DEVELOPMENT OF A NOVEL TECHNOLOGY FOR PRODUCTION AND UTILIZATION OF HYDROCARBON FUELS FROM MIXED PLASTIC WASTE

A thesis submitted to the
UPES

For the award of
Doctor of Philosophy
in
Mechanical Engineering

BY
KRISHNA MOORTHY R

April 2023

SUPERVISOR (S)

Dr. Deepak Kumar

Dr. Bhawna Yadav Lamba

School of Engineering
UPES
Dehradun-248007: Uttarakhand, India

DEVELOPMENT OF A NOVEL TECHNOLOGY FOR PRODUCTION AND UTILIZATION OF HYDROCARBON FUELS FROM MIXED PLASTIC WASTE

A thesis submitted to the
UPES

For the award of
Doctor of Philosophy
in
Mechanical Engineering

BY
KRISHNA MOORTHY R
(SAP ID- 500073637)

April 2023

Supervisor
Dr. Deepak Kumar
Sr Associate Professor

Co-Supervisor
Dr. Bhawna Yadav Lamba
Professor
School of Engineering,
UPES

School of Engineering
UPES
Dehradun-248007: Uttarakhand, India

April 2023

DECLARATION

I declare that the thesis entitled "Development of a novel technology for production and utilization of hydrocarbon fuels from mixed plastic waste" has been prepared by me under the guidance of Dr. Deepak kumar, Senior Associate Professor, Department of Mechanical Engineering, UPES and Dr. Bhawna Yadav Lamba, Professor, Department of Chemistry, UPES. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

Krishna Moorthy R
Department of Mechanical Engineering
School of Engineering
UPES
Dehradun-248007,
Uttarakhand, India.
DATE : 21.11.2024

THESIS COMPLETION CERTIFICATE

We certify that Krishna Moorthy R has prepared his thesis entitled “Development of a novel technology for production and utilization of hydrocarbon fuels from mixed plastic waste”, for the award of PhD degree of the UPES, under our guidance. He has carried out the work at the Department of Mechanical Engineering, UPES.

Supervisor

Dr. Deepak kumar,

Senior Associate Professor,

Department of Mechanical Engineering,

UPES

Co-Supervisor

Dr. Bhawna Yadav Lamba,

Professor,

Department of Chemistry,

UPES

Date:

UPES
UNIVERSITY OF TOMORROW

Great Place To Work. Certified FEB 2024-FEB 2025 INDIA

THESIS COMPLETION CERTIFICATE

We certify that Krishna Moorthy R has prepared his thesis entitled "Development of a novel technology for production and utilization of hydrocarbon fuels from mixed plastic waste", for the award of PhD degree of the UPES, under our guidance. He has carried out the work at the Department of Mechanical Engineering, UPES.

Supervisor

Dr. Deepak kumar,

Senior Associate Professor,

Department of Mechanical Engineering,

UPES

Co-Supervisor

Dr. Bhawna Yadav Lamba,

Professor,

Department of Chemistry,

UPES

Date:

Address: Bidholi Via Prem Nagar, Dehradun - 248 007 (Uttarakhand), India T: +91 135 2770137, 2776053/54/91, 2776201, 9997799474 F: +91 135 2776090/95
Page Address: Kandoli Via Prem Nagar, Dehradun - 248 007 (Uttarakhand), India T: +91 8171979021/2/3, 7060111775

ABSTRACT

This work aimed at efficiently employing the plastic waste sources of energy for power generation with the additional benefit of clean environment. This work focuses on production of hydrocarbon fuel by pyrolysis process with the plastic waste feed. The condensed vapor of pyrolysis gases is called as liquid hydrocarbon fuel which can be used commercial CI Engines, tractors for agricultural farming and generator sets for rural areas. This work also proposes to have utilization of pyro-char for self healing material. The proposed sustainable energy model would provide decentralized energy supply to the local communities and household sector along with the benefits of mitigating environmental pollution.

The liquid hydrocarbon fuel (LHF) derived from mixed municipal plastic waste has a high calorific value and contains a significant composition of cyclic and aliphatic hydrocarbons, making it a viable alternative to fossil fuels. The Pyrolysis of mixed municipal plastic waste (MMPW) from the University of Petroleum and Energy Studies, Dehradun, showed that the resulting liquid hydrocarbon fuel is a potential energy source for heat and power generation. The Liquid hydrocarbon fuel of mixed-plastic waste showed great potential for diesel range hydrocarbon fuels that can be utilized in diesel engines.

When used in a traditional engine, the external mixture formation approach may be effectively deployed at a low cost with minor modifications to the existing intake manifold. Cooled EGR was employed to manage the PCCI combustion up to a 10 % concentration. Because of EGR usage in the PCCI engine, there was a delay in the combustion process. Compared to a traditional engine, the combustion in the PCCI engine occurs early and at a low temperature & pressure. According to the analysis of the testing results, the test engine's brake thermal efficiency with liquid hydrocarbon fuels decreased at intermediate and higher loads. However, while operating within uncertainty limitations, the engine's efficiency with liquid hydrocarbon fuels was nearly as good as the engine's efficiency with diesel fuel at all load activities. With liquid hydrocarbon fuels, the number of carbon-based pollutants that came out of the engine was slightly higher than diesel fuel at intermediate and larger loads, excluding the nitrogen oxides. Lower load activities did not demonstrate substantial differences between the pollutants studied. Nitrogen oxide emissions were significantly decreased while using diesel

blended liquid hydrocarbon fuel vapor at high loads owing to a drop in the temperature of the in-cylinder combustion chamber.

At 30% and 15 % fuel vapor induction, exhaust gas recirculation could be a preferred alternative for diesel PCCI combustion. HC, CO, NOx, and smoke emissions were 0.692 g/kW.h, 0.95 g/kW.h, 5.46 g/kW.h, and 52.69 %, respectively, with 15% fuel vapor and 10% EGR. Whereas HC and CO emissions surged, NOx and smoke emissions declined significantly, replicating earlier observations. The current investigation reveals that the PCCI engine generates a small amount of NOx and smoke emissions compared to ordinary engines. When analyzing the performance obtained with conventional diesel operation to those obtained with engine operation using liquid hydrocarbon fuels, it was discovered that PCCI operation's emission characteristics were reduced. Recovery and recycling of municipal mixed plastic waste to converted to liquid hydrocarbon fuel, on the other hand, showed better emissions behavior in engine operation.

Additionally, activated carbon from mixed municipal plastic waste could be employed as a filler in an epoxy vitrimer composite. The enormous surface area of activated carbon in the AC-epoxy vitrimer biocomposite allows for chain exchanges. Self-healing was observed in virgin epoxy vitrimer at 80 °C for 5 minutes, however when activated carbon was added, the material showed a lower temperature self-healing at 348 K for 5 minutes. Vitrimer composites with 1 wt % AC (EP-1) exhibited an 83% and 75 % recovery efficiency after two successive healings in flexural trials. Composite vitrimer research will be useful in the future to witness ecologically sound vitrimer composite materials for practical uses.

ACKNOWLEDGMENT

I would like to express my heartfelt gratitude to my supervisors Dr. Deepak Kumar and Dr. Bhawna Yadav Lamba, for their continuous encouragement and motivation throughout my thesis work. I am very thankful to them for presenting this promising area of research to me and for their supervision, which I have been getting all these years of my research.

