

I would like to dedicate this dissertation to my family who has supported and encouraged me throughout this endeavour: Thank you for your love and support throughout my entire life and helping me to realize who I am today!



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It is certified that the work contained in the thesis titled “**Study on pyrolysis of sagwan (*Tectona grandis*) sawdust and use of biochar for aqueous Cr(VI) removal**” by “**Goutam Kishore Gupta**” has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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Date: 12/10/2020

Varanasi

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List of abbreviations and symbols

Abbreviations/ symbols	Full form
AD	Anaerobic digestion
ADF	Acid detergent fiber
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
AC	Ash content
BBD	Box-Behnken design
BET	Brunauer–Emmett–Teller
CCD	Central composite design
CrI	Crystallinity index (%)
CHNS	Carbon Hydrogen Nitrogen Sulphur
CV	Co-efficient of variation
DDW	Double distilled water
DTG	Differential thermogravimetric
EY	Energy yield (%)
EDS	Energy dispersive spectrum
FC	Fixed carbon
FTIR	Fourier Transform Infrared Spectroscopy
FWO	Flynn-Wall-Ozawa
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
HHV	Higher heating value (MJ/kg)
I_{002}	Crystalline intensity of diffraction plane (002)
I_{am}	Amorphous intensity of diffraction plane (002)
KAS	Kissinger-Akahira-Sunose
MAI	Mean annual volume increment
MC	Moisture content
Mtoe	Million Tonnes of Oil Equivalent
NDF	Neutral detergent fiber
RSM	Response surface methodology
SD	Standard deviation
SEM	Scanning electron microscope

SS	Sagwan sawdust
TCD	Thermal conductivity detector
TGA	Thermogravimetric analysis
TS	Total solid
VM	Volatile matter
Wt . %	Weight percentage
XRD	X-Ray diffraction
XPS	X-ray photoelectron spectra
λ	X-ray wavelength (0.15406 nm)
k	Rate constant
α	Fractional conversion
E	Activation energy (kJ/mol)
A	Pre-exponential factor (s^{-1})
R	Universal gas constant
β	Heating rate ($^{\circ}C/min$)
T	Temperature (K)
C_0	Initial Cr(VI) concentration (mg/L)
C_t	Cr(VI) concentration at time t (mg/L)
C_e	Cr(VI) concentration at equilibrium (mg/L)
q_e	Equilibrium adsorption capacity (mg/g)
q_t	Adsorption capacity at time t (mg/g)
W_o	Initial mass of the sample
W_i	Mass of the sample at time t
W_f	Final mass of the sample
T_{α}	Temperature at different conversion (K)
T_m	DTG Peak temperature (K)
ΔH	Change in enthalpy (kJ/mol)
ΔG	Change in Gibbs free energy (kJ/mol)
ΔS	Change in entropy (J/mol.K)
K_B	Boltzmann constant ($1.381 \cdot 10^{-23}$ J/K)
h	Plank constant ($6.626 \cdot 10^{-23}$ J.s),

PREFACE

Due to the fast-growing population, technological development and advancement in the living standard of the people, the requirement for energy as well as the price of fossil-derived fuels like petrol and diesel are increasing. The global energy demand has increased from 49 in 2015 to 328 Million Tonnes of Oil Equivalent in 2018. Fossil fuels are predominantly used to fulfil these skyrocketing global energy demands. But major concerns associated with these fossils are that these are neither sustainable nor cleaner energy source. Uses of these fossil fuels release enormous amount of pollutants such as NO_x, SO_x, particulates and CO₂. In light of this, there is a need to develop an alternative renewable energy source for partial fulfilment of required energy demand. Among the available renewable sources of energy, incidentally, biomass has gathered significant attention due to its plentiful amount, low market value, and carbon neutrality.

So, the research objective was decided to perform the pyrolysis of sagwan sawdust for bio-energy generation. The complete research work is summarized in different chapters. **Chapter 1** explains current energy scenario, energy related environmental issues, biomass as a solid waste and also as a source of energy. At present, around 90 % of the energy consumption in developing countries is fulfilled by fossil fuels (coal, petroleum and natural gas). The technological developments, on the other hand, are responsible for depleting the limited fossil fuel reserves along with the release of toxic effluents. The growing demand for energy and environmental concerns have shifted the alertness of researchers to find out a substitute renewable, sustainable, environmental friendly and cleaner energy source for the coming generation. Sagwan wood is used by different industries, especially paper and furniture industries, as it is light wood and has high durability. According to the Food and Agricultural Organisation of the United States

(FAO), after processing only around 28 % of the tree becomes timber and rest is residue. These residues are disposed of to the open atmosphere with no economical value. Every year huge amount of sagwan sawdust is produced and so for its proper utilization, pyrolysis can be performed. This chapter also explains the origin of the problem and objectives of the research work.

Chapter 2 summarizes the literature review associated with the research work. The study includes the selection criteria and feasibility analysis of biomass for pyrolysis as well as the concerned reaction mechanism involved with the pyrolysis process available in literature. The chapter also explains the kinetic and thermodynamic parameters involved in the pyrolysis process. The effect of pyrolysis process parameters on product yield and characteristics were reviewed. Finally, review was done for the utilization of biochar for Cr (VI) removal.

Chapter 3 explains the kinetic and thermodynamic studies of sagwan sawdust pyrolysis for its bio-energy potential. TGA of sagwan sawdust was performed at the heating rates of 5, 10 and 20 °C/min to study its degradation behaviour. Utilizing the TG and DTG data, kinetic and thermodynamic parameters were evaluated using iso-conversional models. The reaction mechanism for the degradation was studied using Z-master plot.

Chapter 4 describes the pyrolysis of sagwan sawdust for the product yield and characterization. The effect of process variables i.e. temperature, fixed bed height, sweeping gas flow rate and particle size on product yield were investigated. Temperature had the most significant role in the pyrolysis process. Characteristics of biochar, bio-oil and pyrolytic gas were studied using different characterization techniques. The pyrolysis of sagwan sawdust is effective in waste treatment, waste minimization as well as in energy generation.

Chapter 5 describes the product distribution and optimization of pyrolysis process variables for maximum bio-oil and minimum biochar yield. The optimization study was performed employing response surface methodology through box-behnken design. The study reports the interaction effect among the process variables for the product yield. The products obtained were also characterized using various characterization techniques.

Chapter 6 describes the utilization of obtained biochar after SS pyrolysis as an adsorbent for Cr (VI) removal from aqueous solution. The study was performed in batch mode varying different parameters i.e. solution pH, initial Cr(VI) concentration, adsorbent dose/Cr(VI) concentration, time and temperature. Further optimization of the process parameters were also done employing response surface methodology through box-behnken design. The kinetics, isotherms, thermodynamics and mass transfer involved in the adsorption process had also been described. The possible reaction mechanism for the adsorption process had also been explained. The regeneration and reusability of the adsorbent had been done in the study.

Chapter 7 describes the summary and future recommendations drawn on the basis of results obtained out of this research work. The results describe sagwan sawdust has the potential to be used as precursor for pyrolysis. In addition, it also helps in waste minimization and waste utilization. Biochar as adsorbent is also in adsorbing Cr(VI) from aqueous solution. In addition, there are certain recommendations that will help in future research work.