

**PRODUCTION OF FUELS AND CHEMICALS THROUGH
CATALYTIC CO-PYROLYSIS OF WASTE BIOMASS AND
WASTE PLASTICS**

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PRODUCTION OF FUELS AND CHEMICALS THROUGH CATALYTIC CO-PYROLYSIS OF WASTE BIOMASS AND WASTE PLASTICS

by

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Certificate

This is to certify that the thesis entitled “**Production of Fuels and Chemicals Through Catalytic Co-pyrolysis of Waste Biomass and Waste Plastics**” submitted by **Mr. T.Nandakumar** to the Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy, is a record of the original bonafide research work carried out by him. He has worked under our supervision and has fulfilled the requirements, which, to our knowledge, has reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.



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“And when you want something, all the universe conspires to help you achieve it”

Paulo Coelho

The Alchemist

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Abstract

Biomass-based fuels and chemicals are going to play a vital role in the decarbonization pathway in achieving Net-Zero Emissions. To achieve the same with the minimum environmental impact on land use patterns and net CO₂ emissions, waste biomass streams should be utilized effectively. Among the various thermo-chemical conversion processes, pyrolysis is a simple but effective method for the production of bio-oil from waste biomass. However, the resultant bio-oil is exceedingly acidic and viscous, contains a high amount of oxygenates, and has a low heating value, therefore, finding limited utilization. The main contributing factor to this low quality is the inherent chemical composition of lignocellulosic biomass, which has a low H/C_{eff} ratio. Therefore compensating the same by co-reaction of waste biomass with high H/C_{eff} materials is expected to alleviate the above issues to some extent. In this aspect, waste plastics such as HDPE, LLDPE, and LDPE with a high H/C_{eff} can form potential co-reactants for biomass co-pyrolysis and are expected to yield valuable chemicals and fuel range carbon molecules.

In this research study, wheat straw (WS) waste biomass co-reacted with recycled waste plastic HDPE in the presence of catalysts to produce valuable chemicals and fuels. In the first work, the effect of various concentrations of metal (1,5, and 10 wt.% Mn, Ni, and Zn) modified HZSM-5 extrudates on the co-pyrolysis of WS and waste HDPE at a feed mix ratio of 3:1 is investigated. The study revealed that metal-impregnated HZSM-5 produced bio-oil with relatively higher proportion of organic-rich phase fractions (16.59 - 31.64%) while simultaneously reduced coke formation by 13.68 - 44.81% compared to the unmodified parent zeolite. Further, 5%Ni followed by 5%Mn incorporated HZSM-5 generated more aliphatic hydrocarbons, whereas, 1%-Zn modified HZSM-5 produced a more relative proportion of valuable aromatics. The catalytic co-pyrolysis also consistently yielded bio-oil with HHV of more than 40 MJ/kg. In addition, more valuable lighter olefins (C₂-C₄) obtained in the gaseous

product with 5% Mn generated more volume of lighter olefins and the LHVs of gaseous products obtained via catalytic process varied between 30-31 MJ/Nm³.

The second study probed thermal behavior, kinetics, and thermodynamic parameters analysis of catalytic co-pyrolysis of wheat straw (WS) and post-consumer recycled high-density polyethylene (HDPE) waste plastic and their blend in the ratio of 3:1 over unmodified and 5%Mn, Ni, and Zn modified HZSM-5 through thermogravimetric analysis (TGA) at differing heating rates of 5, 10, 20 °C/min. The study revealed that the use of catalysts considerably reduced the average activation energy (~ 11.93 -25.50 %) required for the co-pyrolysis process estimated using various model-free methods. In comparison to the non-catalytic co-pyrolysis process, the following performance order is observed in the reduction of activation energy by the catalysts: 5% Zn HZSM-5 > HZSM-5 > 5%Ni-HZSM-5 > 5%Mn-HZSM