In addition to my Supervisors, I would like to show gratitude to Dr. Sunil Rai (Chancellor), Dr. Ram Sharma (Vice-Chancellor and Dean, SoE) at the UPES for their cherished support for my research work.

I would like to express my gratitude to Dr. Devesh Kumar Avasthi (Dean R &D), Dr. Pankaj Kumar Thakur (Associate Dean, R&D) Dr. S.M Tauseef (Associate Dean, R&D), Dr. Ashish Karn (Head of Mechanical Cluster) Dr. Ajay Kumar, Dr. Sravendra Rana and Dr. Shyam Pandey at UPES, for his support during my research.

I would like to extend my special thanks to my dear faculty Dr. Praveen Kumar Ghodke NIT, Calicut and friend Dr. Balaji K who stood with me at each phase of my work.

Thanks to Dr. Sakthi Ganesh Murugesan, Ms. Rakhi Ruhal, Dr. Caneon Kurien, Dr. Debajoyti Bose, Dr. Pinnisetti Swami Sai Ram, Mr. Raghunath, Dr. Meera CS, Dr. Aslesha, Dr. Balaji, Dr. Akhilan raja and Dr. Shiva. I also thank all my faculty colleagues at Department of Mechanical Engineering.

I would like to acknowledge in-house Bio diesel research lab, Central Instrumentation Centre (CIC) and Engine research Lab facility; where I have carried out my research work. I also thank lab technicians Dr. Amit Kumar, Dr. Devendra Rawat, Mr. Charu Pant and Mr. Pradeep singh.

I would like to express my gratitude to R&D Department and SRE Department for their support. I also thank Dr. Vijay.P, Mr. Yogesh sharma, Team SRE and R&D.

DEDICATION

I would like to dedicate and thank you to my Amma R.Gomathy, my Appa K.Rajendran, my Thangachi R.Meenachi Eshwari, my Thangachi R.Samundeeshwari, my Illaal S.Jeya Preethi, my Magavu Prabanjan K.J. and all family Members for their support.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVATIONS

AFD	:	2- Aminophenyl disulfide
A-F	:	Air–fuel ratio
BADGE	:	Bisphenol A diglicidyl ether
BTE	:	Brake thermal efficiency,%
C	:	Carbon
CA	:	Crank angle
CC	:	Combustion chamber
CI	:	Compression ignition
CNT	:	Carbon nanotube
CO	:	Carbon monoxide
DETA	:	Ddiethylenetriamine
DI	:	Direct injection
DMA	:	Dynamic Mechanical Analysis
DSC	:	Differential scanning alorimetry
EGR	:	Exhaust gas recirculation
EGT	:	Exhaust gas temperature
FV	:	Fuel vapor
HC	:	Hydrocarbon
HCCI	:	Homogeneous charge compression ignition
GC-FID	:	Gas chromatograph with a flame ionisation detector
GC-MS	:	Gas chromatograph with Mass spectrometer
GC-TCD	:	Gas chromatograph with a thermal conductivity detector
GO	:	Graphene Oxide
H	:	Hydrogen
N	:	Nitrogen
NOx	:	Oxides of Nitrogen
O	:	oxygen
rGO	:	Reduced Graphene Oxide
PCCI	:	Partially premixed charge compression ignition
TMA	:	Thermogravimetric analyzer

UV–Vis : Ultraviolet–visible spectroscopy

CHAPTER 1 : INTRODUCTION

The population, development activities, changes in lifestyle, and socioeconomic situations all contribute to a rise in solid waste. Energy security and clean environment are the two major thrust areas in the current scenario. Treatment of municipal solid waste (MSW) would satisfy this dual target of energy security and clean environment simultaneously. Plastic waste is categorised as industrial or municipal waste based on its origin; each waste category has various characteristics and features. Waste accounts up a significant portion of municipal waste. It accounts for a significant proportion of solid waste.

Based on information submitted by 35 Indian states and union territories, the Central Pollution Control Board (CPCB) has calculated that India produced 4126997 TPA of plastic waste in 2020–21 and the projected total plastic waste employed to useful product in all 25 States/UTs of India in 2020-21 is 1109180 TPA (Annual Report 2020-21 on Implementation of Plastic Waste Management Rules, 2016 Central Pollution Control Board, n.d.; Overview of Plastic Waste Management, 2013).

States and union territories of India use their plastic waste for a wide range of processes, along with recycling (539447 TPA), reusing plastic in road construction (31578.3 TPA), co-processing plastic as an AFR in cement kilns and power plants (250705 TPA), Waste to Energy plants (135432 TPA), converting plastic waste into liquid fuel through pyrolysis plants (4918 TPA), and others processes (147099 TPA) (Annual Report 2020-21 on Implementation of Plastic Waste Management Rules, 2016 Central Pollution Control Board, n.d.; Overview of Plastic Waste Management, 2013).

Industrial plastic waste (social lead primary waste) is scum generated by the major plastics production, refining, and packaging sectors.

Plastic material is divided into two primary categories: thermoplastics and thermosettings. Thermoplastics account for around 80% of all post-consumer plastics waste created in India, with thermoset accounting for approximately 20%. Polyethylene Terephthalate (PET), Low Density Poly Ethylene (LDPE), Poly Vinyl Chloride (PVC), High Density Poly Ethylene (HDPE), Polypropylene (PP), Polystyrene (PS), and other thermoplastics are recyclable plastics. Thermoset plastics, on the other hand, include epoxy, ester, melamine formaldehyde, phenolic

formaldehyde, silicon, urea formaldehyde, polyurethane, metalized and multilayer polymers, among other things.

The following are some of the environmental consequences resulting from inadequate plastic waste management:

- Littered plastics detract from the aesthetics of the city, obstruct drains, and make valuable public spaces dirty.
- When plastic-containing garbage is burned, it may pollute the air by producing harmful gases.
- Garbage containing plastics causes challenges in garbage processing plants and may also create issues in landfill operations.
- Recycling companies operating in non-conforming regions are causing environmental hazards.

The pyrolysis of plastic waste to produce hydrocarbon fuel is a viable method of extracting energy from waste. Despite the fact that pyrolysis technology is well known in India, significant research challenges such as reactor temperature, pyrolysis vapour retention time, particle size, toxicity, heating rate, catalyst loading, and different plastic waste mixing remain for appropriate pyrolysis system integration in the real market.With this motivation the proposed research is aimed at expeditiously harnessing the plastic waste as sources of energy for alternative fuel instead of diesel with the additional benefit of clean environment.

