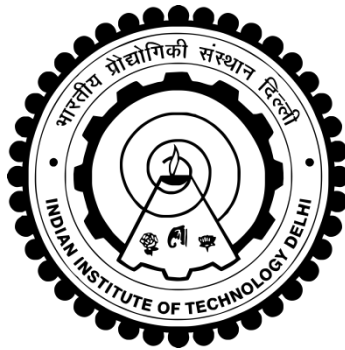


HYDROTHERMAL CONVERSION OF BIOMASS TO BIOFUEL AND ITS CATALYTIC UPGRADATION

DINESH KUMAR



DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI

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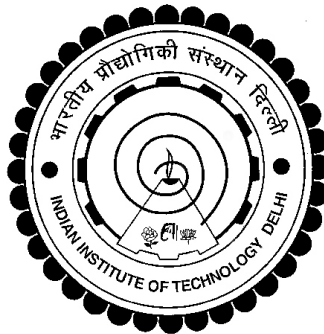
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Department of Chemical Engineering

*Submitted in fulfillment of the requirements
of the degree of*

DOCTOR OF PHILOSOPHY

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

MAY 2016

Dedicated to

Mango & Apple

‘My lovely nieces’

CERTIFICATE

This is to certify that the thesis entitled, “**HYDROTHERMAL CONVERSION OF BIOMASS TO BIOFUEL AND ITS CATALYTIC UPGRADATION**” submitted by ‘**Mr. Dinesh Kumar**’ to the **Indian Institute of Technology Delhi** for the award of Degree of **Doctor of Philosophy** is a record of original bonafide research work carried out by him under my guidance and supervision. The thesis has reached the standards of fulfilling the requirements of the regulations of Indian Institute of Technology Delhi for awarding the degree.

The research report and results presented 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

Professor K. K. Pant

May 2016

Department of Chemical Engineering

Indian Institute of Technology Delhi

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ABSTRACT

Conversion of *Pongamia pinnata*, *Jatropha curcusa* and Tung de-oiled seed cake to biocrude was investigated. Prior to conversion studies, detailed physicochemical characterizations of seed cakes were performed by proximate analysis, ultimate analysis, HHV analysis, SEM, TGA, lignocellulosic content analysis, XRD, FT-IR. The conversion of seed cakes was investigated using pyrolysis (Temperature: 400-600°C), steam pyrolysis (Steam rate: 1-5 cm/sec) and hydrothermal conversion (Pressure: 10-50 kg/cm²) processes. Biocrude obtained was characterized using GC/MS, TGA, CHNO, FT-IR, GC, TAN, density, calorific value, viscosity and silica adsorption chromatography. *Pongamia* cake conversion using hydrothermal process was considered for further investigations due to its maximum conversion to biocrude yield (35.3% ± 1.3%).

Response surface methodology coupled with centre composite design was used for generating quadratic model equations for maximizing biocrude yield and hydrocarbon fraction in the range of boiling range of C₆-C₂₄ straight chain alkanes. Result revealed that temperature and time were the individual significant parameters for biocrude yield whereas pressure was the only individual significant parameter on the C₆-C₂₄ hydrocarbon fraction. Errors between experimentally obtained and predicted values were -12.5% to +11.1% for biocrude yield and 8.5% to -7.5% for C₆-C₂₄ hydrocarbons fraction. Optimized process parameters for the maximum biocrude yield coupled with C₆-C₂₄ hydrocarbons fraction were obtained as T= 400°C (temperature), P= 25 kg/cm² (pressure), t= 35 minutes (reaction time) and W/B ratio = 2.

Biocrude obtained after the thermochemical conversion has high content of heavy hydrocarbons as well as oxygen content, which creates instability issues. To reduce the viscosity, corrosiveness and stability issue, biocrude upgradation studies were conducted using various

methods. The studies were accomplished using three methods available in literature (i) addition of hydrogen donor solvent, (ii) cracking in presence of alkali/alkaline earth metal catalysts in different forms, and (iii) using heteroatom impregnated mesoporous catalyst.

A decrease in the biocrude yield was observed from 35.3% to 32.1%, 31.1% and 27.6% in presence of tetraline, ethanol and acetone respectively. Maximum yield of biocrude (28.2%) was obtained in the presence of KCl as compared to all other catalysts. In presence of alkali a sharp increase in the gaseous products was also observed.

