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Date: *(Mohit Kumar)*

Every challenging work needs self-efforts as well as guidance of elders especially those who are close to our heart.

I dedicate my thesis to the most amazing teacher of my life Prof. S.N. Upadhyay and to my loving family

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List of Abbreviations and Symbols

A	Arrhenius pre-exponential factor, s^{-1}
C_1	Constant
E	Activation energy, kJ/mole
E_α	Activation energy (variation with conversion)
$f(\alpha)$	Reaction model based function of conversion
$g(\alpha)$	Integral conversion function
ΔG	Change in free energy, MJ/mole
ΔH	Change in enthalpy, MJ/mole
k(T)	Temperature dependent reaction rate constant
m_o	Initial weight of sample
m_t	Sample weight at time t
m_f	Final sample weight
P(x)	Conversion function (= x-2e-x)
R	Universal gas constant (=8.314 J/mol.K)
t	Time, s or min
T	Temperature, K
α	Conversion
β	Heating rate
Tm	Peak temperature
$\Pi(x)$	Temperature integral approximation
R^2	Correlation coefficient
n	Order of reaction
TGA	Thermogravimetric analysis
DTG	Derivative of thermogravimetric analysis
FTIR	Fourier transform infrared spectroscopy
MC	Moisture
VM	Volatile matter
FC	Fixed carbon
NIST	National Institute of Standards and Technology
PID	Proportional–integral–derivative
GC	Gas chromatography
NMR	Nuclear magnetic resonance

GC-MS	Gas chromatography–mass spectrometry
k	Rate constant
KAS	Kissinger-Akahira-Sunose
OFW	Ozawa-Flynn-Wall
DAEM	Distributed activation energy model
CR	Coats-Redfern model
MLR	Multiple linear regression model
SB	Sugarcane bagasse
RH	Rice husk
WS	Wheat straw
BT	Banana trunk
AS	Arhar stalk
RS	Rice straw
PMW	Paper mill waste
SCL	Sugar cane leave
PS	Peanut shell

PREFACE

Increasing environmental pollution and related global issues like climate change and global warming coupled with rising cost and finite availability of fossil fuels confined primarily in the politically unstable regions of the world have provided impetus to look for alternative, less polluting and sustainable energy resources. Various carbonaceous wastes such as agricultural residues, municipal solid waste and industrial wastes are being considered as almost carbon neutral and sustainable renewable energy resources. Out of these, lignocellulosic biomass from various sources is being considered as potential substitute for conventional fossil fuels (coal, gas and liquid petro-fuels). Their global availability and renewable nature makes them attractive over other renewable energy sources on several counts. In view of this global efforts are being made to use these as feedstock for producing cleaner fuels and other value added products through biochemical and/or thermo-chemical conversion routes. For a country like India their potential is enormous but still underutilized. In this work lignocellulosic biomasses such as wheat straw (WS), rice straw (RS), banana trunk (BT), rice husk (RH) arhar stalk (AS), sugar cane bagasse (SB), sugar cane leaves (SCL), peanut shell (PS) and paper mill waste (PMW) were used as the target biomasses. In each case representative samples of biomass were collected from agricultural farms. After preparing the powdered sample using clean dry biomass, the proximate, ultimate, and compositional analyses of were carried out. The bulk density and calorific value (higher heating value, MJ/kg) were also measured. The functional groups and crystalline nature of each biomass were determined using FTIR spectroscopic and XRD analyses. The thermal degradation study was carried out using a TGA/DTA unit.

The proximate and ultimate analysis results, higher heating values (HHV) and compositional analysis results for the nine biomasses used in this work were compared with the reported values for other and similar lignocellulosic biomasses. Values of carbon, hydrogen and oxygen percentages were used to prepare van Krevelen plot and compare with that for coal.

The FTIR spectra of all biomasses indicated the presence of alcoholic and phenolic groups, alkanes and alkenes and some aromatic molecules were present in all biomasses. During thermal degradation, maximum weight loss was recorded within the temperature range of 200–500°C in all cases.