In the third study, a novel metal impregnated (5% Mn, Ni, and Zn) -N-doped reduced graphene oxide (RGrO) catalysts synthesized, and its effect on co-pyrolysis of various feed mixes of WS: HDPE was explored through analytical Py-GC/MS experiments. The study disclosed that 50:50 wt.% feed mix provided advantageous conditions and yielded a more relative proportion of aromatics. The order of aromatic yields for a 50:50 feed mix ratio was as follows: Zn@N-RGrO > Mn@N-RGrO > Ni@N-RGrO > No-cat, whereas the Zn and Ni @N-RGrO catalysts also produced a greater proportion of long-chain α -olefins 21.25% (25:75) and 21.21% (75:25). The findings of these studies are not only significant in terms of improving lignocellulosic biomass and waste plastic recycling but also in converting these wastes into valuable biofuels or chemicals. The novel approaches and insights provided by this research study pave the way for more efficient and sustainable utilization of these resources, contributing to the global efforts for a greener future.

Keywords: Co-pyrolysis; Synergic effect; Metal-modified HZSM; TGA kinetics; Metal-modified -N/doped RGO catalyst.

अमूर्त

बायोमास-आधारित ईंधन और रसायन शुद्ध-शून्य उत्सर्जन प्राप्त करने में डीकार्बोनाइजेशन मार्ग में महत्वपूर्ण भूमिका निभाने जा रहे हैं। भूमि उपयोग पैटर्न और शुद्ध CO₂ उत्सर्जन पर न्यूनतम पर्यावरणीय प्रभाव के साथ इसे प्राप्त करने के लिए, अपशिष्ट बायोमास धाराओं का प्रभावी ढंग से उपयोग किया जाना चाहिए। विभिन्न थर्मो-रासायनिक रूपांतरण प्रक्रियाओं में, पायरोलिसिस अपशिष्ट बायोमास से जैव-तेल के उत्पादन के लिए एक सरल लेकिन प्रभावी तरीका है। हालाँकि, परिणामी जैव-तेल अत्यधिक अम्लीय और चिपचिपा होता है, इसमें उच्च मात्रा में ऑक्सीजन होता है, और इसका तापन मान कम होता है, इसलिए इसका सीमित उपयोग होता है। इस निम्न गुणवत्ता का मुख्य योगदान कारक लिग्नोसेल्यूलोसिक बायोमास की अंतर्निहित रासायनिक संरचना है, जिसका एच/सीईएफ अनुपात कम है। इसलिए उच्च एच/सीईएफ सामग्री के साथ अपशिष्ट बायोमास की सह-प्रतिक्रिया द्वारा इसकी भरपाई करने से उपरोक्त मुद्दों को कुछ हद तक कम करने की उम्मीद है। इस पहलू में, उच्च एच/सीईएफ के साथ एचडीपीई, एलएलडीपीई और एलडीपीई जैसे अपशिष्ट प्लास्टिक बायोमास सह-पाइरोलिसिस के लिए संभावित सह-अभिकारक बना सकते हैं और मूल्यवान रसायनों और ईंधन रेंज कार्बन अणुओं का उत्पादन करने की उम्मीद है।

इस शोध अध्ययन में, गेहूँ के भूसे (डब्ल्यूएस) अपशिष्ट बायोमास ने मूल्यवान रसायनों और ईंधन का उत्पादन करने के लिए उत्प्रेरक की उपस्थिति में पुनर्नवीनीकरण अपशिष्ट प्लास्टिक एचडीपीई के साथ सह-प्रतिक्रिया की। पहले काम में, धातु की विभिन्न सांद्रता (1,5, और 10 wt.% Mn, Ni, और Zn) का प्रभाव संशोधित HZSM-5 का फ़्रीड मिश्रण अनुपात पर WS और अपशिष्ट HDPE के सह-पाइरोलिसिस पर प्रभाव पड़ता है। 3:1 की जाँच की जाती है। अध्ययन से पता चला कि धातु-संसेचित HZSM-5 ने कार्बनिक-समृद्ध चरण अंशों (16.59 - 31.64%) के अपेक्षाकृत उच्च अनुपात के साथ जैव-तेल का उत्पादन किया, जबकि साथ ही असंशोधित मूल जिओलाइट की तुलना में कोक गठन को 13.68 - 44.81% तक कम कर दिया। इसके अलावा, 5%Ni के बाद 5%Mn शामिल HZSM-5 ने अधिक स्निग्ध

