

**WASTE PLASTIC CONVERSION INTO
HIGH-VALUE PRODUCTS USING ZEOLITE BASED
CATALYSTS**

UMA DWIVEDI



**CENTRE FOR RURAL DEVELOPMENT AND TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

APRIL 2023

©Indian Institute of Technology Delhi (IITD), New Delhi, 2023

WASTE PLASTIC CONVERSION INTO HIGH-VALUE PRODUCTS USING ZEOLITE BASED CATALYSTS

By

UMA DWIVEDI

CENTRE FOR RURAL DEVELOPMENT AND TECHNOLOGY

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

APRIL 2023

Dedicated to
My Parents

CERTIFICATE

This is to certify that the thesis entitled, **“WASTE PLASTIC CONVERSION INTO HIGH-VALUE PRODUCTS USING ZEOLITE BASED CATALYSTS”** being submitted by **Ms. Uma Dwivedi** to the Indian Institute of Technology Delhi for the award of Doctor of Philosophy is a record of bonafide research work carried out by her under our guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology Delhi.

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.

Dr. S. N. Naik

Professor,

Centre for Rural Development and Technology

Indian Institute of Technology Delhi

New Delhi-110016

Dr. K. K. Pant

Professor,

Department of Chemical Engineering

Indian Institute of Technology Delhi

New Delhi-110016



ACKNOWLEDGMENTS

To begin with, I would like to thank my supervisors, Dr. S. N. Naik, Professor, Center for Rural Development and Technology and Dr. K. K. Pant, Professor, Department of Chemical Engineering, IIT Delhi for their motivation, inspiration, and keen interest throughout my research work. Over the last six years, they have been my mentors and a huge source of inspiration. Despite having very busy schedules, they have always reviewed all my theoretical and experimental results, reports, journal papers and thesis progress and provided their valuable suggestions to improve the quality of my research work. Without their unconditional support, the research work presented here would not have been possible for me. It was a fortunate and unforgettable experience to work under their reflective and admired guidance. Their friendly natures and endless kindness can't be thanked adequately here.

I am profoundly thankful to my supervisors, Dr. S. N. Naik and Prof. K. K. Pant, for providing me the opportunity to avail all the facilities required during the course of my research work.

I am thankful to Prof. V. K. Vijay, Prof. J. K. Sahu and Prof. Divesh Bhatia for their encouragement, constant support, critical reviews, and valuable suggestions throughout my research work. I also wish to thank the other faculty members and office staff of the Department.

Defence Research and Development Organisation-Life Sciences Research Board (DRDO-LSRB) is highly acknowledged for providing funding to avail research facilities during my PhD work.

I was fortunate to have an excellent, exhaustive and friendly environment in the Chemical reaction engineering, Green and Sustainable Engineering and Fluid Extraction laboratories, which facilitated my research work to a great deal.

I am highly thankful to Mr. Vishesh Kumar and Mr. Krishna Kumar for their constant help in every possible way to carry forward my research work.

I am grateful to my colleagues at IIT Delhi, Dr. Rohit Kumar, Dr. Kaushal R. Parmar, Mr. Prashant Jadhao, Dr. Ashish Pandey, Dr. Sonal Asthana, Ms. Akshata, Ms. Shreya, Ms. Deepti, Mr. Rajan, Mr. Shashank, Mr. Sagar, Mr. Akshay, Ms. Shreya Tripathi, Ms. Nidhi Hans, Ms. Vidhi, Dr. Ajay Patel for their help and unconditional support during my research work.

I am also grateful to my close friends Dr. Abhijeet Thaker, Dr. Shabina Ashraf, and Dr. Deepak Jangra, Ms. Ritu for their concern, motivation, and support throughout.

I am also grateful to my extended family members Dr. Umesh Mishra, Dr. Jyoti Shukla, Dr. Pawan Mishra and Dr. Bhavna Dwivedi for their help, support, motivation, and everything throughout my PhD journey.

My appreciation is extended to Mr. Suchit Kumar Pal, Mr. Vijay Pal Singh, Mr. Mewalal Bhaiya, Mr. Ashish for their constant support whenever required.

I am grateful to Indian Institute of Technology Delhi (IITD) for providing me the financial assistantship during my research work.

I remain thankful to the library management staff, IIT Delhi for providing all the necessary material (books, e-journals, e-books etc.) to carry forward my research work.

I wish to thank all the vendors for their timely help in procuring the equipment, accessories, and chemicals I needed for my research work, and help me at short notice with their expertise when any equipment failed to perform.

I have no words to express motivation and inspiration given by my parents to me, whose courage through their life have been a spiritual inspiration to me and holds no bounds. Their encouraging words and deeds through these tough and emotional times will always remain in my heart and soul. I am grateful to my life partner Mr. Sourabh for his encouragement, support, and care throughout my research work. I am also thankful to my brothers (Santosh and Rajesh Bhaiya) for their constant moral support and motivation during my studies. Their success stories have always been a source of inspiration and encouragement throughout my educational

journey. I cannot thank enough my whole family for having faith and trust in all my dreams and allowing to pursue my goals without any bindings.

Herewith I would like to thank all of those, who have directly or indirectly contributed to the realization of this thesis.

Last but not the least, a note of heartfelt devotion to almighty GOD, who has made me capable of accomplishing this task.