The upgradation studies were conducted in presence of siliceous and aluminated mesoporous catalysts e.g. FDU-12, SBA-15 and KIT-6 having large pores. All the catalysts were characterized using SEM, N₂ adsorption-desorption, NH₃-TPD and TPR, BJH, FTIR, ICP, XRD etc. SBA-15 with SAR 30 was considered for detailed studies due to maximum biocrude yield (~33.5%). GC analysis showed an increase of C₁₁-C₁₈ range hydrocarbons (based on boiling point) from 16.3% to 23.7% over Al/SBA-15. Further the optimization of SAR was conducted from 20 to 50 over SBA-15. GC/MS analysis confirmed Al/SBA-15 with SAR 40 as a promising catalyst for maximum increase of hydrocarbons (Aliphatics and benzene type). Three noble metals Pd, Ga and Ru, with 3% (by weight) loading over Al/SBA-15 having SAR 40, were tested for reducing the oxygen content of the biocrude. The performance of 3%Pd/AlSBA-15(SAR 40) was found most suitable in terms of lowest TAN (~20.5 mg KOH/g biocrude), maximum calorific value (~38.4 MJ/kg) and minimum oxygenated compound fraction (~25.5%) as compared to Ga and Ru loaded catalyst.

Further for evaluation of activation energy and rate constant, experiments were conducted between 325-425°C & 20-30 kg/cm². Six lump model which includes one gaseous phase lump,

one solid phase lump and four lumps from liquid phase were generated. Kinetic parameters were evaluated using MATLAB and Marquardt's method considering a combination of 1st and 2nd order kinetics. Estimated activation energy for different lumps were between 9.8 KJ/mol to 33.2 KJ/mol much below than the value available for pyrolysis studies (80-300 KJ/mol). Errors were estimated for each lump and were found from 11% (for lower boiling range hydrocarbons) to 30% for char and gaseous fraction.

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NOMENCLATURE

ANOVA	Analysis of Variance
ASTM	American Standard Test Method
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner Halenda
CCD	Center Composite Design
CF	Calibration Factor
CHNO	Carbon-Hydrogen-Nitrogen-Oxygen
DOE	Design of Experiment
DP	Dipole Moment Unit
EDX	Energy Dispersive X-Ray
FDU	Fudan University
FID	Flame Ionization Detector
FSM	Folded Sheet Mesoporous Materials
FTIR	Fourier Transform Infrared
GC/MS	Gas Chromatography and Mass Spectroscopy
HHV	High Heating Value, MJ/Kg
HMA	Hexagonal Mesoporous Aluminophosphate
HMS	Hexagonal Mesoporous Silica
HY	Linde Type Y Zeolite
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee on Powder Diffraction Standards
KIT	Korean Institute of Technology

MCM	Mobile Composition Of Matter
MFI	Mordenite Framework Inverted
MSU	Michigan State University
NMR	Nuclear Magnetic Resonance
PAH	Polyaromatic Hydrocarbon
RSM	Response Surface Method
SBA	Santa Barbara Amorphous
SAC	Silica Adsorption Chromatography
SAR	Silica To Alumina Ratio
SEM	Scanning Electron Microscope
TAN	Total Acid Number
TAPPI	Technical Association of The Pulp and Paper Industry
TCD	Thermal Conductivity Detector
TEOS	Tetraethyl Ortho Silicate
TGA	Thermogravemetric Analysis
TGF	Transportation Grade Fuel
TMB	Trimethyl Benzene
TMS	Tetramethylsilane
TOC	Total Organic Content
TPR	Temperature Programmed Reduction
XRD	X-ray Diffraction
ZSM	Zeolite Socony Mobil
<i>a</i>	mean aggregate surface area per hydrophilic head group
A_i	Independent variable used for optimization study

A_M	area of an atom, cm^2
B	Biomass weight. g
C	Catalyst weight, g
d	separation of lattice planes or metal particle size, mm
D	Unit of dipole moment
D_M	metal dispersion
E_a	Activation Energy, kJ/mol
E_{Ai}	Individual effect used for Plackett Burman Design
F127	Puronic triblock copolymer
g	Packing factor
H^+	Anionic Silicate species
$I^{-,0,+}$	Anionic, neutral or cationic Silicate species
k_{ij}	Rate constant, min^{-1}
k	number of parameters for process parameter optimization
L	Lump
l	critical hydrophobic chain length
N	Number of Run
P	Operating Pressure, kg/cm^2
P123	Pluronic triblock copolymer
S	Weight of Solvent, g
$S^{+ \text{ or } 0}$	Cationic surfactant
t	Run time, minute
T	Temperature, $^{\circ}\text{C}$
V	effective volume of the hydrophobic chain
V_M	bulk atomic volume of the metals, cm^3

W	Weight of water , g
X	Conversion
y	Wt fractions of individual lump
Y	Response or yield
λ	wavelength of incident radiation
θ	incident Bragg angle
α	Process parameter level used for optimization study
κ	regression coefficients