The proposed work would focus on production of hydrocarbons fuel by pyrolysis process using plastic waste feed. The condensed vapor of pyrolysis gases is called as pyrolysis oil, which can be used in tractors for agricultural farming and generator sets for rural areas. The proposed sustainable energy model would provide decentralized energy supply to the local communities and household sector along with the benefits of mitigating environmental pollution.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

Plastic is an important material in the industrial field and in the human society because of its beneficial properties such as lightweight, cheap cost, and resistance to corrosion(Annual Report 2020-21 on Implementation of Plastic Waste Management Rules, 2016 Central Pollution Control Board, n.d.). Because of the wide scale manufacture and breakdown challenges of plastic materials, garbage generated after their usage poses a significant ecological hazard. To overcome these issues, the scientific community concentrated on converting waste into useful goods, particularly liquid hydrocarbon fuels. Technologies for recycling of individual plastics such as polypropylene (PP), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), polystyrene (PS), and polyethylene terephthalate (PET) are matured. However, there is currently no well-established process for transforming MMPW—a combination of PP, LDPE, HDPE, PET, and PS—into liquid hydrocarbons. Plastics used in wide range of applications in fluid containers, wrapper films, building materials, shopping, and trash bags, outfit, toys, domestic and industrial products generate huge amount of MMPW.

The majority of current research efforts are focused on tertiary recycling, with the goal of introducing recycling technology into the petrochemical industry's everyday operations. Many generations of experience have been gained in the use of various established plastic waste treatment technologies such as incineration, landfill, gasification, plasma gasification, combustion, glycolysis, hydrolysis and aminolysis towards the yield of gaseous/fuel products which can be utilised to produce heat and power. However, these conventional technologies suffer many hurdles to penetrate the market for real ground utilization due to huge investments, practical implications and environmental issues. In order to overcome these hurdles, researchers are focusing on alternate options for plastic waste treatment such as fast pyrolysis technology.

Among all the available technologies to treat MMPW, pyrolysis technology is a promising option to attain high yields of valuable products(Williams & Williams, 1998). In view of ecological security and reduction of non-recoverable conventional fuels, conversion of MMPW into valuable hydrocarbon fuels has attracted world. Few studies have discovered hypotheses and innovations for transforming discarded plastics to liquid products. Many patents on altering over

invention have been filed. Various experimental reactors have been established across the globe. Recent investigations on the pyrolysis of certain kinds plastic materials have been conducted (Adrados et al., 2012; P. Ghodke & Mandapati, 2018; I. Kayacan & Doğan, 2008; Thahir, Altway, Juliastuti, et al., 2019; Williams & Williams, 1998).

There are no commercial plans for converting MMPW into liquid fuel due to its variable temperature, breakdown behavior, and complicated chemical structure. There have been several proposed recycling routes to reduce MMPW, from primary recycling to secondary recycling technologies (Dayana Anuar Sharuddin et al., n.d.). Incineration (S. Kumar et al., 2013a; Kunwar et al., 2015; Lopez et al., 2017; Y. Yang et al., 2012), gasification (Brajendra K.Sharma, Bryan R.Moser, Karl E.Vermillion, Kenneth M.Doll et al., 2014; Buckley, 1991; Mahadevan et al., 2015; Parikh et al., 2004), plasma gasification (Adelawon et al., 2022; Igathinathane et al., n.d.; Y. Zhang et al., n.d.), combustion (Bimbela et al., 2014; Tan et al., 2021), pyrolysis (Alper et al., 2015; Khuenkaeo & Tippayawong, 2020; Kiliç et al., 2014), glycolysis (Onwudili et al., 2009; Pinto et al., 1999), hydrolysis (Ng et al., 1995; Shah et al., 2010), aminolysis (Demirbas, 2004) , and hydrogenation (Chin et al., 2014) are all examples of thermochemical recycling routes for plastic waste that yield gaseous/fuel products (İ. Kayacan & Doğan, 2008). Thermochemical degradation techniques such as pyrolysis provide one of the most dependable answers to this problem. Due to its complicated chemical makeup and varying thermal and decompositional behaviours, MMPW cannot be directly converted into a liquid fuel.

Pyrolysis is one of the important thermochemical conversions that involves heating of MMPW at moderate temperatures range of 573–823K in the inert atmosphere to produce oils, gases, and solid carbon black(P. Ghodke & Mandapati, 2018; Thahir, Altway, & Rachmania Juliastuti, 2019). The use of catalyst brings down the temperature and pyrolysis can occur at considerably lower temperature. The inorganic substances produced by pyrolysis retain unmodified and may be employed in chemical alteration, road construction, or as binders for other polymers(Adrados et al., 2012). In any case, few considerations are describing the process technology and the product characteristics of MMPW pyrolysis. Sharuddin et al. 2016 used pyrolysis technology to convert plastic waste into several forms of fuel, including all by product and streamlined the quantities of liquid hydrocarbon fuels(Dayana Anuar Sharuddin et al., n.d.). Product elasticity might be attained in the pyrolysis process by adjusting operational factors such

as heating rate, pressure, pyrolysis temperature, and catalyst. Product elasticity might be attained in the pyrolysis process by adjusting operational factors such as heating rate, pressure, pyrolysis temperature, and catalyst. Conclusions arrived by Sharuddin et al. 2016, MMPW pyrolysis reduces the dependence on fossil fuel, environmental problems and rise in energy demand issues(Dayana Anuar Sharuddin et al., n.d.). In slow pyrolysis with short residence time, wax formation is favorable, higher temperatures and longer residence times favor BTX (Benzene, Toluene, and Xylene) products (Lopez et al., 2017). Kunwar et al. (2016) highlight the pyrolysis technique and appropriate variables for the transformation of plastic waste to oil in their study on plastic waste to oil. The study suggests that parameter variations such as catalysts, reactor design, heating value, and plastic/catalyst ratio be used to improve overall plastic waste processing to gasoline or diesel range fuels. Catalysts with high acidic characteristics and surface area may increase the transition of plastic waste to oil, while FCC catalysts have been considered for the synthesis of aromatic and gaseous hydrocarbons. The research addressed various issues with the use of MMPW in this review, one of which is the presence of PVC, which creates HCl throughout the process, and provided a viable way to manage the PVC in the MMPW. Product improvement was also suggested by alternative heating methods such as IR, microwave heating for higher heating rates(Kunwar et al., 2015). It could be observed from the above literature review that catalyst plays a vital role in pyrolysis process. In last years, there are few reports on the tuning of the present catalyst which are efficient enough concerning previously reported catalysts. In recent years, focus had turned towards the clay catalyst to reduce the costing of process and for green approach. Apart from the catalyst, several factors affect the products like resident time, type of reactor, temperature, and pressure.

Hence, the present study focused on various parameters affecting the pyrolysis process such as temperature, reactor design, pressure, resident time, product, and catalyst characterization. In addition, insights on recent advancements and modifications of catalyst and comparative assessment of different catalysts have also been addressed.

2.2 Composition and Physical Properties of MMPW

Kayacan and Doan (2008) used a TMA in a N_2 environment to determine physical properties of plastic waste (Akubo et al., 2019). A first-order decomposition reaction and the integral technique were used to analyse the kinetic parameters of the plastic waste pyrolysis process

(Akubo et al., 2019; Kaminsky & Kim, 1999; Overview of Plastic Waste Management, 2013; K. B. Park et al., 2019) . TG analyses were carried out at various heating rates of 10, 15, and 20 K min^{-1}. The combustion temperature was set at 1273 K in the presence of oxygen to determine the ash content of MMPW. Table 1.1 (Jung et al., 2010) depicts the detailed characterisation of MMPW.