Uma Dwivedi

ABSTRACT

Among waste plastic treatment methods, plastic transformation into liquid hydrocarbons is the most promising route. Considering environmental and commercial aspects, plastic to liquid process is beneficial as it is a sustainable route producing liquid fuel (energy) from low-cost waste plastics. The process simultaneously overcomes challenges associated to waste plastic decomposition and increasing energy demand. Research communities are continuously working in this area and different processes have been explored. High temperature pyrolysis is well adopted for the plastic to liquid conversion using fixed and fluidized bed reactor units. In view of improving quality of liquid products, heterogeneous catalysts have been incorporated along with thermal treatment. Zeolites (USY/ZSM-5), $\text{SiO}_2\text{-Al}_2\text{O}_3$, and FCC type catalysts have been considered. Despite, available vast studies, plastic to liquid process is still facing limitation towards successful industrial implementation. Major obstacles are associated to high temperature requirement, poor liquid yield, higher selectivity of undesired heavier hydrocarbons and short catalyst cycle length. These aspects must be in consideration while developing suitable route and catalyst for plastic to liquid technology. In this context, present research work has been constructed exploring two-stage thermo-catalytic cracking of plastics towards production of fuel (such as Diesel and Gasoline) range of hydrocarbons using modified zeolite catalysts at relatively lower temperature.

As a first step, degradation profiles of polymers (PP, LDPE, and HDPE) with respect to temperature, heating rates and catalyst were investigated using thermogravimetric analyzer (TGA). Performing TGA experiments in presence and absence of catalyst (ZSM-5), polymer degradation kinetics was studied using non-isothermal models. Kissinger-Akahira-Sunose (KAS), Starink, and Ozawa-Flynn-Wall (OFW) as non-isothermal models were tested to predict the kinetic parameters using TG thermal and catalytic degradation profiles upon polymer cracking. For the thermal decomposition of polymers temperature range was set up

to 800 °C varying heating rates (specifically at 1, 2, 5, 10, 20, 30, 40, and 50 °C/min). Activation energy corresponding to polymer degradation profiles was measured using iso-conversional methods. In kinetic results, activation energies for thermal decomposition of PP, LDPE and HDPE polymers were obtained as; 178 kJ/mol, 200 kJ/mol and 216 kJ/mol respectively. The values indicated that PP polymer requires low temperature to degrade, which is believed to be due to the branched structure of polypropylene. While the LDPE and HDPE plastics possessing linear structures require higher energy for degradation. In contrast, activation energies for catalytic degradation of the PP, LDPE and HDPE polymers were found as 130 kJ/mol, 140 kJ/mol and 145 kJ/mol respectively which was comparatively lower than the values observed in absence of catalyst. This corroborated that presence of catalyst strongly facilitated polymer cracking. In addition, degradation temperature range was found to be optimized between 300 to 400 °C for the selected polymers (PP, LDPE, and HDPE). Overall obtained kinetic parameters using iso-conversional methods applied to TGA degradation profiles were very informative to carry forward the research work.

In parallel efforts, experimental studies were conducted to produce fuel range hydrocarbons degrading polymer mixtures (PP, LDPE, and HDPE). A bottom-up two-stage cracking approach was adopted using relatively lower pyrolysis temperature. Collected liquid products upon thermal and thermo-catalytic cracking at 350 °C were analysed using GC-MS, NMR, and IR techniques. In thermo-catalytic cracking, catalyst to plastic feed ratio was taken as 1:30. Catalytic cracking showed higher selectivity towards desired fuel range hydrocarbons as compared to the thermal cracking. Cat A (HZSM-5) and Cat B (5%Fe/HZSM-5) were used for the catalytic cracking in which Cat B resulted into 76 wt.% of liquid yield which was comparatively higher than that using Cat A (60 wt.%). Further, the GC-MS results confirmed that the liquid product collected upon catalytic cracking consisted of higher selectivity of fuel range (C₆-C₂₀) hydrocarbons; 66.39% with Cat B and 47.33% with Cat A. Whereas in case of

thermal cracking, selectivity towards C₆-C₂₀ range hydrocarbons was comparatively low (27.39%). FT-IR, ¹H and ¹³C NMR studies also indicated that the product obtained upon catalytic cracking possesses similar characteristics to that of conventional fuel (Diesel). XRD, NH₃-TPD, BET, FE-SEM, HR-TEM, XPS, and H₂-TPR techniques were used to examine the physiochemical properties of catalysts correlating with cracking performance. Characterization of commercial fuel (Diesel) was also performed to compare fuel properties of the liquid products obtained in the study.

In view of tuning hydrocarbon composition of liquid product, third study was performed using zeolite catalyst of different framework and SiO₂/Al₂O₃ ratio (30 and 55). Cat A (ZSM-5) and Cat C (MCM-22) having framework code MFI and MWW respectively were compared towards polymer (PP:LDPE:HDPE, 1:1:1) degradation at 350 °C using two-stage cracking approach. Obtained results revealed that upon polymer cracking, Cat C selectively provided C₇-C₁₂ range (which is specifically a gasoline range) of hydrocarbons (99.12 %) as compared to Cat A which resulted into C₁₃-C₂₀ range of hydrocarbons (73.19 %). This was attributed to unique framework (MWW) structure of Cat C having two independent pore channels. GC-MS, ¹H, ¹³C NMR, and FT-IR techniques confirmed presence of diesel and gasoline range hydrocarbons using Cat A and Cat C respectively. Moreover, activity results indicated that acidity content over these catalysts on varying SiO₂/Al₂O₃ also affects the liquid yield and hydrocarbon distribution. For both Cat A and Cat C, lower SiO₂/Al₂O₃ (30) exhibiting higher acidity resulted into better yield towards fuel range of hydrocarbons compared to that for SAR-55. Physio-chemical properties of the catalysts were investigated using XRD, NH₃-TPD, N₂-physisorption (BET), FE-SEM, and EDX techniques and correlated with activity results.

