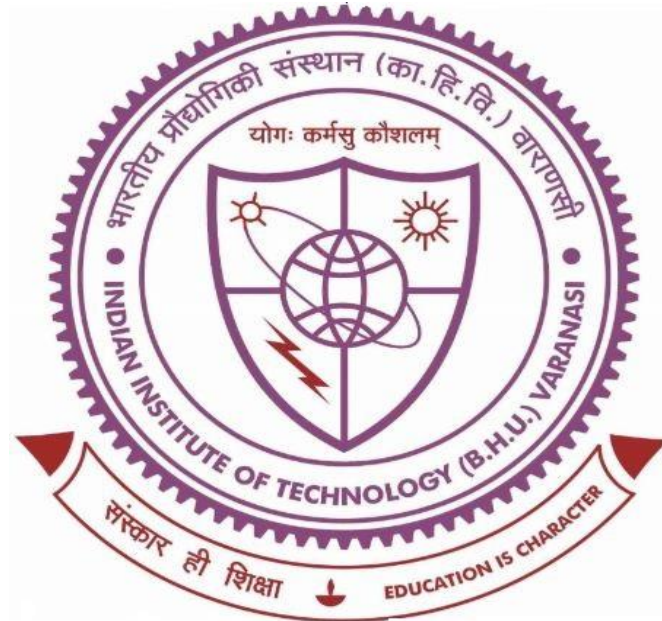


**STUDY OF KINETICS, THERMODYNAMICS, PROCESS  
PARAMETER VARIATION AND COMPARISON OF NON-  
CATALYTIC AND CATALYTIC PYROLYSIS OF *MELIA*  
*AZEDARACH* SAWDUST**



**Thesis submitted in partial fulfilment  
for the award of degree**

**Doctor of Philosophy**

By

**Nidhi Agnihotri**

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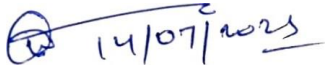
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# CERTIFICATE

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It is certified that the work contained in this thesis entitled "**Study of kinetics, thermodynamics, process parameter variation and comparison of non-catalytic and catalytic pyrolysis of *Melia azedarach* sawdust**" by **Nidhi Agnihotri** has been carried out under my supervision, and it has not been submitted elsewhere for a degree.

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## DECLARATION BY THE CANDIDATE

I, **Nidhi Agnihotri**, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of **Prof. Monoj Kumar Mondal** from July 2018 to July 2023, at the **Department of Chemical Engineering & Technology**, Indian Institute of Technology (Banaras Hindu University) 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 this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in the journals, books, magazines, reports, dissertations, thesis, 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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Date: 14/07/23

Varanasi



(Nidhi Agnihotri)

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## List of Abbreviation and Symbols

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<b>Abbreviations/ Symbols</b>	<b>Full form/Meaning</b>
A	Pre-exponential factor ( $s^{-1}$ )
AC	Ash content
BC	Bio-char
BC-C	Catalytic bio-char
BC-N	Non-catalytic bio-char
BET	Brunauer–Emmett–Teller
BO	Bio-oil
BO-C	Catalytic bio-oil
BO-N	Non-catalytic bio-oil
Btu	British thermal units
CPI	Comprehensive pyrolysis index
Cu	Copper
DTG	Derivative Thermogravimetry
E	Activation energy (kJ/mol)
EIA	Energy Information Administration
EY	Energy yield

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FC	Fixed carbon
FTIR	Fourier transforms infrared spectra
FWO	Flynn–Wall–Ozawa
GC-MS	Gas chromatography–mass spectrometry
h	Plank’s constant ( $6.626 \times 10^{-34}$ J.s)
HHV	Higher heating value (MJ/kg)
ICTAC	International Confederation of Thermal Analysis and Calorimetry
IUPAC	International Union of Pure and Applied Chemistry
$k$	Rate constant
KAS	Kissinger–Akahira–Sunose
$K_B$	Boltzmann constant ( $1.381 \times 10^{-23}$ J/K)
LHV	lower heating value
MAS	<i>Melia azedarach</i> sawdust
MAS-N	Native <i>Melia azedarach</i> sawdust
MAS-C	Cu impregnated <i>Melia azedarach</i> sawdust
MC	Moisture content
$M_f$	Weight loss (wt.%)

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NMR	Nuclear Magnetic Resonance
R	Universal gas constant (J/mol.K)
$-R_a$	Average decomposition rates
$-R_p$	Maximum average decomposition rate
SEM	scanning electron microscope
t	Time (s)
T	Temperature (K)
TGA	Thermogravimetric analysis
$T_i$	Initial devoatisation temperature
$T_p$	Peak temperature
VM	Volatile matter
$W_f$	Final mass of the sample left as residue after reaction (mg)
$W_i$	Initial mass of sample (mg)
$W_t$	Mass of sample at time t (mg)
XRD	X-ray diffraction
$\alpha$	Fractional conversion
$\beta$	Rate of heating ( $^{\circ}\text{C}/\text{min}$ )