Ultimate analysis or elemental analysis of any MMPW can be determined using CHNS (carbon, hydrogen, nitrogen, sulfur) analyzer. It is very important to determine the elemental composition of MMPW to determine the theoretical heating value or calorific value. Parikh et al. (2005) provided a formula to calculate the energy content of fuel with excess moisture, based on its chemical composition (Undri et al., 2014). Czajka et al., 2016 employed the LECO TruSpec analyzer to do the final analysis, which included total carbon, hydrogen, sulphur, and nitrogen content according to standard PN-EN 15,104:2011, sulphur content according to PN-EN 15,289:2011, and oxygen content estimated by difference of total (Aishwarya & Sindhu, 2016). Yang et al. (2013) conducted the Conradson Carbon Residue (CCR) test using the conventional ASTM D189 procedure, in which a carefully balanced sample is placed in a crucible and heated vigorously by a direct burner. The experiment would perform under room temperature, the black carbon residue remaining after the reaction/cracking and coking final sample is weighed and expressed as a mass percentage of the original feed sample(S. Kumar et al., 2013a; Y. Yang et al., 2012).

Table 2.1 Characteristic properties of different plastic residues (B. K. Sharma et al., 2014)**.**

Properties	PP	LDPE	HDPE	PS	PE	MMPW
Volatile matter(wt%)	99.44	96.76	97.5	52.01	96.76	83.44
Fixed carbon(wt%)	0.00	1.68	1.01	47.99	1.68	10.82
Bulk Density (kg m^{-3})	481	689	713	641	689	737
Ash (wt%)	0.67	1.57	0.2	0.0	1.57	11.10
Conradson Carbon residue(wt%)	0.22	0.67	0.53	0.65	0.67	1.01

Heating value (MJ kg^{-1})	45.3-46.4	34.7- 46.6	49.4	37.7-42.1	34.7-46.3	14.4 to 45.3
Carbon (wt%)	77.52-86.1	69.67- 85.7	83.9	83.10- 92.7	69.67-85.4	70.14
Hydrogen(wt%)	14.22-13.7	10.12-13.0	14.9	7.82-7.9	10.12-14.4	6.81
Oxygen(wt%)	7.46 -0.2	0.9-18.55	0.74	0-8.88	0.03-18.55	14.73
Nitrogen(wt%)	0.1	0.09	0.05	0.21	0.09	3.27
Sulfur(wt%)	0.0	0.0	0.0	0.0	0.0	0.0

The calorific value of MMPW can be determined by using an oxygen bomb calorimeter. Various formulae for calculating heating values from their elemental composition have been proposed by many authors(Buckley, 1991; Parikh et al., 2004). Mahadevan et al. (2015) have determined the specific heat capacity (higher heating value) using a Parr 1341 Oxygen Bomb Calorimeter (Mahadevan et al., 2015). The density of solid materials is usually measured as bulk/average density. The density of materials affects the economics of complete process and technology, mainly collection and separation, transportation of feedstock and storage in bunkers/silos and finally loading the material into the reactor. Igathinathane et al. 2010 observed the permeability of material affects the feed gas flow rate(Igathinathane et al., n.d.). This ultimately influences reaction parameters such as thermal conductivity, heating rate, reaction efficiency and emissions(Igathinathane et al., n.d.; Y. Zhang et al., n.d.). Therefore, understanding the physical characteristics of any solid fuel is important in the utilization of heat and power generation systems. It is noted that knowing the physical parameters such as high heating value, viscosity, proximate and ultimate analysis of MMPW contributes for its effectual employment through thermo - chemical techniques.

2.3 Thermal pyrolysis of MMPW

As considerable activation energy is needed to break the Carbon-Carbon and Carbon-Hydrogen bond in an inert environment like nitrogen gas, heat is the primary factor in thermal pyrolysis and the breakdown of hydrocarbon chains. Demirbas (2004) described the process of pyrolyzing plastic waste, in which polymeric materials are heated to high temperatures to break down their massive molecular structures into smaller molecules, resulting in a variety of liquid

hydrocarbons upon condensation. Any solid fuel may be pyrolyzed into a liquid, a solid, and a gas. The liquid byproduct of pyrolyzing MMPW contains hydrocarbons in the gasoline and diesel ranges. Pyro-char, a byproduct of the process, might be employed as a road base or as a feedstock in other petrochemical procedures (López, de Marco, Caballero, Laresgoiti, et al., 2011) . To understand better Adrados etal. 2012 describe the thermochemical phenomena of MMPW by considering simulated homogeneous and known composition of plastic waste. The plastic waste mixture was defined that are usually present in municipal waste(Adrados et al., 2012).

Slow pyrolysis occurs under circumstances of modest temperature (200-400 °C), long residence time (20-60 min), and slow heating rate (0.1-10 °C min^{-1}). Fast pyrolysis occurs under circumstances of intermediate temperature (450-500 °C), moderate heating rate (10-100 °C min^{-1}) and minimum residence time (10-20 min)(Adelawon et al., 2022; Alper et al., 2015; Bimbela et al., 2014; Khuenkaeo & Tippayawong, 2020; Kiliç et al., 2014; Tan et al., 2021).

A considerable number of studies have been reported on the utilization of used plastic of particular kinds in different reactors. For example, on wudili et al., 2009 explored the pyrolysis of PE, PP, PS, and PET in Parr mini autoclave at 773 K and found that the yields of heavy crude plastic oil around 90–95 wt%, 5–10 wt% of gases and up to 1wt% solid residue which indicate all the feed is converted into products(Onwudili et al., 2009). Similarly, Pinto et al. (1999) conducted the pyrolysis of municipal plastic waste (MSW) comprising of polyethylene (PE), polypropylene (PP), and polystyrene (PS) in 1dm^3 autoclave with varying compositions of N_2, they observed for plastic particle size of 3 mm, optimum conditions for maximum yield was at temperature of 703 K and pressure of 3.5 MPa with the residence time of 20 min. Total conversion was higher than 90 % and the main product was liquid, and gas yield was lower than 10 %. Plastic oil produced was aliphatic hydrocarbon carbon ranging from C5-C11 along with branched and cycled alkanes in low concentration(Pinto et al., 1999).

Abbas and Shubar (2008) conducted experiments in an autoclave reactor with HDPE plastic and observed the highest yield of 70 wt% at 753 K with a residence time of 20 minutes. At 708 K and 5.5-6.0 MPa of N_2 gas pressure for 1 hour, Siddiqui and Redhwi, 2009 investigated the thermal plus catalytic pyrolysis of PS in the presence of LDPE, HDPE, PP, and PET plastics in a 25 cm^3 stainless steel micro reactor. Experiments were performed with ratios of 1:1, 1:2, and 1:3,

however the highest production of plastic oil was found with a ratio of 1:1. Using hydro treating catalysts, solvents, the catalyst based on feed, a one-hour residence period, 5.5-6.0 MPa pressure, and optimal temperature of 703-713 K, the author also identifies the useful products (de Marco et al., 2009; Sarker et al., 2012). Thermogravimetric examination of PS, PE, and PP municipal plastic waste subjected to non-catalytic pyrolysis was investigated by Bosmans et al., 2014. The final stages of deterioration were seen at temperatures between 447 and 500 K.