In fourth study, attempts were made to produce value-added carbon nanotubes (CNTs) from plastic degradation along with liquid and gas products varying Fe content of Cat B. Being a profound source of carbon, plastics can be used as an effective raw material for the fabrication

of CNTs on which research communities are rigorously working due to its unique conducting and adsorbent properties. Effect of Fe loading (2 to 15 wt.%) was investigated towards CNTs formation upon two-step catalytic degradation of polymer mixture (PP, LDPE, and HDPE) at slightly higher temperature 400 °C. It was found that with the increase in Fe content, fraction of filamentous carbon (CNTs) was noted over spent catalyst surface and was confirmed by HR-TEM and FE-SEM analysis. At 400 °C, 5 wt.% of Fe addition showed higher deposition of CNTs over the catalyst due to possessing uniform distribution of Fe species. Formation of CNTs was further supported by I_D/I_G ratio as obtained via Raman profiles collected for spent Cat B having different Fe content. A gradual increase in I_D/I_G ratio (0.2 to 0.7) was obtained with the increase in Fe content which indicated that at higher loading (>5 wt. %), more deformed carbonaceous species (disordered sp^2 carbon) generated due to agglomeration of Fe species. In addition, yield and selectivity of liquid hydrocarbons was obtained comparatively higher for 5 wt.% Fe loaded Cat B at 400 °C which was in line with the second study. Hydrogen (H_2) selectivity was also found to be higher (51.34%) using 5 wt.% Fe loaded Cat B as compared to the rest catalysts. Overall, 5 wt.% Fe loading was optimum in terms of desired acidity and uniform metallic (Fe) distribution to produce fine CNTs at 400 °C along with liquid and H_2 production.

सार

प्लास्टिक का तरल हाइड्रोकार्बन में परिवर्तन सभी अपशिष्ट प्लास्टिक उपचार विधियों में सबसे आशाजनक मार्ग है। पर्यावरण और वाणिज्यिक पहलुओं के संदर्भ में, प्लास्टिक से तरल प्रक्रिया फायदेमंद है क्योंकि यह कम लागत वाले अपशिष्ट प्लास्टिक से तरल ईंधन (ऊर्जा) का उत्पादन करने वाला एक स्थायी मार्ग है। यह प्रक्रिया एक साथ अपशिष्ट प्लास्टिक अपघटन और बढ़ती ऊर्जा मांग से जुड़ी चुनौतियों पर काबू पाती है। अनुसंधान समुदाय इस क्षेत्र में लगातार काम कर रहे हैं और विभिन्न प्रक्रियाओं का पता लगा गया है। उच्च तापमान पाइरोलिसिस प्रक्रिया को फिक्स्ड और फ्लुइडाइज रिएक्टर इकाइयों का उपयोग करके प्लास्टिक से तरल बनाने के लिए अच्छी तरह से अपनाया जाता है। तरल उत्पादों की गुणवत्ता में सुधार के संदर्भ में, थर्मल उपचार के साथ विषम उत्प्रेरक को शामिल किया गया है। जिओलाइट्स (USY/ZSM-5), SiO_2 - Al_2O_3 और FCC प्रकार के उत्प्रेरकों का उपयोग किया गया है। उपलब्ध विस्तार अध्ययन के बावजूद, प्लास्टिक से तरल प्रक्रिया अभी भी सफल औद्योगिक कार्यान्वयन की दिशा में बाधाओं का सामना कर रही है। प्रमुख बाधाएं उच्च तापमान की आवश्यकता, खराब गुणवत्ता वाले तरल, अवांछित भारी हाइड्रोकार्बन की उच्च चयनात्मकता और उत्प्रेरक की अस्थिरता से जुड़ी हैं। प्लास्टिक से तरल प्रौद्योगिकी के लिए उपयुक्त मार्ग और उत्प्रेरक विकसित करते समय इन पहलुओं पर विचार किया जाना चाहिए। इस संदर्भ में, अपेक्षाकृत कम तापमान पर, संशोधित जिओलाइट उत्प्रेरक का उपयोग करके ईंधन रेंज (जैसे डीजल और गैसोलीन) के

हाइड्रोकार्बन के उत्पादन के लिए प्लास्टिक के दो-चरणों में थर्मो-कैटेलिटिक क्रैकिंग की खोज के लिए प्रस्तुत शोध कार्य संपन्न किया गया है।

पहले कदम के रूप में, बहुलक (PP, LDPE और HDPE) के क्षरण प्रोफाइल की तापमान, ताप दर और उत्प्रेरक के संबंध में थर्मोग्रैविमेट्रिक विश्लेषण (TGA) का उपयोग करते हुए जांच की गई है। उत्प्रेरक (ZSM-5) की उपस्थिति और अनुपस्थिति में TGA का प्रयोग करते हुए, नॉन-आइसोथर्मल मॉडल का उपयोग करके बहुलक क्षरण कैनेटीक्स का अध्ययन किया गया। नॉन-आइसोथर्मल मॉडल के रूप में Kissinger-Akahira-Sunose (KAS), Starink, और Ozawa-Flynn-Wall (OFW) का परीक्षण पॉलीमर क्रैकिंग पर TGA थर्मल और कैटेलिटिक क्षरण प्रोफाइल का उपयोग करके कैनेटीक् मापदंडों की भविष्यवाणी करने के लिए किया गया था। पॉलिमर थर्मल अपघटन के लिए तापमान रेंज 800 °C तक अलग-अलग ताप दर (विशेष रूप से 1, 2, 5, 10, 20, 30, 40, और 50 °C/min) प्रयोग करते हुए स्थापित किया गया था। बहुलक क्षरण प्रोफाइल के अनुरूप सक्रियण ऊर्जा को आइसो-रूपांतरण विधियों का उपयोग करके मापा गया था। कैनेटीक् परिणामों में, PP, LDPE और HDPE पॉलिमर के थर्मल अपघटन के लिए क्रमशः 178 kJ/mol, 200 kJ/mol और 216 kJ/mol सक्रियण ऊर्जा प्राप्त की गई। सक्रियण ऊर्जा परिणामों ने संकेत दिया कि PP बहुलक क्षरण के लिए कम तापमान की आवश्यकता होती है, जिसका कारण PP की शाखित संरचना है। जबकि रैखिक संरचनाओं वाले LDPE और HDPE प्लास्टिक को क्षरण के लिए उच्च ऊर्जा की आवश्यकता होती है।

