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.

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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.

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

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NOMENCLATURE

RSM	Response surface methodology
HHV	Higher heating value (MJ/kg)
X_1	Torrefaction temperature (°C)
X_2	Residence time (min)
X_3	Heating rate (°C/min)
X_4	Nitrogen sweeping rate (ml/min)
RPS	Raw pigeon pea stalk
REC	Raw eucalyptus
TPS-X_1-X_2-X_3	Torrefaction of pigeon pea stalk at temperature X (°C), residence time X_2 (minutes) and heating rate X_3 (°C/min)
TEC-X_1-X_2-X_3	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-X_1-X_2-X_3-X_4	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-X_1-X_2-X_3-X_4	Pyrolysis of raw eucalyptus at temperature X (°C), residence time X_2

	(minutes), heating rate X_3 (°C/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 (°C), residence time X_2 (minutes), heating rate X_3 (°C/min), and X_4 (ml/min)
PTPS-X_1-X_2-X_3-X_4	Pyrolysis of torrefied eucalyptus (TECO) at temperature X (°C), residence time X_2 (minutes), heating rate X_3 (°C/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

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
$\mathbf{n_i}$	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 CH_4 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.