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It is certified that the work contained in the thesis titled **'Pyrolysis behaviour of low value biomass towards renewable fuel and valuable chemicals'** by **Ahmad Nawaz** has been carried out under my supervision. This work has not been submitted elsewhere for a degree. It is further certified that the student has fulfilled all the requirements of the comprehensive examination, Candidacy, and SOTA for the award of Ph. D. degree.

Supervisor 16/8/22

Dr. Pradeep Kumar (Associate Professor)
Department of Chemical Engineering & Technology
Indian Institute of Technology (BHU), Varanasi – 221005, India

DECLARATION BY THE CANDIDATE

I, **Ahmad Nawaz**, certify that the work embodied in this thesis is my bonafide work and carried out by me, under the supervision of **Dr. Pradeep Kumar** from **December 2017 to August 2022** at the '**Department of Chemical Engineering & Technology**,' Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. 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 willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports, dissertations, thesis, etc., or available on websites and have not included them in this thesis and have not cited as my work.

Date: 16/8/22

Place: Indian Institute of Technology (BHU), Varanasi

Ahmad Nawaz
(**Ahmad Nawaz**)

CERTIFICATE FROM THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my knowledge.

16/8/22
Head of the department
Prof. V.L Yadav
Department of Chemical Engineering & Technology
Indian Institute of Technology (BHU)
Varanasi – 221005, India

विभागाध्यक्ष / Head
रासायनिक अभियांत्रिकी एवं प्रौद्योगिकी विभाग
Dept. of Chemical Engg. & Tech.
भारतीय प्रौद्योगिकी संस्थान / Indian Institute of Technology
काशी हिन्दू विश्वविद्यालय / Banaras Hindu University
वाराणसी / Varanasi-221005

16/8/22
Supervisor
Dr. Pradeep Kumar (Associate Professor)
Department of Chemical Engineering & Technology
Indian Institute of Technology (BHU), Varanasi – 221005, India

Associate Professor
Deptt. of Chemical Engg. & Tech.
Indian Institute of Technology
Banaras Hindu University
वाराणसी/Varanasi-221005

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Date:

Place: IIT (BHU) Varanasi (**Ahmad Nawaz**)

Dedicated

To

My Beloved Parents

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List of Abbreviations

Abbreviation	Nomenclature
MMT	Million Metric Tons
MTOE	Million Tons of Oil Equivalent
TMT	Thousand Metric Tons
GHG	Green House Gas
MW	Mega Watt
MNRE	Ministry of New Renewable Energy
IREDA	Energy Development Agency Limited
MPa	Mega Pascal
HTC	Hydrothermal Carbonization
TGA	Thermogravimetric analysis
DTG	Differential Thermogravimetric
FTIR	Fourier Transform Infrared Spectroscopy
GCMS	Gas Chromatography Mass spectroscopy
NMR	Nuclear magnetic resonance
RSM	Response Surface Methodology
OFAT	One Factor At a Time
CCD	Central Composite Design
ANOVA	Analysis of Variance
LS	*Lagerstroemia speciosa*
MS	Mustard straw
SB	*Sesbania bispinosa*
MC	Moisture content
AC	Ash content
VM	Volatile matter
FC	Fixed carbon
C, H, N, and S	Carbon, Hydrogen, Nitrogen, and Sulfur
EA	Elemental analyzer
HHV	Higher heating value
ATR	Attenuated total reflection
OFW	Ozawa Flynn Wall

KAS	Kissinger Akahira Sunose
TM	Tang Method
ST	Starink method
VZK	Vyazovkin method
CR	Coats Redfern
PID	Proportional Integral Derivative
rpm	Revolution per minute
ASTM	American Society for Testing and Materials
EDX	Energy Dispersive X-ray
FE-SEM	Field Emission Scanning Electron Microscopy
NIST	National Institute of Standards and Technology
ICTAC	International Confederation of Thermal Analysis and Calorimetry
MCT	Molecular collision theory

List of symbols

Symbol	Nomenclature
A	Pre-exponential factor (s^{-1})
T	Temperature (degree Celsius or kelvin)
E	Activation energy (kJ/mol)
E_α	Activation energy (variation with conversion)
α	Conversion
t	Time (second or minute)
K(T)	Temperature dependent rate constant
m_i	Initial weight
m	Instantaneous weight
m_∞	Final weight
R	Universal gas constant (8.314 J/mol.K)
β	Heating rate (°C/min)
f(α)	Reaction model based function of conversion
g(α)	Integral conversion function
C	Constant
ΔG	Change in Gibb's free energy (kJ/mol)
ΔH	Change in enthalpy (kJ/mole)
ΔS	Change in entropy (J/mol.K)
h	Plank's constant (6.626×10^{-34} Js)
K_b	Boltzmann constant (1.381×10^{-23} J/K)
T_m	Peak temperature
R^2	Regression coefficient

Preface

Energy is regarded as a critical component for the worldwide development and financial prosperity of present-day society. However, rising energy use in recent years has resulted in issues such as depletion of fossil-based energy resources and ecological destruction. The agricultural, industrial, transportation, and residential sectors have an increased energy demand. Over the last two to three decades, significant global research and development efforts have been devoted to developing different renewable energy supplies to meet energy demand while decreasing environmental challenges. Renewable energy resources such as biomass, solar, wind, and hydro have been identified as potential possibilities for a country like India. Lignocellulosic biomass has received substantial consideration over other renewable energy resources due to its inherent advantages. Biomass has drawn the attention of policymakers and academics worldwide among the many categories of renewable energy sources because of its renewable and sustainable character and its continuous and extensive availability in various forms. In this thesis, three different types of low-value biomass such as *Lagerstroemia speciosa* (LS), mustard straw (MS), and *Sesbania bispinosa* (SB), were chosen as a feedstock for pyrolysis in order to determine their bioenergy potential. The LS biomass was collected from the campus of IIT (BHU) Varanasi, whereas the MS and SB biomass was collected from the village (Bindwal) of Azamgarh district, Uttar Pradesh, India. The samples were dried and then powdered to get the desired particle size. Further, physicochemical characterization such as proximate, ultimate, and fiber analyses were carried out. The calorific value and bulk density were also measured to determine the energy content and ease in storage and transportation, respectively. The FTIR spectroscopy was carried out to determine the different functional groups attached to the respective biomasses, whereas thermogravimetric analysis was carried out to determine the thermal stability of the biomass.