इसके विपरीत, PP, LDPE और HDPE पॉलिमर के उत्प्रेरक क्षरण के लिए सक्रियण ऊर्जा क्रमशः 130 kJ/mol, 140 kJ/mol और 145 kJ/mol पाई गईं जोकि उत्प्रेरक की अनुपस्थिति में देखे गए मूल्यों से तुलनात्मक रूप में कम थीं। इसने पुष्टि की कि उत्प्रेरक की उपस्थिति ने पॉलिमर क्रैकिंग को दृढ़ता से सुगम बनाया। इसके अलावा, चयनित पॉलिमर (PP, LDPE, और HDPE) के लिए क्षरण तापमान 300 से 400 °C के बीच अनुकूलित पाया गया। समग्र रूप से, TGA क्षरण प्रोफाइल पर लागू आइसो-रूपांतरण विधियों का उपयोग करते हुए प्राप्त कैनेटीक पैरामीटर प्रस्तुत कार्य को आगे बढ़ाने के लिए बहुत जानकारीपूर्ण थे।

समानांतर प्रयासों में, ईंधन श्रेणी के हाइड्रोकार्बन का उत्पादन करने के लिए प्रायोगिक बहुलक (PP, LDPE, और HDPE मिश्रण) क्षरण अध्ययन किए गए थे। अपेक्षाकृत कम पाइरोलिसिस तापमान का उपयोग करके एक बॉटम-अप टू-स्टेज क्रैकिंग दृष्टिकोण अपनाया गया था। 350 °C तापमान पर, थर्मल और थर्मो-कैटेलिटिक क्रैकिंग द्वारा एकत्रित तरल उत्पादों का GC-MS, NMR और FT-IR तकनीकों का उपयोग करके विश्लेषण किया गया। थर्मो-कैटेलिटिक क्रैकिंग में, प्लास्टिक और उत्प्रेरक के अनुपात को 1:30 के रूप में लिया गया था। थर्मल क्रैकिंग की तुलना में कैटेलिटिक क्रैकिंग ने वांछित ईंधन रेंज हाइड्रोकार्बन के प्रति उच्च चयनात्मकता दिखाई। कैटेलिटिक क्रैकिंग के लिए Cat A (HZSM-5) और Cat B (5%Fe/HZSM-5) का उपयोग किया गया था, जिसमें Cat B ने 76 wt.% द्रव यील्ड दिया, जोकि Cat A (60 wt.%) का उपयोग करते हुए प्राप्त द्रव यील्ड की तुलना में अधिक था।

इसके अलावा, GC-MS परिणामों ने पुष्टि की, कि उत्प्रेरक क्रैकिंग द्वारा एकत्रित तरल उत्पाद में ईंधन रेंज (C_6-C_{20}) हाइड्रोकार्बन की उच्च चयनात्मकता शामिल है; Cat B के साथ 66.39% और Cat A के साथ 47.33% प्राप्त हुई, जबकि थर्मल क्रैकिंग में, C_6-C_{20} रेंज हाइड्रोकार्बन के प्रति चयनात्मकता (27.39%) तुलनात्मक रूप से कम थी। FT-IR, 1H और ^{13}C NMR अध्ययनों ने यह भी संकेत दिया कि उत्प्रेरक क्रैकिंग द्वारा प्राप्त उत्पाद में पारंपरिक ईंधन (डीजल) के समान गुण हैं। क्रैकिंग परिणामों से संबंधित उत्प्रेरकों के भौतिक-रासायनिक गुणों की जांच करने के लिए XRD, NH_3 -TPD, BET, FE-SEM, HR-TEM, XPS, और H_2 -TPR तकनीकों का उपयोग किया गया था। प्राप्त तरल उत्पादों के गुणों की तुलना करने के लिए व्यावसायिक तरल ईंधन (डीजल) का विश्लेषण भी किया गया है।

तीसरे अध्ययन में, तरल उत्पाद की गुणवत्ता में परिवर्तन के संबंध में, दो विभिन्न संरचना और SiO_2/Al_2O_3 अनुपात (30 और 55) वाले जिओलाइट उत्प्रेरक का उपयोग किया गया था। उत्प्रेरकों, Cat A (ZSM-5) और Cat C (MCM-22), जो कि क्रमशः MFI और MWW संरचना कोड रखते हैं, की तुलना दो-चरण क्रैकिंग दृष्टिकोण का उपयोग करते हुए $350\text{ }^{\circ}C$ तापमान पर बहुलक (PP: LDPE: HDPE, 1:1:1) क्षरण के लिए की गई थी। प्राप्त परिणामों से पता चला कि Cat C ने Cat A की तुलना में पॉलिमर क्रैकिंग होने पर, चुनिंदा रूप से C_7-C_{12} रेंज के हाइड्रोकार्बन (जो विशेष रूप से एक गैसोलीन रेंज है) की चयनात्मकता (99.12%) दिखाई, जबकि Cat A के द्वारा $C_{13}-C_{20}$ रेंज (73.19%) के हाइड्रोकार्बन प्राप्त हुए। Cat C

के दो स्वतंत्र चैनलों वाले अद्वितीय (MWW) संरचना के कारण ही यह परिणाम प्राप्त हुए।

