

Development of an Integrated Process for Upgradation of Biomass and Bio-liquids via Thermo-catalytic Route

Lignocellulosic biomass is among the most abundant renewable carbon feedstocks for fuels and chemicals, yet its recalcitrance, compositional heterogeneity and structural anisotropy continue to hinder efficient conversion. Pretreatment, thermochemical conversion, and catalytic upgrading are usually studied in isolation and are seldom linked to in situ diagnostics or predictive modelling, so the kinetic and transport insights gained at one stage rarely inform the design of the next. This thesis treats these stages as one connected value chain and develops an integrated biorefinery framework, applied to the model woods *Pinus sylvestris* (softwood) and *Fagus sylvatica* (hardwood) and to residues central to the Indian bioeconomy: babool, coir pith, rice straw, and walnut and pistachio shells.

Intrinsic thermal behaviour is established first. Non-isothermal thermogravimetry of *V. nilotica* is interpreted through an independent-parallel-reaction scheme, with the derivative signal deconvoluted on physical grounds into hemicellulose, cellulose and lignin pseudo-components. Iso-conversional analysis and a distributed activation-energy model resolve reactivity as a continuous distribution of activation energies, providing the kinetic baseline for all reactor-scale observations. Two low-cost fractionation routes are then developed for pine and beech: metal-based deep eutectic solvents, which delignify and demineralise simultaneously, and the protic ionic liquid [DMBA][HSO₄], which yields a cellulose-rich pulp by IonoSolv fractionation. Compositional assays, HSQC NMR, GPC and XRD confirm up to 70% delignification.

The methodological core is a non-invasive, time-resolved X-ray imaging study of devolatilisation. Cineradiography of packed beds and X-ray radiography of single particles in a fluidised bed, coupled with infrared thermography, directly contrast softwood and hardwood. Mass and volume are strongly decoupled: mass loss reaches 75–85% on heating to 500 °C, yet the bed contracts by only about 15% because a rigid, porous char skeleton preserves the particle envelope, quantified non-invasively for the first time as a volume-retention factor $f_v \approx 0.83$. A validated one-dimensional transient model gives an apparent activation energy of about 24 kJ mol⁻¹, far below the intrinsic 100–250 kJ mol⁻¹, showing that conversion of thermally thick particles is heat-transfer rather than chemically controlled. Thermal imaging links volatile-venting geometry to wood anatomy and permeability anisotropy.

XGBoost models, built as strictly separate pipelines, predict product yields for pyrolysis and hydrothermal liquefaction from feedstock composition and operating conditions and identify the governing parameters. These are grounded in the slow pyrolysis of *V. nilotica* and in hydrothermal and solvothermal liquefaction of coir pith, optimised using response-surface methodology, with mass and energy balances and lumped kinetics. Finally, pyrolysis bio-liquid is hydrotreated over NiMo/ γ -Al₂O₃ prepared under acidic and basic conditions, while NiMo on walnut- and pistachio-shell activated carbon and on a composite AC-Al₂O₃ support is evaluated with lignin-derived phenoxy model monomers, removing up to 25% of the oxygen and turning a waste residue into a tailored catalyst support. Together, the work advances a mechanistically grounded, data-informed basis for the integrated valorisation of lignocellulosic residues.

Keywords: *lignocellulosic biomass; integrated biorefinery; devolatilization kinetics; machine learning; hydrotreatment.*