The thermal degradation behaviour of sugarcane (*Saccharum officinarum* L) leaves (SCL) was investigated using DTA/TGA unit and fixed bed pyrolyser. Analysis of the pyrolysis kinetics had been carried using iso-conversional model free methods as well as multiple linear regression method. Apparent activation energy values evaluated from iso-conversional methods ranged from 214.9 to 239.6kJ/mol where as in the case of multiple linear regression analysis it ranged from 25.06 to 57.23kJ/mol.The multi-step reaction mechanism had been investigated using the Criado method. Effect of pyrolysis process parameter such as temperature, heating rate (15-30ºC/min), bed height (4-16cm) and particle size (0.710-0.180mm) were studied systematically. The maximum bio-oil and bio-char yields were found to be 44.78% (550ºC) 36.82% (350ºC), respectively. Physicochemical properties of bio-oil compared well with conventional diesel fuel. The chemical properties were estimated using FTIR, ^{1}HNMR and GC–MS. The bio-char was characterized through proximate and ultimate analyses, HHV evaluation as well as FTIR, SEM-EDX, ICP-AES, BET surface area and XRD analyses. The GC-MS analysis of bio-oil confirmed the presence of aromatic derivatives, phenols, ketones, and oxygenated compounds of high molecular weight as possible useful chemical products. The pyrolytic gases were analysed using gas chromatography. With increase in the pyrolysis temperature, the composition of hydrogen and hydrocarbons increased significantly while the formation of carbon dioxide got reduced. In addition, quantity of hydrogen and methane and HHV (MJ/kg) value indicated a good fuel property.

India is the second largest producer in Asia. After harvesting the fruit, the trunk and leaves are just left in the field as a litter. This biomass may be a good source of energy and chemicals. In view of this was used as the second target biomass. The thermo-chemical characterization (proximate and ultimate analyses and higher heating value) of banana trunk biomass waste was carried out. The thermo-gravimetric and differential scanning calorimetric (DSC) investigations were made at the heating rates of 10, 15, 20 and 25^{o}C/min. The TGA data had been used to carry out kinetic analysis and evaluate the kinetic and thermodynamic parameters using iso-conversional models. The values of activation energy increased with increasing conversion (α) irrespective of the model used. The average values of activation energies (E_α) were found to be 386.21, 355.43, 385.77, 355.01, 379.67, and 292.78kJ/mol for Flynn-wall-Ozawa (FWO), Starink, Kissinger-Akahira-Sunose (KAS), Tang, Vyzovkin and Vyzovkin AIC models, respectively. The average values of change in enthalpy, Gibbs free energy, and entropy too had been calculated. The reaction mechanisms of pyrolysis had been predicted using Criado's method.

India is one of the largest growers of peanut. Waste biomass after harvesting peanut pods (straw) and the peanut shell after taking out the seeds is neither properly collected nor used as a fuel in spite of its availability in large amount and expected good fuel property. In view of this the peanut shell biomass was taken as the third biomass. The pyrolysis of peanut shell (PS) had been investigated using a TGA/DTG unit and a fixed-bed pyrolyser at heating rates of 10, 15 and 20°C/min and in the temperature range of ambient to 800°C. The kinetic analysis of thermal degradation had been carried out using iso-conversional models. Effects of temperature, heating rate, and nitrogen gas flow rate on bio-oil and bio-char yields had been studied. The Box-Behenken design (BBD) of response surface methodology (RSM) had been used to optimize the process parameters. Bio-oil and biochar were characterized in terms of conventional thermo-chemical characteristics. The GC-MS spectrometric, Fourier transform infra-red spectroscopic, and nuclear magnetic resonance spectroscopic analyses had been used to know the chemical constituents of bio-oil.

The fourth biomass used as the target biomass was the paper mill waste (PMW) available in large amount from paper mills. The thermal degradation behaviors of PMW had been investigated in presence and absence of catalyst Montmorillonite clay in the temperature range of ambient to 1000°C and at the heating rates of 20, 25and 30°C/min. Proximate and ultimate analyses and evaluation of calorific value (HHV) of PMW were carried out using standard ASTM protocols. The thermo-gravimetric analysis (TGA) and differential thermogravimetric (DTG) data obtained under both situations had been used to evaluate the kinetic and thermodynamic parameters and elucidate the reaction mechanism. The clay had also been characterized using TGA/DTG analysis, Fourier Transform Infra-Red (FTIR) spectroscopic analysis and X-ray diffraction (XRD), Energy dispersive spectroscopy (EDS), and scanning electron microscopic (SEM) techniques. The activation energy, pre-exponential factor and thermodynamic parameters had been evaluated using the model-free iso-conversional methods of Flynn-Wall-Ozawa (FWO) and Vyazovkin and the distributed activation energy model (DAEM). The Montmorillonite clay had influenced the degradation process appreciably through its catalytic action.

The work presented in the thesis is well documented and following publications have come out of it:

Manuscripts Published in Peer-reviewed Journals

[1] Mohit Kumar, Shivesh Sabbarwal, P.K. Mishra, S.N. Upadhyay., **2019.**Thermal Degradation Kinetics of Sugarcane Leaves (Saccharum officinarum L) using Thermo-gravimetric and Differential Scanning Calorimetric Studies **Bioresource Technology** 279, 262–270.