^1H , ^{13}C NMR, और FT-IR तकनीकों ने क्रमशः Cat A और Cat C के द्वारा प्राप्त डीजल और गैसोलीन श्रेणी के हाइड्रोकार्बन की पुष्टि की। इसके अलावा, गतिविधि के परिणामों ने संकेत दिया कि $\text{SiO}_2/\text{Al}_2\text{O}_3$ परवर्तित करते हुए उत्प्रेरकों की अम्लता भी तरल यील्ड और हाइड्रोकार्बन वितरण को प्रभावित करती है। Cat A और Cat C दोनों उत्प्रेरकों के साथ, कम $\text{SiO}_2/\text{Al}_2\text{O}_3$ (30) पर उच्च अम्लता रखते हुए, अधिक $\text{SiO}_2/\text{Al}_2\text{O}_3$ (55) की तुलना में ईंधन रेंज के हाइड्रोकार्बन की बेहतर उपज प्राप्त हुई। XRD, NH_3 -TPD, BET, FE-SEM और EDX तकनीकों का उपयोग करके उत्प्रेरकों के भौतिक-रासायनिक गुणों की जांच की गई और गतिविधि परिणामों के साथ सहसंबद्ध किया गया।

चौथे अध्ययन में, Cat B के Fe भाग को परिवर्तित करते हुए, तरल और गैस उत्पादों के साथ-साथ प्लास्टिक क्षरण से मूल्यवर्धित कार्बन नैनोट्यूब (CNTs) का उत्पादन करने का प्रयास किया गया है। कार्बन का एक गहरा स्रोत होने के नाते, प्लास्टिक को एक प्रभावी कच्चे माल के रूप में CNTs के निर्माण के लिए इस्तेमाल किया जा सकता है, जिस पर अनुसंधान समुदाय कड़ाई से काम कर रहे हैं। CNTs के उत्पादन की दिशा में, बहुलक मिश्रण (PP, LDPE, और HDPE) के दो-चरणीय उत्प्रेरक क्षरण पर Fe भाग (2 से 15 wt.%) के प्रभाव की जांच 400 °C तापमान पर की गई है। अध्ययन में यह पाया गया कि Fe भाग में वृद्धि के साथ, प्रयुक्त उत्प्रेरक की सतह पर फिलामेंटस कार्बन (CNTs) का अंश है और इसकी पुष्टि

HR-TEM और FE-SEM तकनीक द्वारा की गई। 5 wt.% भाग के उपयोग पर, Fe के समान वितरण के कारण, 400 °C तापमान पर, उत्प्रेरक ने CNTs का उच्च जमाव दिखाया। आगे के अध्ययन में, CNTs के गठन को I_D/I_G अनुपात द्वारा समर्थित किया गया, जोकि विभिन्न Fe भाग वाले स्पेंट उत्प्रेरकों के लिए एकत्रित Raman प्रोफाइल के माध्यम से प्राप्त किया गया। Fe भाग में वृद्धि के साथ, I_D/I_G अनुपात में एक क्रमिक वृद्धि (0.2 से 0.7) देखी गई, जिसने संकेत दिया कि उच्च Fe भाग (>5 wt.%) पर, Fe के भारी जमाव के कारण अधिक विकृत कार्बनयुक्त प्रजातियां (विकृत sp^2 कार्बन) उत्पन्न होती हैं। इसके अलावा, तरल हाइड्रोकार्बन की यील्ड और चयनात्मकता, 5 wt.% Fe भाग वाले Cat B के लिए 400 °C पर तुलनात्मक रूप से अधिक प्राप्त की गई थी जोकि दूसरे अध्ययन के अनुरूप थी। बाकी उत्प्रेरकों की तुलना में 5 wt.% Fe भाग वाले Cat B का उपयोग करके हाइड्रोजन (H_2) की चयनात्मकता (51.34%) भी अधिक देखी गई। कुल मिलाकर, 5 wt.% Fe भाग वाला उत्प्रेरक, वांछित अम्लता और समान Fe वितरण रखते हुए, तरल और H_2 उत्पादन के साथ-साथ 400 °C पर बेहतर गुणवत्ता वाली CNTs का निर्माण करने के लिए उच्चतम पाया गया।

TABLE OF CONTENTS

	Page No.
Certificate	i
Acknowledgments	ii
Abstract	v
सार	ix
List of Figures	xxi
List of Tables	xxvii
Nomenclature	xxix
CHAPTER 1: INTRODUCTION	1-12
1.1 Background	2
1.2 Waste plastics processing	5
1.2.1 Thermal cracking of plastics	6
1.2.2 Thermo-catalytic cracking	8
1.2.3 Process for thermo-catalytic cracking	9
1.3 Challenges and motivation	10
1.4 Objective of the present study	11
1.5 Structure of the thesis	12
CHAPTER 2: LITERATURE REVIEW	13-57
2.1 Waste plastics	14
2.1.1 Statistics in India	15
2.1.2 Effect of waste plastics on environment	17

2.2	Plastic composition and classification	22
2.2.1	Types of polymers	23
2.3	Waste plastic processing	24
2.3.1	Conventional methods	24
2.3.2	Non-conventional methods	25
2.3.2.1	Thermal cracking	27
2.3.2.2	Thermo-catalytic cracking	29
2.3.2.3	Catalytic cracking versus thermal cracking	31
2.4	Catalysts for plastic cracking	33
2.4.1	Solid acid catalysts	33
2.4.1.1	Effect of metal addition	42
2.4.1.2	Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of zeolite	43
2.4.1.3	Catalyst deactivation	46
2.5	Effect of operating parameters	50
2.5.1	Effect of temperature	50
2.5.2	Effect of residence time	51
2.5.3	Effect of pressure	53
2.6	Kinetics of plastic degradation	54
2.7	Gaps and motivation for the present study	56
CHAPTER 3: EXPERIMENTAL DETAILS		59-69
3.1	Methodology	60
3.2	Catalyst preparation	61
3.2.1	Material procurement and pre-treatment	61

