THERMOCATALYTIC CONVERSION OF LIGNO(HEMI)CELLULOSIC BIOMASS TO GREEN FUELS

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by

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Certificate

This is to certify that the thesis entitled 'THERMOCATALYTIC CONVERSION OF LIGNO(HEMI)CELLULOSIC BIOMASS TO GREEN FUELS' submitted by 'Mr. Pravakar Mohanty' to the Indian Institute of Technology (IIT) Delhi, for the award of the Degree of Doctor of Philosophy, is a record of the original bona fide research work carried out by him under our supervision and guidance. The thesis has reached the standards of fulfilling the requirements of the regulations relating to the degree.

The results contained in this thesis have not been submitted in part or full to any other university or institute for the award of any degree or diploma.

New Delhi
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Abstract

The biofuel generated from ligno(hemi)cellulosic biomass has created significant interest as an alternative fuel for the future due to much concerns over energy security and climate change. These issues have stimulated the direction of developments towards new and renewable energy side. Understanding the need of green energy, the main objective of the present study is to develop a suitable thermochemical cum thermocatalytic system for the conversion of ligno(hemi)cellulosic biomass into green fuel. Three different kind of biomass feedstock such as pine wood (coniferous), wheat straw, and timothy grass (herbaceous) were investigated and detailed physicochemical characterization of these were performed along with its biochar produced during pyrolysis. Their compositional and structural characteristics were analyzed by using different analytical techniques such as proximate, ultimate analysis (CHNSO), ICP-MS, particle size, FTIR analysis, Raman spectroscopy, TG-DTA, XRD, SEM-EDX, GC-MS, ESI-MS and HPLC etc. Investigations were performed by the pyrolysis of selected biomass at different heating rate methods (i) slow heating rate (2°C/min) (SHR) pyrolysis to generate chars and (ii) high heating rate (450°C/min) (HHR) pyrolysis that yielded low yield of char, pyrogas and high yields of pyrooil. The HHR pyrolysis of PW, TG and WS resulted the biochar yield of 24.0±2.1, 22.0±1.9 and 21.0±2.4 wt.% and biooil yield of 48.0±2.9, 42.0±3.2 and 40.0±2.6 wt.% respectively. Relatively high yield of biooil and biochar from PW was because of its

recalcitrant and rigid morphology.

Through this study by applying different heating rates of 5, 10, 20, 30 and 40 °C/min in TG-DTA, the pyrolysis characteristics of all three feedstocks were investigated and the distributed activation energy model has discussed. Kinetics of these three biomass were evaluated both experimentally and mathematically, where the kinetic parameters were determined by using nonlinear least squares regression of the experimental data assuming first-order kinetics. From kinetic rate constants, it was observed that the predominant reaction pathway were from biomass feedstock (A) to gas (C_1-C_4) rather than (A) to biooil (B) at temperatures range of 400 to 450°C. In addition the intermediate pyrolysis, in a horizontal pyroformer (pilot plant study with two axial screws configuration pyrolyser) was also carried out by using wheat straw followed by biodiesel quenching to produce a stable, high energy content green fuel (37±0.5 MJ/kg). The different fuel properties, average molecular weight of pyroil and the blend mixture of biodiesel and pyroil were performed.

Investigations were made in which the biocrude was converted into green liquid fuel through catalytic route at different reaction temperatures, weight hourly space velocities (WHSV), solvent to biocrude ratio and catalyst to biocrude ratio using a fixed bed reactor by utilizing Pd/MCM-41 and Pd/SBA-15 mesoporous catalyst. This Pd was loaded on MCM-41 and SBA-15 supports by wet impregnation method and all these catalysts were characterized with XRD, N_2 physical adsorption, TPR, and SEM-EDX analysis. Effect of reaction temperatures (380-480°C), and WHSV (15-30h^{-1}) on Pd/MCM-41 and Pd/SBA-15 were studied for the conversion of biocrude to green fuel like gasoline, kerosene, and diesel range of hydrocarbons with an average heating value of 41±0.5 MJ/kg. The highest yield of organic liquid product (OLP) was obtained on Pd/MCM-41 at temperature of 430°C with WHSV 15h^{-1}. In case of Pd/MCM-41 catalyst the values of activation energy and order of reaction were found to be 52.1 kJ/mol and 1.4 respectively.

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