Miskolczi et al. (2004), studied the pyrolysis of HDPE and PP waste generate of hydrocarbon fuels in a pilot size shell and tube reactor at 798 K temperature either with or without ZSM-5 catalyst. Increased gas, gasoline, and light oil yields were observed when a catalyst was employed. They also found that, depending on the conditions, plastic wastes might be turned into gasoline at a yield of 20–48% and light oil at a yield of 17–36% (Bujak, 2015) . Adnan et al., 2015 observed the highest production of the hydrocarbon fuels during the pyrolysis of PET in the temperature range 373-753 K. The analysis also reported the existence of insoluble compounds including waxy higher hydrocarbons, gums, and coke (D. Chen et al., 2015a) . Used Plastic has been pyrolyzed at a low temperature (548 K) in a batch reactor (Shah et al., 2010). The 3 mm length feedstock was used with a mix of LDPE and PP and observed the yield of the plastic oil was 48.6 % with a non-catalytic pyrolysis technique(Shah et al., 2010). Thermal decomposition of virgin PE was investigated by Ng et al., 1995, with parametric condition of pressure range of 1.38–16.13 MPa, residence time of 10 min and temperature range of 373–873 K. Maximum liquid production was observed at 743 K and chemical composition analysis revealed that the product constitutes of α- olefins along with branched hydrocarbons(Ng et al., 1995). Demirbas, 2004, studied the pyrolysis of PP, PE and PS to obtain the gasoline-range hydrocarbons at 720–760 K and reported that by using fractional distillation some of hydrocarbon compund generated from plastic oil(Demirbas, 2004).

To overcome the requirement of high temperatures for pyrolysis process, catalyst can be used. A catalyst, which ultimately diminishes the temperature for the reaction, is reducing the prerequisite activation energy for bond breaking and pyrolysis can occur at substantially lower temperature.

2.3.1 Effects of temperature

Temperature has a major role in how easily a polymer will breakdown during the pyrolysis process. There exists Vander Waals interaction between polymer molecules. Since the bond between C-C is non-polar, it is very strong and requires a large amount of energy to break it. The stability of the C-C bond requires a high temperature of 573−1073 K. The thermal decomposition of various polymers varies throughout a wide range of temperature. Also, studies show that at different heating rates, the process of liquid fuel may effect. For example, heating rates increase the weight loss and reaction rate for the pyrolysis of HDPE(Chin et al., 2014). Another investigation found that 773 K is best for extracting the most liquid hydrocarbon fuel. The yield of liquid products decreases as the temperature rises over 873 K (Donaj et al., 2012; Kaminsky & Zorriqueta, 2007). Similarly, a thermal degradation temperature range of 623-773 K (Gerasimov & Volkov, 2015) for both polystyrene and PP.

Silvarrey and Phan 2016, conducted PE waste pyrolysis in TGA equipment and observed that degradation peak starts at 623 K and reaches maximum degradation at 693 K and degradation finishes at 793 K(Diaz Silvarrey & Phan, 2016). A single decomposition peaks were observed for PE, PP, PS pyrolysis however for PVC waste two decompositions peaks were observed which infers HCl release correspond to first peak and remaining polyene decomposition as the second peak. Additionally, for a mix of all the plastic waste pyrolysis, 99.4 wt% decomposition was observed at temperature 773 K(Diaz Silvarrey & Phan, 2016). Encinar and González 2008, performed the experiments both isothermal and non-isothermal mode using thermogravimetric and observed the effects temperatures. It was observed that polyethylene below 698 K, mass conversion was low. However, the reaction was fast above the 723 K and maximum conversion was occurred up to 99.6 wt%. If the process temperatures are below 698 K multiple peaks were observed in the corresponding DTG curve of the PP pyrolysis process(Encinar & González, 2008). There are three distinct reaction stages in the pyrolysis of low-density polyethylene, as seen by three distinct breakdown peaks in the DTG curve at 660, 698, and 791 K (Almeida & De Fátima Marques, 2016). According to Walendziewski and Steininger (2001), pyrolysis of polyethylene occurs between 643 and 723 K (Degnan, 2000).

2.3.2 Effects of pressure and residence time

Murata et al. (2003) have carried out studies on the effect of pressure in the process of pyrolysis. For HDPE, they reported that gaseous products increased from 6 % to 13 % at 683 K and

observed a specific small increment of 4 % to 6 % at 713 K, and as the pressure increased from 1 to 8 bars maximum yields were obtained. They also have shown that when the pressure was high, lower molecular weight products resulted in the liquid fuel(Murata et al., 2004). At low temperatures, the effect of pressure becomes less apparent and residence time shows greater impact.

The amount of time that feeds spend within the reactor is known as their "residence time." More thermally stable products, such as lower molecular weight hydrocarbons, are formed when particles are kept in the reactor for longer (Elordi et al., 2009; Renzini et al., 2011). Research shows that the distribution of a product at different temperatures depends on the residence period, with lower yields for the liquid product over longer residence times. Higher liquid yields with longer residence time of 2.56s below 958 K and has no effect of residence time above 958 K (Y. H. Lin & Yen, 2005) were found in studies on HDPE waste pyrolysis done by Mastral et al., 2003 to understand the effect of residence time on product distribution.

2.3.3 Effect of types of reactors

Different type of reactor has an impact on the process and product yields. By keeping reactants in the reactor for longer periods of time, the batch-scale reactor can achieve high conversion rates despite being a closed-loop, isolated system. Large-scale systems have high labor costs and difficult in maintenance, which is considered as the main disadvantage of large-scale continuous reactors. In contrast, a semi-batch reactor permits the addition of reagents and the discharge of products simultaneously and is suitable for manufacturing on a micro level (Fogler & Fogler, 1999). Both reactors have been used for small scale laboratory production and the temperature range lies in 573−1073 K.

For substantial rates of reactant conversion, a reactor in which there is neither an inflow nor an outflow of component is used. Nevertheless, the most significant drawback associated with these reactors is the variable quality of the output of each cycle, as well as the high employment cost and large-scale manufacturing(Anene et al., 2018). Unlike Batch reactors, semi-batch reactors allow either reactant addition or product removal continuously. In semi-batch reactors, the selectivity of the reaction may be a benefit, but the expense of manpower can be a negative. Both reactors have the benefit of being able to regulate the operating parameter, in addition to having the simplest design possible (J. J. Park et al., 2003), (Fogler & Fogler, 1999). Fixed-bed reactors

are widely used for batch-type pyrolysis of MMPW(Akubo et al., 2019). Fixed-bed reactors are easy to design, operate, with constraint of irregular feed particle size and shape cause problem during the feeding into the system and surface area availability for process reaction. In MMPW pyrolysis process, for fixed-bed reactor yields a maximum hydrocarbon fuel of 70–75 wt% without catalyst and 85–90 wt% with catalyst.

To overcome the problems faced in the fixed-bed reactor, a fluidized bed reactor is used by many authors(K. B. Park et al., 2019). Kaminsky et al. (1999) used inert gas to fluidize the reaction bed, causing the feed particles to float in a fluid state along with the catalyst. Thus, provides better mixing of catalyst and feed in the reactor, thereby increasing surface area for the reaction/process in fluidized-bed pyrolysis of MMPW(Kaminsky & Kim, 1999). Because the fluidized-bed reactor maintains consistent conditions throughout the process and has efficient heat and mass transmission, it is able to limit the amount of product variation. The authors Jung et al. (2010) used fluidized bed reactors to conduct pyrolysis on waste PP and PE materials. It was observed that process reaction temperature was constant with better heat and mass transfer, and shorter residence time which results in consistency of liquid product produced from PP with a yield of 87 wt% and HDPE with yield of 85 wt% at 773 K(Jung et al., 2010).