हाइड्रोकार्बन उत्पन्न किया, जबकि, 1%-Zn संशोधित HZSM-5 ने मूल्यवान एरोमैटिक्स का अधिक सापेक्ष अनुपात उत्पन्न किया। उत्प्रेरक सह-पायरोलिसिस से भी लगातार 40 एमजे/किलोग्राम से अधिक के एचएचवी के साथ जैव-तेल प्राप्त होता है। इसके अलावा, 5% एमएन के साथ गैसीय उत्पाद में प्राप्त अधिक मूल्यवान हल्के ओलेफिन (सी₂-सी₄) ने हल्के ओलेफिन की अधिक मात्रा उत्पन्न की और उत्प्रेरक प्रक्रिया के माध्यम से प्राप्त गैसीय उत्पादों के एलएचवी 30-31 एमजे/एनएम³ के बीच भिन्न थे।

दूसरे अध्ययन में गेहूं के भूसे (डब्ल्यूएस) के उत्प्रेरक सह-पायरोलिसिस और उपभोक्ता के बाद पुनर्नवीनीकरण उच्च घनत्व पॉलीथीन (एचडीपीई) अपशिष्ट प्लास्टिक के थर्मल व्यवहार, कैनेटीक्स और थर्मोडायनामिक पैरामीटर विश्लेषण की जांच की गई और उनके मिश्रण को 3: 1 के अनुपात में असंशोधित किया गया। और 5%Mn, Ni, और Zn ने 5, 10, 20 °C/मिनट की अलग-अलग हीटिंग दरों पर थर्मोग्रैविमेट्रिक विश्लेषण (TGA) के माध्यम से HZSM-5 को संशोधित किया। अध्ययन से पता चला कि उत्प्रेरकों के उपयोग से विभिन्न मॉडल-मुक्त तरीकों का उपयोग करके अनुमानित सह-पाइरोलिसिस प्रक्रिया के लिए आवश्यक औसत सक्रियण ऊर्जा (~ 11.93 -25.50%) कम हो गई। गैर-उत्प्रेरक सह-पाइरोलिसिस प्रक्रिया की तुलना में, उत्प्रेरक द्वारा सक्रियण ऊर्जा की कमी में निम्नलिखित प्रदर्शन क्रम देखा जाता है: 5% Zn HZSM-5 > HZSM-5 > 5%Ni-HZSM-5 > 5%Mn -HZSM

तीसरे अध्ययन में, एक नवीन धातु संसेचित (5% एमएन, नी, और जेडएन) -एन-डोपड कम ग्राफीन ऑक्साइड (आरजीआरओ) उत्प्रेरक को संश्लेषित किया गया, और डब्ल्यूएस: एचडीपीई के विभिन्न फ़ीड मिश्रणों के सह-पाइरोलिसिस पर इसके प्रभाव का पता लगाया गया। विश्लेषणात्मक पीई-जीसी/एमएस प्रयोग। अध्ययन से पता चला कि 50:50 वजन% फ़ीड मिश्रण ने लाभप्रद स्थिति प्रदान की और सुगंधित पदार्थों का अधिक सापेक्ष अनुपात प्राप्त किया। 50:50 फ़ीड मिश्रण अनुपात के लिए सुगंधित उपज का क्रम इस प्रकार था: Zn@N-RGrO > Mn@N-RGrO > Ni@N-RGrO > उत्प्रेरक के बिना, जबकि Zn और Ni @N-RGrO उत्प्रेरक ने भी लंबी-श्रृंखला α का एक बड़ा अनुपात उत्पन्न किया। -ओलेफिन्स 21.25% (25:75) और 21.21% (75:25)।

इन अध्ययनों के निष्कर्ष न केवल लिग्नोसेल्यूलोसिक बायोमास और अपशिष्ट प्लास्टिक रीसाइक्लिंग में सुधार के संदर्भ में महत्वपूर्ण हैं, बल्कि इन कचरे को मूल्यवान जैव ईंधन या रसायनों में परिवर्तित करने में भी महत्वपूर्ण हैं। इस शोध अध्ययन द्वारा प्रदान किए गए नए दृष्टिकोण और अंतर्दृष्टि इन संसाधनों के अधिक कुशल और टिकाऊ उपयोग का मार्ग प्रशस्त करते हैं, जो एक हरित भविष्य के लिए वैश्विक प्रयासों में योगदान करते हैं।