3.2.2	Synthesis of Metal supported zeolite catalyst (Fe/HZSM-5)	62
3.3	Characterization techniques	63
3.4	Reactor setup and activity test	67
CHAPTER 4: RESULTS AND DISCUSSION		70-164
4.1	Degradation of polymers: Thermal and catalytic cracking route	71
4.1.1	Degradation kinetics of polymers via Thermo-gravimetric analysis (TGA)	72
4.1.2	Iso-conversional methods	80
4.1.2.1	Model selection and kinetic analysis	80
4.1.2.2	Activation energy	82
4.1.2.3	Pre-exponential factor	84
4.1.3	Summary	87
4.2	Two-stage thermo-catalytic cracking of plastics	88
4.2.1	Activity Test and Product Analysis	88
4.2.1.1	Product distribution and selectivity	88
4.2.1.2	Proximate and heating value analysis	90
4.2.1.3	FT-IR Technique	91
4.2.1.4	GC-MS analysis and carbon atom selectivity	92
4.2.1.5	GPC and SimDist analysis	95
4.2.1.6	^1H and ^{13}C NMR spectroscopy	96
4.2.2	Catalyst characterizations	98
4.2.2.1	X-ray diffraction pattern	98
4.2.2.2	MP-AES and X-ray photoelectron spectroscopy	100

4.2.2.3	BET surface area and pore volume analysis	101
4.2.2.4	NH ₃ -TPD analysis	102
4.2.2.5	H ₂ -TPR analysis	104
4.2.2.6	FT-IR Technique	105
4.2.2.7	FE-SEM analysis	106
4.2.2.8	HR-TEM analysis	107
4.2.2.9	TGA and DTG analysis	110
4.2.2.10	Catalyst stability test	108
4.2.3	Summary	110
4.3	Effect of framework structure and Si/Al ratio of catalyst on product distribution	112
4.3.1	Catalyst characterization	112
4.3.1.1	X-ray diffraction	112
4.3.1.2	Surface area and pore volume analysis: N ₂ adsorption-desorption isotherm	113
4.3.1.3	NH ₃ -TPD analysis	116
4.3.1.4	FE-SEM/EDS analysis	118
4.3.2	Catalyst activity test and product analysis	121
4.3.2.1	Product distribution and selectivity	121
4.3.2.2	GC-MS analysis and carbon atom selectivity	122
4.3.2.3	¹ H and ¹³ C NMR spectroscopy	128
4.3.2.4	FT-IR Technique	130
4.3.2.5	Proximate and heating value analysis	132
4.3.3	Summary	133

4.4	Waste Plastics transformation into value added Carbon nanotubes (CNTs) and hydrogen	134
4.4.1	Catalyst characterization	135
4.4.1.1	X-ray diffraction pattern	135
4.4.1.2	Acidity analysis via NH ₃ -TPD	136
4.4.1.3	BET surface area and pore volume analysis	138
4.4.1.4	H ₂ -TPR analysis	139
4.4.1.5	UV-DRS absorption	140
4.4.1.6	FE-SEM micrographs	141
4.4.1.7	HR-TEM micrographs	143
4.4.2	Product analysis: Gas, liquid, and solid	144
4.4.2.1	Product distribution	144
4.4.2.2	Gas product analysis	145
4.4.2.3	Liquid product analysis	147
4.4.2.3.1	Elemental and heating value analysis	147
4.4.2.3.2	FT-IR technique	148
4.4.2.3.3	GPC and SimDist analysis	149
4.4.2.3.4	GC-MS analysis	151
4.4.2.3.5	NMR analysis	154
4.4.2.4	Solid (coke) residues analysis	156
4.4.2.4.1	TGA and DTG analysis	156
4.4.2.4.2	HR-TEM analysis	158
4.4.2.4.3	FE-SEM analysis	159
4.4.2.4.4	Raman analysis	161

4.4.2.4.5 XRD pattern	162
4.4.3 Summary	163
CHAPTER 5: CONCLUSIONS AND FUTURE RECOMMENDATION	165-171
5.1 Conclusions	168
5.2 Future recommendations	171
REFERENCES	
APPENDIX	

LIST OF FIGURES

Figure No.	Title	Page No.
Fig. 1.1	Adverse effect of waste plastics on environment	2
Fig. 1.2	Global plastic production in Million Metric Tons	3
Fig. 1.3	Global plastic consumption per capita of population	3
Fig. 1.4	Polymer types and its applications	4
Fig. 1.5	Waste plastics processing methods	6
Fig. 1.6	Schematic of thermal cracking route for polymers	7
Fig. 1.7	Zeolite framework channels	8
Fig. 1.8	Schematic of depolymerization via acid catalyzed route	9
Fig 2.1	Global data on plastic waste generation	15
Fig. 2.2	Plastic waste generation in India	16
Fig. 2.3	Effects of plastic wastes on environment	18
Fig. 2.4	Percentage of individual wastes contribution in total waste generated in the country	20
Fig. 2.5	Percentage of individual wastes contribution in total municipal solid waste (MSW)	21
Fig. 2.6	Distribution percentage of polymers in the total plastic waste generated in India	23
Fig. 2.7	ZSM-5 framework structure	35
Fig. 2.8	Hydrocarbon yields obtained during HDPE cracking at 360 °C over different catalysts	36
Fig. 2.9	Framework structure of Y zeolite	37