Conical spouted bed reactors (CSBRs) manage a wide range of particle sizes and delivering effective mixing (Choi et al., 2010). Olazar et al., 2009 decided to employ CSB reactors rather than fluidized bed reactors since the earlier had a reduced potential for bed dispersion and a reduced attrition rate (Marcilly, 2000). CSBR offer numerous benefits over fluidized-bed reactors, such as high thermal rates and little defluidization limitations, while also being able to withstand large feeds like as PE and PP at a certain temperature. These advantages may be found in both the design and operation of the reactors. The operation of the CSBR had, however, provide a few challenges, the most notable of which were catalyst entrainment, catalyst feeding, and the collection of finished products (liquid fuel and solid pyrochar). The slow pyrolysis process at low temperatures generally one which CSBR favours the most since it results in the production of waxes using plastic waste pyrolysis technologies. Experiments were conducted by Aguado et al., 2002, to create waxes using the CSBR reactor from HDPE, LDPE, and PP pyrolysis at temperatures ranging from 723 to 873 K. At a temperature of 723 K, they found that the HDPE and LDPE pyrolysis produced waxes yield of around 80 wt%, while the PP pyrolysis

produced 92 wt% (Chitnis & Sharma, 1997). Elordi et al., 2007 carried out the HDPE pyrolysis process in CSBR using the HY zeolite catalyst at 773K. They found that the process produced liquid fuel at a rate of around 68.7 wt%, the majority of which was gasoline fraction (C5–C10) fuel (Gil et al., 2007).

The usage of conventional thermal pyrolysis approaches has been found to be inferior to the microwave-assisted technology in a number of respects. This method enhances the pace of reactions by rapidly heating materials in an energy-efficient manner, resulting in enhanced production speed as well as reduced production costs (Budsaereechai et al., 2019; Lewandowska et al., 2002; Manos et al., 2001). Because microwave pyrolysis involves the quick and direct transmission of heat to the feed materials using microwave radiation, it is possible to avoid the loss of heat energy while still carrying out the fast pyrolysis process. Major limitations of the microwave pyrolysis process, there is no sufficient data available on dielectric properties of mixed plastic waste materials. Undri et al., 2014 performed microwave pyrolysis for HDPE and PP waste using carbon and tires as absorbers in the microwave power range of 1.2–6.0 kW(Undri et al., 2014). According to the findings, HDPE pyrolysis produced the maximum output of liquid fuel at 83.9 wt%, while PP pyrolysis produced a yield of 74.7 wt%. Similarly, some other authors(Aishwarya & Sindhu, 2016; Ludlow-Palafox & Chase, 2001) performed the microwave pyrolysis of HDPE and toothpaste packaging at 775−873 K. They found 100 % conversion of plastic waste, producing 79−82 wt% of liquid product and 19−21 wt% of gaseous product in-case of HDPE pyrolysis. Many parameters influence the microwave pyrolysis process such as inert nitrogen gas flow rate, type of absorber and microwave rotation design. Internal chambers of rotary drums, furnaces, or kilns built of steel drums are lined with refractory materials that have high resilience and are resistant to corrosion. They are intended for prolonged residence durations of around twenty minutes or more and have inclined low speed spinning movements. Because of the significant temperature differential that occurs inside the system, rotary kilns produce a product that is subject to a broad range of variations. Punkkinen et al., 2017, performed (Werther & Ogada, n.d.) the plastic waste pyrolysis in a rotary kiln designed with screens for solid circulation at 823–953 K(Punkkinen et al., n.d.).

From the results, it was observed that the products obtained from rotary kiln pyrolysis yields around 38.12 wt% liquid, 49.09 wt% solid, 2.39 wt% of gaseous fuel product. Table 2.2 summarzes the effect of different reactor types on pyrolysis process.

Table 2.2 Different types of reactors and their effects on pyrolysis process.

Type of plastic	Type of reactor	Process temperature	Process pressure	Residence time	Product yield	Other remarks
Municipal solid waste (MSW) and mixed plastic waste (MPW) (Miskolczi et al., 2013a)	Batch fixed reactor	773-873 K	Atmospheric pressure	111 min at 773 K,89 min at 823 K	MPW yields are higher compared to MSW. Also, observed catalyst addition increases the yields rapidly in the thermo-catalytic pyrolysis process	The surface structure and physical form of the chars were modified by catalysts used in the process, (Ni–Mo)
Wood, paper, municipal plastic waste (Jiang, 2006)	An electrically induced heated fixed bed reactor	The reaction temperature was changed from 773-1173 K	Atmospheric pressure	up to 50 min	Pyrolysis gas composition was CO, H_2, CH_4, and CO_2. The liquid products are hydrocarbons	Pyrolysis temperature affects product outcomes. Observed increases in the gas product, decrease the yield of liquids and char.
MSW fractions and mixed waste plastics(Dahlbo et al., 2018)	Batch reactor with three-section, with individual temperature controllers	Pyrolysis was performed up to 823 K (with Heating rate of 20–25 K min^{-1})	Atmospheric pressure	30 min	N. A	

Virgin plastic: 40 wt% PE, 35 wt% PP, 18 wt% PS, 4 wt% PET, and 3% PVC(López, de Marco, Caballero, Laresgoiti, et al., 2011)	Mettler Toledo TGA/SDTA851 analyzer and an unstirred stainless steel reactor in semi-batch operation	823 K	Atmospheric pressure	30min	Liquid: 42.9 wt%, Gases: 56.2 wt%, Solid: 0.9 wt%	
Pre-treated domestic refuse; MPW (Gerasimov & Volkov, 2015)	Rotary drum,	723-773 K	Atmospheric pressure	50-60 min	The char with a calorific value of around 10 GJ/t.	
A mixture of LDPE and PP (Escola et al., 2011)	Batch and semi-batch reactor	673 K,	Atmospheric pressure	90min	54% Liquid yield	
PE (de Marco et al., 2009)	Batch and semi-batch reactor	733 K	Atmospheric pressure	30min	40% Gases, 55% Liquid, 5% Solid	
Cleaned PP waste (Sarker et al., 2012)	Batch and semi-batch reactor	633 K	Atmospheric pressure		2%Gases, 92% Liquid, 6% Solid	
LDPE and PP (Jung et al., 2010)	Fluidized bed reactor	953 K,			42.8% Gases, 56.7% Liquid, 0.5%Solid	fluidizing bed reactor, product gases are used as fluidizing gas
Shredded MSW, + 50% waste plastics (Bujak, 2015)	Rotary kilns,	773-823 K	Atmospheric pressure	60 min	Power from steam Turbine	The pyrolysis gas passed through a cyclone before the

						boiler Flue gas scrubbing system of the coal-fired power plant
Industrial waste, spent tires, industrial plastic waste and domestic solid waste (D. Chen et al., 2015b)	Rotary kiln, pyrolysis	773-823 K	Atmospheric pressure	45– 60 min	CO/H_2-rich fuel gas	Gaseous products are utilized to produce heat and process the pyrolysis process.
Shredded waste, and industrial waste (Porzio et al., 2016)	A rotary kiln	723-873 K	Atmospheric pressure	45 min	N.A	Pyrolysis process carried out with process heat from the drying zone. Char separation is carried out using cloth filters.
Mixed waste, MSW, industrial and hospital waste (Malkow, 2004a)	Conical shape, inclined and rotary kiln.	873-973K	Atmospheric pressure		steam; ash and metals	

2.3.4 Effect of catalysts

Typically, catalyst effects the rate of the reaction either positively or negatively without being consumed. The positive catalyst reduces the activation energy requirement hence enhancing the rate of reaction. The catalyst in the pyrolysis process helps eliminate the need for very high temperatures and makes the process more uncomplicated. Catalyst also affects/controls the product composition and gives higher selectivity for the desired chemicals(Marcilla et al., 2007). Usage of the catalyst reduces the cost of energy due to low temperature reactions in the pyrolysis and enables for commercial applications.