संकेत शब्द : सह-पाइरोलिसिस; सहक्रियात्मक प्रभाव; धातु-संशोधित HZSM; टीजीए कैनेटीक्स; धातु-संशोधित -एन/डोपड आरजीओ उत्प्रेरक।

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List of Abbreviations

Abbreviation	Definition of the term
AP	Aqueous rich Phase
BET	Brunauer-Emmet- Teller
BJH	Barrett-Joyner-Halenda
BTX	Benzene-Toluene -Xylene
DTG	Differential Thermogravimetric
EDS	Energy Dispersive X-ray spectroscopy
FID	Flame Ionisation Detector
FM	Friedman
FT-IR	Fourier Transform - Infrared Spectroscopy
GC/MS	Gas chromatography–Mass spectrometry
GRP	Gross Residue Potential
HDPE	High Density Polyethylene
HHV	Higher Heating Value
HR-TEM	High Resolution -Transmission Electron Microscopy
H-ZSM -5	Protonated - Zeolite Socony Mobil-5
ICP-AES	Inductively Coupled Plasma -Atomic Emission Spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
KAS	Kissinger-Akahira-Sunrose
LDPE	Low Density Polyethylene
LHV	Lower Heating Value
LLDPE	Linear Low Density Polyethylene
MAH	Monocyclic Aromatic Hydrocarbons
NMR	Nuclear Magnetic Resonance
OECD	Organization for Economic Co-operation and Development
OFW	Ozawa-Flynn-Wall
OP	Organic rich Phase
PA	Polyacrylate
PAH	Polycyclic Aromatic Hydrocarbon
PC	Polycarbonate
PET	Polyethylene Terephthalate
PP	Poly Propylene
PS	Poly Styrene
PUF	Polyurethane Foam
PVC	Poly Vinyl Chloride
Py-GC/MS	Pyrolysis–gas chromatography-mass spectrometry
RGA	Refinery Gas Analyser
RGrO	Reduced Graphene Oxide
SDG	Sustainable Development Goals
SEM	Scanning Electron Microscopy
SRP	Surplus Residue Potential
TCD	Thermal conductivity Detector
TGA	Thermo Gravimetric Analysis
TPD	Temperature Programmed Desorption
TPR	Temperature Programmed Reduction
UV-Vis -DRS	Ultraviolet-visible Diffuse Reflectance Spectroscopy
WS	Wheat Straw
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

List of Symbols

Symbols	Definition of the term
α	Degree of Conversion
A_0	Pre-exponential factor of the Arrhenius equation (s^{-1})
β	Heating rate ($^{\circ}C/min.$)
E_a	Apparent activation energy (kJ/mol)
E_{α}	Apparent activation energy at a particular degree of conversion (kJ/mol)
$f(\alpha)$	Differential form of reaction model
$g(\alpha)$	Integral form of the reaction model
ΔG	Change in Gibbs Free Energy (kJ/mol)
ΔH	Change in Enthalpy (kJ/mol)
h	Planck's constant (Js)
$k(T)$	Rate constant
K_B	Boltzmann constant (JK^{-1})
m/z	Charge to Mass ratio
$p(u)$	Temperature integral
R	Universal gas constant, (kJ/mol K)
ΔS	Change in Entropy (J/mol.K)
T_{max}	Maximum degradation temperature of the DTG curve
T_p	Peak decomposition temperature ($^{\circ}C$)
Vol.%	Volume percentage
$W_1\%$	The weight percentage of WS
$W_2\%$	The weight percentage of HDPE
wt.%	Weight percentage
ΔW	Differences in weight loss
W_{exp}	Actual weight loss of the blend
W_{cal}	Calculated weight loss of the blend
W_1	Weight loss of WS
W_2	Weight loss of HDPE
x_1	Weight fraction of WS
x_2	Weight fraction of HDPE
ΔX	Synergy parameter
X_{cal}	Calculated peak area percentage
X_{exp}	Experimental peak area percentage
X_{HDPE}	Peak area percentage of identified groups during HDPE pyrolysis
X_{ws}	Peak area percentage of identified groups during WS pyrolysis