



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: **Catalytic and Non-Catalytic Co-Pyrolysis of Torrefied Bamboo Biomass and Plastic: Synergism, Kinetics and Reaction Mechanism**

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SHORT ABSTRACT

The depletion of fossil fuels and environmental deterioration leads researchers to search for alternative, renewable, sustainable, and eco-friendly energy resources. The lignocellulosic biomass (LCB) is one of the most promising renewable resources for the production of biofuels, due to its mass availability, eco-friendliness, and CO₂ neutrality. The LCB consists majorly of hemicellulose, cellulose, lignin and minor amounts of extractives and ash. The solid biomass cannot directly be used as fuel in industrial applications, because of several drawbacks including hygroscopic nature, high moisture content, high oxygen content, low heating value, lower grindability, low bulk density, fewer compositional homogeneity and lower resistance to biological degradation. Recently, the thermochemical conversion processes such as catalytic and non-catalytic (co-)pyrolysis has increased attention to convert biomass into biofuel. The biofuel obtained from the pyrolysis of raw biomass is inferior and the process itself is inefficient due to heteropolymeric nature of the hemicellulose present in the biomass. Therefore, it was hypothesized that the selective removal of hemicellulose by wet-torrefaction

would help in improving the biofuel quality as well as overall economics of the process due to extra useful product (xylose) formation in the process. Addition of plastic also improves the biofuel characteristics and mitigates the plastic pollution. Further, addition of catalyst improves the biofuel quality by forming desired products such as aromatics (BTEX).

The overall aim of this thesis is to develop wet-torrefaction process to selectively remove the hemicellulose in the form of xylose and to form the hydrochar with better pyrolysis characteristics. Further, to explore the potential of various zeolite catalysts (MesoHY and HZSM-5) for the catalytic co-pyrolysis (CCP) of wet-torrefied bamboo biomass and plastic (linear low-density polyethylene, LLDPE), TGA was carried out in the temperature range of 30 to 900°C with four heating rates (5–40°C) under argon atmosphere. The kinetic parameters were determined using three models based on the isoconversional method: Kissinger-Akahira-Sunose (KAS), Flynn–Wall–Ozawa (FWO), and Friedman (FM) models. The reaction mechanisms for individual and mixed samples were predicted using the Criado's master plot.

Initially, the co-pyrolysis of bamboo sawdust (BSD) and LLDPE was studied. A blend containing 25 wt.% BSD and 75 wt.% LLDPE (BP1:3) showed the highest synergism as compared to other blends studied. The activation energy drop (36% with respect to biomass) was the highest with this blend. The mean values of apparent activation energy (\bar{E}_α) for the decomposition of blends (BP3:1 (75 wt.% BSD and 25 wt.% LLDPE), BP1:1 (50 wt.% BSD and 50 wt.% LLDPE) and BP1:3) are determined to be 357, 371 and 143 kJ mol⁻¹ from KAS, 368, 400 and 165 kJ mol⁻¹ from OFW and 468, 356 and 255 kJ mol⁻¹ from FM, respectively. The reaction follows a multistep mechanism. The decomposition of the blend BP1:3 follows a nucleation growth (A2) model in the lower conversion range and diffusion (D2) model in the higher conversion range.

As a next study, the bamboo saw dust (BSD) was wet-torrefied to selectively remove hemicellulose in the form of xylose (85 wt.%) at 140°C and duration of time 30 min with formic acid:BSD 1:1 and NaCl:BSD 3:1 w/w. and solid part act as hydrochar or Torrefied biomass saw dust (TBSD). Further, the pyrolysis and co-pyrolysis behavior of TBSD, LLDPE, and their blends were studied. The blend with one part hydrochar and three parts LLDPE (TBP1:3) showed the

highest positive synergism. The \bar{E}_α of co-pyrolysis of blends (TBP3:1, TBP1:1, and TBP1:3) were found to be 232, 261, 247 kJ mol⁻¹, respectively. The Criado's master plot showed the reaction mechanism of co-pyrolysis to be multistep. For example, the blend TBP1:3 followed the trend of two-dimensional Avrami-Erofeyev model (A2) at lower conversions, diffusion-reaction model (D2) at high conversions and end with a first-order reaction.

The torrefied BSD (TBSD) was catalytically co-pyrolyzed with LLDPE over HZSM-5 and MesoHY. The peak decomposition temperature of catalytic pyrolysis of LLDPE over MesoHY was reduced by 251°C than that of HZSM-5 and the enhancement can be attributed to the topology of MesoHY. The apparent activation energies (E_α) of catalytic pyrolysis (CP) of TBSD, and LLDPE were 187 and 147 kJ mol⁻¹ over HZSM-5 from KAS model. In addition, \bar{E}_α of blends TBP3:1, TBP1:1 and TBP1:3 were 163, 135 and 133 kJ mol⁻¹, respectively. While \bar{E}_α of blends (TBP3:1, TBP1:1, and TBP1:3) were found to be 176, 133, and 122 kJ mol⁻¹ in presence of MesoHY, respectively. The CCP of TBP1:3 and TBP1:1 showed synergism between TBSD and LLDPE in terms of \bar{E}_α and TBP1:3 showed the highest synergism with the least \bar{E}_α over HZSM-5. A multistep mechanism was observed in both CP of individual samples and CCP of blends, as analysed by Criado's master plot over both zeolites. For example, the CCP of TBP1:3 followed geometric (volume) contraction (R3) and first-order reaction models at low and high conversions in presence of MesoHY.

Keywords: Wet-torrefaction of bamboo sawdust; Linear low-density polyethylene (LLDPE); Catalytic co-pyrolysis; Biofuel; Criado's master plot; Reaction mechanism