[2] Mohit Kumar, S.N.Upadhyay, P.K. Mishra., **2019.** A Comparative Study of Thermochemical Characteristics of Lignocellulosic Biomasses **Bioresource Technology Reports** 2019:100186. doi:10.1016/j.biteb.2019.100186.

[3] Mohit Kumar, P.K. Mishra, S.N. Upadhyay, **2019.** Pyrolysis of *Saccharum munja*: Optimization of Process Parameters using Response Surface Methodology (RSM) and evaluation of kinetic parameters**. Bioresource Technology Reports** 2019; 8:100332. doi:10.1016/j.biteb.2019.100332.

[4] Mohit Kumar, S.N. Upadhyay, P.K .Mishra. **2020.** Thermal Degradation of Rice Husk: Effect of Pre-treatment on Kinetic and Thermodynamic Parameters. **Fuel 268, 117164** https://doi.org/https://doi.org/10.1016/j. fuel.2020.117164.

[5] Mohit Kumar, S.N.Upadhyay, P.K. Mishra., **2020.** Effect of Montmorillonite Clay on Pyrolysis of Paper Mill Waste **Bioresource Technology 2020:12316.** https://doi.org/10.1016/j.biortech.2020.123161

[6] Mohit Kumar, Shusheel Kumar Shukla, P.K. Mishra, S.N. Upadhyay **2020.** Analysis of thermal degradation of banana (Musa balbisiana) trunk biomass waste using iso-conversional models **Bioresource Technology 310,**123393 https://doi.org/10.1016/j.biortech.2020.123393

[7] Mohit Kumar, Neha Srivastava, P.K. Mishra, S.N. Upadhyay. (2021) Thermal degradation of dry kitchen waste: Kinetics and product distribution, **Biomass Conversion**

and Biorefinery 10.1007/s13399-021-01309-z

[8] Garvit Bhardwaj, **Mohit Kumar**, P.K. Mishra, S.N. Upadhyay., (2021). Kinetic Modelling of slow pyrolysis of Waste Papers, **Biomass Conversion and Biorefinery https://doi.org/10.1007/s13399-021-01363-7**

[9] Mohit Kumar, Durga Rai, Garvit Bhardwaj, P.K. Mishra, S.N. Upadhyay., (2021). Pyrolysis of Peanut Shell: Kinetic Analysis and Optimization of Thermal Degradation Process**, Industrial Crops & Products [Under review]**

[10] Dan Bahadur Pal, **Mohit Kumar**, P. K. Mishra, S. N. Upadhyay. (2021). Kinetics of Thermal Degradation of Mango, Jackfruit and Jamun Seeds kernel, **Biomass conversion and Biorefinery [Under revision]**

[11] Mohit Kumar, P.K. Mishra, S.N. Upadhyay., (2021). Pyrolysis of sugarcane (*Saccharum officinarum* L.) leaves: Product formation and characterization, **Biomass & Bioenergy [Under review]**

[12] Mohit Kumar, Rahul Yadav, P.K. Mishra, S.N. Upadhyay (2021). Effect of Chemical Treatment on Thermal Degradation Behavior of Litchi Seed Biomass **Journal of Environmental Management (Under review)**

[13] Tanya Gupta, **Mohit Kumar**, S.N. Upadhyay, P. K. Mishra, Amit K. Jaiswal (2021) Effect of Hot Water Extraction on Pyrolysis of Green Coconut Husk: Kinetics and Thermodynamic Parameters Analysis **Journal of Environmental Chemical Engineering [Under Review]**

[14] Mohit Kumar, S.N. Upadhyay, P. K. Mishra, Amit K. Jaiswal (2021) Advances in Thermochemical Conversion of Lignocellulosic Biomass into biofuel, **Book Chapter [Submitted]**

[15] Mohit Kumar, P.K. Mishra, S.N. Upadhyay., (2021) Recent trends of In-depth kinetic analysis of thermal degradation of lignocellulosic biomass. **Sustainable Energy & Fuel (Ready to submit).**

Manuscripts in advance stage of preparation

1. Mohit Kumar, Garvit Bhardwaj, P.K. Mishra, S.N. Upadhyay., 2021 (manuscript under preparation)

2. Mohit Kumar, P.K. Mishra, S.N. Upadhyay., 2021 (manuscript under preparation)

3. **Mohit Kumar**, P.K. Mishra, S.N. Upadhyay., 2021 (Manuscript prepared)