



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

Name of the Student : Gaffer Ahmed

Roll Number : 186107005

Programme of Study : Ph.D.

Thesis Title:

Single and Co-Feed Pyrolysis of *Erythrina Indica* and *Azadirachta Indica*: Analysis of Products, Kinetics and Thermodynamics

Name of Thesis Supervisor(s) : Prof. Nanda Kishore

Thesis Submitted to the Department/ Center : Chemical Engineering

Date of completion of Thesis Viva-Voce Exam : August 01, 2024

Key words for description of Thesis Work : Biomass conversion, Single-feed pyrolysis, Co-feed pyrolysis, *Erythrina indica*, *Azadirachta indica*, Biofuels, Solvent extraction, Bio-oil phase separation, Fuel phase, Non-fuel phase, Biochar, Non-condensable gases, Economic analysis, Kinetics and Thermodynamics

SHORT ABSTRACT

Growing concerns over fossil fuel utilization and their impending scarcity have spurred a transition towards renewable energy sources. Biomass has gained remarkable traction due to its widespread availability and adaptability. Pyrolysis, amid various biomass conversion routes, boasts advantages like moderate operating conditions, facile handling and efficient product distribution. However, commercialization faces hurdles due to the large fraction of non-fuel phase in pyrolytic bio-oil. This thesis focusses on the fuel phase extraction of bio-oil obtained from pyrolytic conversion of *Erythrina indica* (EI) and *Azadirachta indica* (AI) biomass using dichloromethane and n-hexane at four vol.% (10, 20, 30 and 40%) of solvent relative to the volume of pyrolytic raw bio-oil. Average yields of bio-oil, biochar and non-condensable gases from EI biomass pyrolysis were 26.873 wt.%, 42.870 wt.% and 30.257 wt.%, respectively; for AI biomass, the values were 27.286 wt.%, 41.053 wt.% and 31.662 wt.%. n-hexane proved superior for isolating fuel phases, showing improved properties in terms of density, viscosity and calorific value compared to dichloromethane and without using any solvent for separating the fuel phases. Fuel phases extracted using 30 vol.% and 40 vol.% n-hexane depicted properties similar to conventional gasoline. The average calorific values of biochar from EI and AI biomass were 28.030 MJ/kg and 28.500 MJ/kg, respectively, and for non-condensable gases, the respective values were 14.486 MJ/Nm³ and 14.882 MJ/Nm³. EI and AI biochar exhibited physiochemical properties, flowability and combustion indices comparable to conventional coal. In the non-condensable gases obtained from EI and AI biomass pyrolysis, approximately 50-65% (by volume) of the gases were constituted by combustible gases including H₂, CO and CH₄. Co-feed pyrolysis of EI and AI biomass yielded bio-oil, biochar and non-condensable gases in the range of 29.512-32.399 wt.%, 38.249-42.480 wt.% and 26.901-30.730 wt.%, respectively. The 1:1 co-feed ratio showed optimal outcomes, with a maximum calorific value of 36.798 MJ/kg for the fuel phase (extracted using 10 vol.% of n-hexane) and 29.233 MJ/kg for biochar and 13.761 MJ/Nm³ for non-condensable gases. Economic analysis for setting a 10-ton batch-type pyrolysis plant indicated viable projects with positive net present values by the end of the project. Payback periods were 3.90 years for EI, 6.46 years for AI and 4.05 years for their 1:1 co-feed ratio.

The kinetics and thermodynamics of the single-feed and co-feed processes were investigated at heating rates of 10, 20, 30 and 40°C/min. Five iso-conversional methods—differential Friedman method (DFM), Kissinger-Akharria-Sunose (KAS), Ozawa-Flynn-Wall (OFW), Starink (STK) and distributed activation energy model (DAEM)—were used to evaluate the kinetic and thermodynamic properties. Average values of activation energy for EI and AI biomass pyrolysis ranged from 176.861 kJ/mol to 184.787 kJ/mol and 187.613 kJ/mol to 196.635 kJ/mol, respectively. The corresponding average values of enthalpy change, Gibbs free energy change and entropy change for EI biomass varied from 171.781 kJ/mol to 179.890 kJ/mol, 168.191 kJ/mol to 170.083 kJ/mol and 0.003 kJ/mol·K to 0.019 kJ/mol·K, respectively. Meanwhile, for AI biomass, the corresponding values varied from 182.425 kJ/mol to 191.638 kJ/mol, 167.288 kJ/mol to 173.742 kJ/mol and 0.014 kJ/mol·K to 0.039 kJ/mol·K, respectively. Strong correlations ($R^2 > 0.98$) in kinetic plots indicated excellent agreement of the iso-conversional methods for both biomasses. Complex reaction mechanisms, as revealed by Criado's master plots and integral approach, were observed for both EI and AI biomass pyrolysis. Synergistic effect of co-feed pyrolysis was observed in the average activation energy required at various co-feed ratios. The co-feed ratio of EI:AI-1:1 displayed average values of activation energy and enthalpy change in the range of 169.643 kJ/mol to 179.808 kJ/mol and 164.421 kJ/mol to 174.819 kJ/mol, respectively. Based on product properties, economic analysis and potential applications, one may consider co-feed pyrolysis of EI and AI at a 1:1 ratio as a better choice.