2.3.4.1 Types of catalyst

Catalysts are of two kinds - Homogeneous (dissolves with reactant and solvent) and heterogeneous (does not dissolve). The most significant drawback of homogeneous catalysts that they difficult to separate from the reaction mixture after the reaction has taken place, in contrast to heterogeneous catalysts, which are often solid and hence simple to separate. $TiCl_4$, $AlCl_3$, $FeCl_3$, and $TiCl_3$ together function as a powerful Lewis acid and acceptor of electron pairs. They have the potential to disperse their charges differently throughout the polymer chain if they degrade in liquid resin. After charge distribution, they accept hydride ion to produce carbonium ion(Donaj et al., 2012; Kaminsky & Zorriqueta, 2007). Ivanova et al., 1990 used $AlCl_3$ as a catalyst (Homogeneous), which required lower temperatures and higher yields of the gaseous product but the poor selectivity of monomer compared with the un-catalyzed process (Ivanova et al., 1990). Thus, the main area for research in catalysis remains with the development of Heterogeneous catalysts.

There are many case studies of heterogeneous catalysts in the scientific literature. Some of these include zeolites, Nanocrystalline zeolite (HUSY, n-HZSM-5, H, HMOR), silica-alumina, alumina, FCC (Fluid Catalytic Cracking), MCM-41, cement powder (J. J. Park et al., 2003), Clay/Sand, kaolin (Miskolczi et al., 2013b), SBA-16, metal oxides, and molecular sieves, among others. Acidic property, pore size, adsorption property, and surface area of the catalyst are some of the properties that influence the process. All the catalysts that were named above exhibit these characteristics uniquely, and their effects on reaction speeds, product ranges, and other characteristics may be seen.(Donaj et al., 2012).

Mechanism of cracking incorporates the development of carbenium ion with isomerization, β-cleavage, random bond scission, oligomerization/alkylation, hydrogen transferal, aromatization which is governed by acidity, density, and acid sites on the surface of the catalyst(Almeida & De

Fátima Marques, 2016). Since Lewis and Brnsted acid sites, thought to be present within the apertures of materials like zeolites (S. Kumar & Singh, 2011), affect the acidity of solid crystalline catalysts, the pore size of the catalyst must be large enough. Isomerized products are formed when hydrogen ions are donated to polyolefin at the highly acidic spots on the catalyst's surface. The catalyst becomes inactive due to high acidity and pore size (Jamradloedluk & Lertsatitthanakorn, 2014). In recent years, researchers have focused on tailoring catalysts to produce pyrolysis products with specific properties (Duangchan & Samart, 2008; Sharypov et al., 2002) . These novel catalysts have produced intriguing outcomes, demonstrating high levels of efficiency and output.

2.3.4.2 Zeolite catalyst

Zeolites are structures of alumino-silicate minerals having microporous sites used as commercial adsorbents and catalysts(Degnan, 2000). It has a three-dimensional framework with an oxygen atom link in the tetrahedral site. Different zeolite has a different ratio of silica-alumina and the specific ratio has different reactivity. Even this was well demonstrated by Artetxe et al., 2013 that with different ratios of SiO_2/Al_2O_3 30, 80, 280 using catalyst HZSM-5 zeolite. SiO_2/Al_2O_3 = 30 has the greatest acid strength and also has a higher BET surface area and average pore diameter. While SiO_2/Al_2O_3 = 280 has the least acidic strength(Artetxe et al., 2013).

With a SiO_2/Al_2O_3 ratio of 30, the most acidic catalyst is the most important functional site for breaking waxes, leading to increased yields of light olefins and decreased yields of the C12-C20 heavy fraction. The yields of the C12–C20 and C5–C11 fractions are decreased by 28 wt% and 28 wt%, respectively, while the production of light olefins chemicals is increased by 58 wt% as a result of the reduction in SiO_2/Al_2O_3.

Elordi et al., 2009, presented a report of comparison between HZSM-5, Hβ, Hγ acid zeolite catalyst on CSBR for HDPE. HZSM-5, Hβ, Hγ have SiO_2/Al_2O_3 ratio of 30, 75, 5.2 and BET surface area 182, 231, 221 $m^2\ g^{-1}$ respectively(Elordi et al., 2009). Since the Hγ catalyst possesses bigger microspore's possibly causes bimolecular cracking and hydrogen transfer reactions whereas monomolecular cracking taking place in HZSM-5. HZSM-5 giving more gaseous olefins and less coke precursor reactions, but reaction with Hγ giving more paraffin and coke formation. Hβ catalyst with mild acid strength and pore size shows normal results of additional catalysts. The Major disadvantage of Hβ and Hγ catalyst is its deactivation due to coke production whereas HZSM-5 is producing much lower amount.

Renzini et al., 2011 studied the performance of H–ZSM-11 (H–Z) and BETA (H-B) zeolites for LDPE and other plastics. The fresh H-B zeolite catalyst possesses better catalytic action than the fresh H–Z zeolite. The microporous structure of H–Z hinders has a large opening of polymeric molecules to the internal acidic sites and are 10 membered ring structure. Whereas H-B, having higher accessibility to its active sites was more active, has 12 membered rings as pore. Since H-B is more Lewis/Brønsted acid than H–Z catalyst (Renzini et al., 2011). Product distribution using (Table 1.3) HZSM-5, HUSY, HMOR catalyst for PP has been shown by Lin and Yen, 2005 (Y. H. Lin & Yen, 2005). According to the results in Table 2.3, the liquid product yields employing HZMS-5 were the highest when compared to HUSY and HMOR. The thorough analysis of fuel source generated by catalytic pyrolysis process of PP waste gives hydrocarbons ranging from C1-C4 and C5-C9 in amounts of about 60-67 wt% and 26-28 wt %, respectively, utilising the HZSM-5 and HMOR catalysts. HUSY formed C1-C4 and C5-C9 hydrocarbon molecules with roughly 30-37 and 52-55 wt percent, respectively. Table 2.3 compares the yields of the product produced with various catalysts.