Fig. 2.10	TGA describing LDPE polymer degradation over different acid catalysts	38
Fig. 2.11	Schematic of Bronsted acid sites over zeolite framework	43
Fig. 2.12	Cracking of polypropylene plastic at 380 °C using different catalysts (USY (▲), and Silica-Alumina 13%, (■), (◇ 1g; ○ 1.5 g; □ 1.75 g; Δ 2 g) were introduced for comparison	45
Fig. 2.13	Coke deposition study for ZSM-5, HY, H-Modernite, and Silica-Alumina catalysts at 450 °C with TOS	47
Fig. 2.14	Performance study of HZSM-11 zeolite at 500 °C for the set of cycles during LDPE plastic cracking using 2:1 ratio of plastic to catalyst	49
Fig. 2.15	Proposed reaction paths for thermal pyrolysis of polyolefins	55
Fig. 3.1	Block flow diagram for processing of plastic waste	61
Fig. 3.2	Schematic representation of Fe/HZSM-5 catalyst preparation	63
Fig. 3.3	Fixed bed reactor set-up for catalyst activity analysis	68
Fig. 4.1	Degradation profiles of (a) PP, (b) LDPE and (C) HDPE at different heating rates	74
Fig. 4.2	Degradation profiles of (a) PP:HZSM-5, (b) LDPE:HZSM-5, and (c) HDPE:HZSM-5 (30:1) ratio at three different heating rates	78
Fig. 4.3	Activation energy distribution using different isoconversional methods comparing thermal and catalytic cracking for PP, LDPE and HDPE	84
Fig. 4.4	Distributed pre-exponential factor $A_f(\alpha)$ values for PP, LDPE, and HDPE polymers	85
Fig. 4.5	(a) Product distribution and (b) carbon atom distribution obtained	90

	in TC, Cat A-TCC and Cat B-TCC	
Fig. 4.6	FT-IR spectra of liquid products obtained in TC, Cat A-TCC, Cat B-TCC and Commercial Diesel	92
Fig. 4.7	Hydrocarbon components in GC-MS of (a) liquid (Cat A-TCC), (b) liquid (Cat B-TCC) and (c) liquid (TC) and corresponding carbon number selectivity for (a') liquid (Cat A-TCC), (b') liquid (Cat B-TCC) and (c') liquid (TC)	94
Fig. 4.8	(a) ^1H , (b) ^{13}C NMR spectra of liquid (Cat A-TCC), (c) ^1H , (d) ^{13}C NMR spectra of liquid (Cat B-TCC), (e) ^1H , (f) ^{13}C NMR spectra of liquid (TC), and (g) ^1H , (h) ^{13}C NMR spectra of commercial diesel fuel	98
Fig. 4.9	XRD patterns of (a) Fresh Cat A and Cat B, (b) Expanded view of (a) for 2 Theta 25-40°, (c) Fresh and spent Cat A and (d) Fresh and spent Cat B	100
Fig. 4.10	XPS profile of fresh-Cat B catalysts in Fe2p region	101
Fig. 4.11	NH_3 -TPD profile of (a) Cat A-fresh, (b) Cat B-fresh, (c) Cat A-spent, and (d) Cat B-spent	103
Fig. 4.12	H_2 -TPR profiles of fresh Cat B catalysts and pure iron oxide (inset)	105
Fig. 4.13	FT-IR spectra of fresh and spent catalysts (Cat A and Cat B)	106
Fig. 4.14	FE-SEM images of fresh and spent catalysts (Cat A and Cat B)	107
Fig. 4.15	HR-TEM images of fresh and spent catalysts (Cat A and Cat B)	108
Fig. 4.16	(a) TGA, and (b) DTG profiles of spent catalysts (Cat A and Cat B)	109
Fig. 4.17	Selectivity towards carbon atom distribution for (a) Fresh and	110

	spent Cat A and (b) Fresh and spent Cat B	
Fig. 4.18	XRD patterns of Cat A (SAR 55, 30), and Cat C (SAR 55, 30)	113
Fig. 4.19	N ₂ adsorption-desorption isotherms of Cat A (a) SAR 55, (b) SAR 30 and Cat C (c) SAR 55, (d) SAR 30	115
Fig. 4.20	NH ₃ -TPD profiles of Cat A (a) SAR 55, (b) SAR 30 and Cat C (c) SAR 55, (d) SAR 30	117
Fig. 4.21	FESEM images, EDS spectrum and corresponding mapping of Cat A (a) SAR 55, (b) SAR 30 and Cat C (c) SAR 55, (d) SAR 30	120
Fig. 4.22	(a) Product distribution, and (b) Carbon atom distribution for Cat A (SAR 30, 55), and Cat C (SAR 30, 55), and (b)	122
Fig. 4.23	Mass-spectrum of liquid products obtained for Cat A (a) SAR 55, (b) SAR 30, and Cat C (c) SAR 55, (d) SAR 30 and corresponding carbon number selectivity in Cat A (a') SAR 55, (b') SAR 30 and Cat C (c') SAR 55, (d') SAR	127
Fig. 4.24	¹ H and ¹³ C NMR spectra of liquid products for Cat A (a, a') SAR 55, (b, b') SAR 30, and Cat C (c, c') SAR 55, (d, d') SAR 30	130
Fig. 4.25	FTIR spectra of liquid obtained for Cat A (a) SAR 55, 30, and Cat C (a) SAR 55, 30	131
Fig. 4.26	XRD patterns of (a) Cat A, and Cat B having different Fe loading (2, 5, 10, and 15 wt%), and (b) expanded view of XRD pattern between 25 to 40, 2 Theta (Deg) for all catalysts	136
Fig. 4.27	NH ₃ -TPD profiles of Cat A, and Cat B having different Fe loading (2, 5, 10, and 15 wt%)	138
Fig. 4.28	H ₂ -TPR profiles of Cat B having different Fe loading (2, 5, 10, and 15 wt%)	140