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$\Delta G$	Change in Gibbs free energy (kJ/mol)
$\Delta H$	Change in enthalpy (kJ/mol)
$\Delta S$	Change in entropy (J/mol.K)
$\Delta T_{1/2}$	Temperature range of half-peak width
$T_\alpha$	Temperature at a specific conversion $\alpha$

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## **PREFACE**

Fossil fuel-based energy is exhaustible and accompanied by adverse impacts at local, regional, and global levels for environment, ecology, human beings and flora and fauna. Climatic conditions of the planet are being burdened due to population. Generating energy from waste biomass is a sustainable, novel and renewable green-energy generation approach for addressing energy-linked environmental impacts focusing on generation of wealth-from-waste. Lignocellulosic biomass is the most abundant, renewable, sustainable, and carbon neutral feedstock for the production of bio-energy, bio-fuels and high value bio-products. Pyrolysis is a thermochemical route for transforming biomass into biofuels (pyrolysis liquid called as bio-oil, solid bio-char and gases) at high temperature and inert atmospheric conditions. Often, bio-oil is the main targeted product of pyrolysis, but it has several drawbacks like high oxygen content and water content, high acidity and viscosity. Catalytic pyrolysis is used to enhance product quality. Bio-oil has potential for generating bio-energy and chemical feedstocks. Bio-char can be used as a substrate for activated carbon and other applications.

In view of the above stated issues, the objectives of this study were decided, to carry out pyrolysis of *Melia azedarach* sawdust for evaluation of its bio-energy generation potential and also to further carry out catalytic pyrolysis for attaining improved pyrolytic yields. The complete research work of thesis entitled “**Study of kinetics, thermodynamics, process parameter variation and comparison of non-catalytic and catalytic pyrolysis of *Melia azedarach* sawdust**” can be summarized as follows:

**Chapter 1** explains the present energy scenario, emissions and other issues arising due to it and how this demand and emission is projected to rise in near future. Importance of biomass as a renewable energy source, its characteristics, various pathways for

conversion of biomass into bio-energy, etc. have also been discussed in this chapter. Utilization of waste biomass for energy generation can fulfil the aspiration of creating wealth from waste. It will serve the dual purpose of energy generation and waste management simultaneously.

**Chapter 2** is dedicated to the review of biomass pyrolysis in the available literature. A holistic review related to various aspects of biomass pyrolysis including physicochemical properties, its thermal degradation kinetics, effect of variation in operating parameters on biomass pyrolysis and catalytic pyrolysis have been summarized in this chapter.

**Chapter 3** is related to the evaluation of physicochemical properties of *Melia azedarach* sawdust, its thermal degradation characteristics, thermo-kinetic analysis, thermodynamic parameters and reaction mechanism associated with the thermal decomposition of *Melia azedarach* sawdust. Thermogravimetric analysis of *Melia azedarach* sawdust was performed at three distinct heating rates of 10, 20 and 30 °C/min under inert atmosphere of N<sub>2</sub> gas. TG/DTG curves, Iso-conversional models and z-master plot were employed for the study of this section.

**Chapter 4** explains effect of operating process parameters on pyrolysis products yield distribution of *Melia azedarach* sawdust. Influence was analysed for various parameters including temperature, sweeping gas flow rate, bed height, particle size, heating rate and pyrolysis time. Pyrolytic products yield varied significantly with variation in pyrolysis temperature as compared to other parameters. Further, characterization of bio-oil and bio-char was carried out by employing different characterization techniques.

**Chapter 5** deals with comparative study for non-catalytic and catalytic pyrolysis of *Melia azedarach* sawdust using copper (Cu) metal as a catalyst. Thermal degradation performance of catalytic and non-catalytic *Melia azedarach* sawdust was examined by thermogravimetric analysis. Effect of variation in temperature and biomass to catalyst

ratio on catalytic pyrolysis was explored. Study on characterization of resultant bio-oil and bio-char has also been discussed in this chapter.

**Chapter 6** summarizes conclusions of this thesis entitled “**Study of kinetics, thermodynamics, process parameter variation and comparison of non-catalytic and catalytic pyrolysis of *Melia azedarach* sawdust**”. Also, recommendations for future studies have been provided. Based on this study it was concluded that *Melia azedarach* sawdust has significant potential for generation of bio-energy via pyrolysis. Using catalyst can impart improvements in pyrolytic products and can enhance production of targeted products.

