysis of raw biomass and co-combustion with coal. The present scope of research work also covers the optimization and the statistical analysis for both torrefaction and pyrolysis process using response surface methodology (RSM). The present study includes the energy and the exergy aspects of torrefaction and pyrolysis process in order to improve the existing process by introducing energy recuperation from byproducts, and thus decreasing the energy consumption and helping in achieving an energy efficient process for obtaining high grade bio-fuels from biomass.

Torrefaction of pigeon pea stalk and eucalyptus have been carried out in a quartz tube reactor. For the torrefaction process, temperature (X_1) varied from 200-300 °C; residence time (X_2) varied from 0-60 min, and heating rate (X_3) varied from 5-20 °C/min. Based on the statistical analysis, for both biomass materials, the impact of operating parameters on responses (HHV and energy yield) have been found as $X_1 > X_2 > X_3$. Based on ANOVA and validation of optimum condition, it can be attributed that reduced quadratic models for HHV and energy yield of torrefied pigeon pea stalk and eucalyptus have been efficient to

operate in the design space. The optimum torrefaction condition for pigeon pea stalk and eucalyptus have been obtained at 248 °C, and 253 °C, respectively, with residence time at 60 min, and heating rate at 20 °C/min. Maximum increase in HHV for torrefied pigeon pea stalk and eucalyptus have been 43.53 and 39.49 %, respectively, as compared to their raw biomass. The solid fuel properties like HHV, FR, CI, and VI have been improved for the torrefied biomass, making it compatible with the existing coal based power plants available in South Asian and African countries. FTIR results confirmed the removal of oxygen containing functional groups in pigeon pea stalk and its extent increased with severity of torrefaction. XRD analysis showed a decrease in crystallinity index for torrefied biomass as compared to raw biomass. SEM micrographs indicated increase in porosity and generation of cracks for torrefied biomass. HHV and water content of liquid product have been in the range of 6.91-11.94 MJ/kg and 50.2-84.3 wt%, respectively. GC-MS results suggested the high presence of phenol and furan derivatives with acetic acid and ketones derivatives being on the lower side. Kinetic parameters revealed that the total activation energy decreased by 54.4 % and 45 % for eucalyptus and pigeon pea stalk, respectively, at the most severe torrefaction condition as compared to their respective raw biomass.

Pyrolysis have been performed for the torrefied biomass obtained at the optimum condition. Statistical analysis revealed that impact of operating parameters on bio-oil yield (BY) for both types of biomass has been $X_1 > X_3 > X_2 > X_4$ (where X_4 denotes nitrogen sweeping rate). Based on maximum bio-oil yield (BY), the optimum conditions have been obtained at 461 °C, 1 min, 42.3 °C/min, and 73 ml/min for pigeon pea stalk and at 442 °C, 0 min, 55.4 °C/min, and 42 ml/min for eucalyptus. On comparing the BY obtained from

torrefied to that of raw biomass at the same condition revealed that BY has been decreased substantially. However, the fuel properties of bio-oil obtained from the pyrolysis of torrefied biomass have been significantly improved as compared to bio-oil obtained from raw biomass. Both elemental and FTIR analysis confirmed that oxygen content in the bio-oil from pyrolysis of torrefied biomass decreased significantly.

In torrefaction process energy and exergy values of solid products have been decreased, whereas for non-condensable gases (NCG) and liquid, these values have increased with increase in temperature. Energy and exergy values of solid have been the highest followed by liquid and then NCG. CO has been the main contributor in the total energy and exergy of NCG. Exergy efficiency of solid product has been in the range of 52 to 54% under moderate torrefaction. Irreversibility has been found to be increased with increase in temperature. Recuperation of energy from byproducts (liquid and NCG) could increase the energy recovery in solid by 8 to 9 %. The present study shows that the moderate torrefaction condition for biomass seems to be the most promising condition in achieving a balance between overall efficiency and desired physicochemical properties. During the energy and exergy analysis for the pyrolysis of torrefied biomass there was a significant increase in the chemical energy of CH₄ which confirmed the quality enhancement of pyrolytic gas on using torrefied biomass as a feed. Similarly the energy or exergy value of bio-char from torrefied biomass also witnessed a sharp increase in its value. However, on analyzing the energy-exergy value of bio-oil there was a decrease in its value for the torrefied biomass as compared to raw biomass feed but considering the yield of bio-oil the quality of bio-oil increased significantly in terms of HHV.