Fig. 4.29	DRS profiles of Cat A, and Cat B having different Fe loading (2, 5, 10, and 15 wt%)	141
Fig. 4.30	FE-SEM images of fresh Cat A, and Cat B having different Fe loading (2, 5, 10, and 15 wt%)	142
Fig. 4.31	HR-TEM images of fresh Cat A, and Cat B having different Fe loading (2, 5, 10, and 15 wt%)	143
Fig. 4.32	Product distribution for Cat A and Cat B having different Fe loading (2, 5, 10, and 15 wt%)	145
Fig. 4.33	(a) Gas composition for Cat A and Cat B having different Fe loading (2, 5, 10, and 15 wt%), and (b) H ₂ gas selectivity	146
Fig. 4.34	FT-IR spectra of liquid products obtained in for Cat A and Cat B having different Fe loading (2, 5, 10, and 15 wt%)	149
Fig. 4.35	Mass-spectrum of liquid products obtained for (a) Cat A, and (b) Cat B (5 wt% Fe loading) and corresponding carbon number selectivity in (a') Cat A, and (b') Cat B (5 wt% Fe loading)	153
Fig. 4.36	¹ H and ¹³ C NMR spectra of liquid products for (a) Cat A, and (b) Cat B (5 wt% Fe loading)	155
Fig. 4.37	(a) TGA of the spent catalysts Cat A and Cat B having different Fe loading (2, 5, 10, and 15 wt%) and (b), (c) DTG-TGA profiles of Cat A and Cat B (5 wt% Fe loading)	157
Fig. 4.38	HR-TEM images of the spent catalysts Cat A and Cat B having different Fe loading (2, 5, 10, and 15 wt%)	159
Fig. 4.39	FE-SEM images of the spent catalysts Cat A and Cat B having different Fe loading (2, 5, 10, and 15 wt%)	160
Fig. 4.40	Raman spectra of the spent catalysts Cat A and Cat B having	162

different Fe loading (2, 5, 10, and 15 wt%)

Fig. 4.41 (a) XRD patterns of Spent Cat A and Cat B having different Fe loading (2, 5, 10, and 15 wt%), and (b) Expanded view of 2 Theta deg between 25-40° 163

LIST OF TABLES

Table No.	Title	Page No.
2.1	Product distribution on thermal decomposition of different polymers	27
2.2	Types of catalyst used for plastic cracking reported in the literature	39
4.1	Thermo-gravimetric analysis: Degradation temperature range, onset, and end temperatures for thermal cracking of LDPE, HDPE, and PP plastics	75
4.2	Thermo-gravimetric analysis: Degradation temperature range, Onset, and end temperatures for catalytic cracking of LDPE, HDPE, and PP plastics.	79
4.3	Range of kinetic parameters obtained using Ozawa-Flynn and Wall (OFW), Kissinger-Akahira-Sunnose (KAS), and Starink methods.	86
4.4	Elemental analysis and heating value of liquid products obtained in TC, Cat A-TCC, Cat B-TCC and Commercial Diesel	91
4.5	GPC analysis of liquid products obtained in Liquid (TC), Liquid (Cat A-TCC), and Liquid (Cat B-TCC)	95
4.6	Distillation fraction yields (wt. %) of liquid products obtained in TC, Cat A-TCC, and Cat B-TCC using simulated distillation	95
4.7	Physiochemical properties of fresh and spent catalysts (Cat A and Cat B)	102
4.8	NH ₃ consumption of fresh and spent catalysts (Cat A and Cat B)	104
4.9	Physiochemical properties of Cat A (SAR 55, 30) and Cat C (SAR	114

	55, 30)	
4.10	NH ₃ consumption of Cat A (SAR 55, 30) and Cat C (SAR 55, 30)	117
4.11	Elemental (CHNS) analysis and heating value of liquid products obtained for Cat A (SAR 55, 30), and Cat C (SAR 55, 30) along with commercial diesel and gasoline fuels	132
4.12	NH ₃ consumption of Cat A, and Cat B having different Fe loading (2, 5, 10, and 15 wt%)	138
4.13	BET Surface area and pore volume of Cat A, and Cat B having different Fe loading (2, 5, 10, and 15 wt%)	139
4.14	Elemental analysis and heating value of liquid products obtained for Cat A and Cat B having different Fe loading (2, 5, 10, and 15 wt%)	147
4.15	GPC analysis of liquid products obtained for Cat A and Cat B (5 wt% Fe loading)	150
4.16	Distillation fraction yields (wt. %) of liquid products for Cat A and Cat B (5 wt% Fe loading) using simulated distillation	151

NOMENCLATURE

W_i	Initial weight
W_t	Weight at time (t)
W_∞	Residue weight at end of reaction
E_a	Activation energy
T_o	Onset temperature
T_e	End temperature
$k(T)$	Rate constant
$f(\alpha)$	Reaction model
S_{BET}	BET surface area (m ² /g)
S_{micro}	Micropore surface area (m ² /g)
S_{ext}	External surface area (m ² /g)
V_{micro}	Micropore volume (cm ³ /g)
I_D	Intensity of D band in Raman spectra
I_G	Intensity of G band in Raman spectra
$Af(\alpha)$	Pre-exponential factor

Greek letters

λ	Wavelength
θ	Diffraction angle
α	Conversion
β	Heating rate

Acronyms

PP	Polypropylene
LDPE	Low density polyethylene
HDPE	High density polyethylene
PVC	Polyvinyl chloride
MFI	Zeolite framework code
MWW	Zeolite framework code
AE	Activation energy
MSW	Municipal solid waste
TGA	Thermo-gravimetric analysis
DTG	Differential thermal gravimetry
SAR	Silica alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$)
MCM-22	Mobil Composition of Matter-22
ZSM-5	Zeolite Socony Mobil-5
MWW	Framework code (International zeolite association)
MFI	Framework code (International zeolite association)
BET	Brunauer-Emmett-Teller
NMR	Nuclear magnetic resonance
GC-MS	Gas chromatography mass spectrometry
FE-SEM	Field Emission Scanning Electron Microscope
EDS	Energy-dispersive X-ray spectroscopy
TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
HR-TEM	High Resolution-Transmission electron micrographs
TCD	Thermal Conductivity Detector

FID	Flame Ionization Detector
OFW	Ozawa-Flynn and Wall
KAS	Kissinger-Akahira-Sunnose