Chapter-1 deals with the introduction of energy scenario in India. This chapter describes the production and consumption of different petroleum products in India. Further, the classification and properties of the available biomass resources have been described. The chemical composition of the biomass, such as hemicellulose, cellulose, and lignin, and the technologies applied for converting biomass into valuable products were presented.

Chapter-2 mainly deals with the physicochemical characteristics of different types of biomasses reported in previously published literature. The kinetic analysis of different types of biomasses using different models was studied. The thermal pyrolysis based on different operating conditions of various types of biomass and their optimum pyrolytic yield were presented. The yield of pyrolysis products, for example, type of biomass, catalyst employed, heating rate, feedstock size, sweeping gas (N_2) flow rate, reactor layout, and temperature, were studied. The pyrolysis products were optimized using response surface methodology (RSM) based on central composite design (CCD). The research gaps were identified from the literature. The scope and objectives of the present research work are described.

Chapter-3 deals with material and methods, collection, and preparation of the biomass. The preliminary characterization of the sample such as proximate analysis (moisture content, volatile matter, ash, and fixed carbon content), ultimate analysis (carbon, hydrogen, nitrogen, and sulfur), calorific value, bulk density, fiber analysis (cellulose, hemicellulose, and lignin) were carried out using the standard protocols, whereas thermal degradation analysis was carried out using a thermogravimetric analyzer. Fourier transform infrared spectroscopy (FTIR) was employed for the determination of functional groups present in the biomass. The kinetic and thermodynamic parameters were also calculated using the respective equations. This chapter also comprises the details of the experimental setup used in different experimental works.

Chapter-4 aims to investigate the thermochemical characteristics and thermal degradation behavior of LS biomass. LS sample was characterized by proximate study, elemental study, calorific value, fiber analysis, and thermal stability study, whereas; isoconversional models such as Ozawa-Flynn-Wall (OFW), Kissinger Akahira Sunose (KAS), Vyazovkin (VZK), Tang method (TM), and Starink method (ST) were used for performing the kinetic study. The physicochemical study of LS revealed its bioenergy capability to create renewable fuel and valued compounds. Further, isoconversional models such as OFW, KAS, TM, ST, and VZK yielded average activation energy of 164, 154.35 154.63, 154.61, and 141.93 kJ/mol. The master plot and thermodynamic study of LS confirmed that the pyrolysis process passed through multifaceted reaction mechanisms. Important pyrolysis parameters such as heating rate, temperature, and inert gas (N_2) flow rate were optimized using the Response Surface Methodology (RSM). The experimental findings revealed that the optimum condition for the maximum bio-oil yield (45.6%) production was: temperature = 550°C, heating rate = 65°C/min, and N_2 flow rate = 60ml/min; however, at this condition, the predicted bio-oil yield using RSM was 44.98%. The obtained bio-oil was characterized based on its physicochemical properties such as GCMS, FTIR, and 1H-NMR.

Chapter-5 aims to investigate the thermochemical characteristics and thermal degradation behavior of mustard straw. The model-free methods of Ozawa-Flynn-Wall (OFW), Kissinger Akahira Sunose (KAS), and Vyazovkin were employed for kinetic analysis and Coats-Redfern (CR) method was employed for elucidating the reaction mechanism. Response surface methodology (RSM) with a central composite design technique was employed to optimize the pyrolysis process parameters to gain the maximum amount of bio-oil. The highest bio-oil yield (44.69%) was obtained at the heating rate of 25 °C/min and a temperature of 500°C under inert conditions (N_2 gas flow rate=100 ml/min). Further, FTIR and GCMS analysis of bio-oil revealed the presence of different functional groups and valuable chemicals, whereas physicochemical characterization revealed its fuel characteristic. The results confirmed the suitability of mustard straw as a feedstock for obtaining cleaner fuel and value-added products.

Chapter-6 deals with the aim of optimizing the process parameters and experimental situations for the pyrolysis of *Sesbania bispinosa* (SB) to acquire the utmost bio-oil yield. A stainless steel fixed bed reactor was employed for pyrolysis to attain the pyrolysis product. The thermogravimetric analyzer (TGA) was employed to measure the thermal degradation profile at dynamic heating rates. The model-free approaches of Ozawa Flynn Wall (OFW), Kissinger Akahira Sunose (KAS), Tang (TM), Starink (ST), and Vyazovkin (VZK) were used to predict kinetic parameters. The average activation energy obtained was 181.37, 180.63, 180.91, 180.90, and 161.31 kJ/mol using the OFW, KAS, TM, ST, and VZK methods, respectively. The thermal pyrolysis results revealed that the highest bio-oil yield (42.53 wt. %) was achieved at a temperature of 585 °C, a heating rate of 60 °C/min, and an inert flow rate of 125 ml/min. Characterization results of biochar confirmed its candidacy to be used in different industrial applications.

Chapter-7 presents the overall summary, including important conclusions and the scope of future work.