Table 2.3 Products yield plastic waste pyrolysis process at an optimum temperature (Y.-H. H. Lin & Yen, 2005)

Type of catalyst	HUSY (Y. H. Lin & Yen, 2005)	HZSM-5	HMOR	Y-Zeolite(Bagri & Williams, 2002)	HNZ (J. J. Park et al., 2003)	Silica sand(Obeid et al., 2014)	Cement(Obeid et al., 2014)
Liquid (%)	89.49	94.77	88.29	84.23	65.43	40	82
Gaseous(%)	3.75	2.31	4.54	11.54	18.95	51	18
Residue(%)	6.76	3.92	7.17	4.23	15.62	9	0
Coke(%)	3.44	1.25	3.21	0	0	0	0

HUSY produced extensive molecular range compare to HZSM-5 and HMOR catalyst. However, both HUSY and HMOR are deactivated during the reaction(Y. H. Lin & Yen, 2005).

Adnan et al., 2015, studied the effects of polystyrene (PS) and polyethylene terephthalate (PET) interactions in the presence of 20 wt% Al-Al_2O_3 supported catalysts. PET was pyrolyzed at a temperature of 773 K and a residence period of 60 minutes to generate the by product. Based on

the liquid composition, significant interactions were identified. PET content boosts gas production, and single-ring aromatic hydrocarbons (C6-C9), mainly styrene monomers, dominate in the liquid product (D. Chen et al., 2015a). Sriningsih et al. (2014) investigated the liquid product breaking of low-density PE polymers over bi-functional catalysts Ni/Z, Ni-Mo/Z, Co/Z, and Co-Mo/Z. Furthermore, the hydrotreating/hydrocracking operation were effectively performed out at 623 K with 20 mL min^{-1} of hydrogen gas for one hour of residence time. At 623 K, the transformation of LDPE across Co-Mo/Z produces a greater selectivity of gasoline of 71.49 % (P. K. Ghodke, 2021b) .

Lopez-Urionabarrenechea et al. (2012) have documented the pyrolysis of polyethylene, polypropylene, and polystyrene waste at 713 K for 30 mins utilising ZSM-5 zeolite as a catalyst. During the pyrolysis process, several valuable chemicals for commercial applications like aromatic compounds are produced (S. Kumar et al., 2013b). When coupled with polystyrene plastic, commercial chemicals such as benzoic acid, naphthalene, naphthalene derivatives, biphenyls, tetra-phenyls, and quarter-phenyls are detected in the pyrolysis result of plastic trash. Aromatic hydrocarbons, notably styrene monomer and styrene oligomers, are prevalent among the hydrocarbons generated. The catalyst to input ratio of 1:1 produced the highest yield of liquid output pyrolysis and was shown to be an uneconomical method.

Bagri and Williams, 2002, conducted the catalytic pyrolysis of LDPE in a fixed bed reactor at temperatures of 673, 723, 773, 823 and 873 K independently with presence of ZSM-5 and Y zeolite. Pyrolysis process of LDPE to product yield 46 wt% liquid product and zero char and negligible gas yield. Performance of Y- zeolite catalyst was observed the liquid yields reduced to 84 wt% and increase the char product. As the temperature of the reaction bed climbed, the gas production increased but the liquid product production dropped. The employment of catalysts improves the aromatic hydrocarbon content in pyrolysis oil (Chintala, Godkhe, et al., 2018).

Vasile et al. (2001) used H-ZSM-5 and P-ZSM-5 zeolite catalysts to pyrolyze a mixture of all type of polymers. The enhanced gaseous products found in this pyrolysis process reduce the liquid production rates. The composition of the produced hydrocarbon is determined by the reactivity and acidity of the catalyst (Chintala, Godkhe, et al., 2018). Park et al., 2003, performed pyrolysis in a semi-batch fixed bed reactor with a HNZ catalyst and a temperature range of 723-773 K. to generated liquid production maximum was observed (Panda et al., 2012).

In conclusion, zeolite catalysts are efficient for hydrocarbon production. However, some zeolites are producing char that leads to catalyst deactivation but HZSM performing better. Miskolczi et al. (2009) investigated the pyrolysis of mixed plastics waste in such a pilot-scale reactor at 723 - 796 K temperature in the appearance and without of the catalyst ZSM-5. The use of zeolite catalysts boosts the yields of liquid products including gasoline and light oil (Walendziewski, 2005).

2.3.4.3 Fluid catalytic cracking (FCC)

The most significant catalyst for the upgrade process of hydrocarbon products involves fluid catalytic cracking. It converts high molecular weight and high boiling hydrocarbons into important fuel products. FCC has been created by combining zeolite and non-zeolite acidic crystals in a matrix. Because of its excellent product selectivity and thermal stability, zeolite-Y was the primary component of the FCC catalyst (Kalargaris et al., 2017) . Many zeolite catalysts have significant production costs; in this case, FCC catalyst has an economic benefit since it creates wasted catalyst that is still active in other processes. M. Olazar et al. 2014, reported a reduction in the acidity of the FCC catalyst due to the steaming of catalyst bed (Table 2.4). This reduces the yields of C_1–C_4 compounds(Abbas-Abadi et al., 2014). In this case, steaming of FCC lump formation, it affects the yields of liquid product. It has been discovered that the output rates for utilising a fresh catalyst and a catalyst that has been subjected to moderate steaming have been respectively, 35 and 38 wt %. During the reaction process, it causes a considerable decrease in the catalyst activity that was utilised in conjunction with intense steaming (22 wt %). Interestingly it is found that, fresh catalyst yield the diesel fraction of 13 wt%, mild steamed FCC catalyst yields diesel fraction up to 40 wt%, and a severe steaming yields highest as 69 wt% (Table 2.4).

Table 2.4 Product distribution of FCC in a fresh and steaming state (Abbas-Abadi et al., 2014)

Type of FCC catalyst	C_1–C_4 (gaseous)(wt%)	C_5–C_9 (medium gasoline) (wt%)	C_{10}+ (diesel) (wt%)
Fresh FCC	52	35	15
Mild steaming	25	38	40
Severe steaming	5	20	70

Coke deactivates the catalyst, rendering it ineffective for breaking waxes. Monitoring catalyst activity revealed that a chemical equilibrium catalyst has been a promising alternative for plastic waste pyrolysis (Kalargaris et al., 2017). Abbas-Abadi et al. (2013) demonstrated the influence of the catalyst/PP ratio (Table 2.5) on product distribution using the FCC catalyst (Sayin et al., 2009).10 wt% of the catalyst is best to obtain condensed product compare to 20, 40 and 60 wt% of catalyst. To conclude the FCC catalyst, we can say that the usage of 'spent FCC catalyst' added advantage to it. This catalyst has greater efficiency in liquid oil production.

Table 2.5 Product analysis from catalyst/ PP ratio

Catalyst / PP ratio	Condensed product yield (%)	Non-condensable product yield (%)	Coke yield (%)	Olefins (%)	Paraffins (%)	Naphthenes (%)	Aromatics (%)	Olefin/ Paraffin (%)
0	95.2	4.4	0.4	Nd	Nd	Nd	Nd	Nd
0.1	92.3	4.1	3.6	44.63	32.87	17.23	5.27	1.36
0.2	85.2	9.6	5.2	46.57	29.36	17.28	6.79	1.59
0.4	79.3	13.8	6.9	48.04	24.77	18.34	8.85	1.94
0.6	76.7	14	9.3	50.08	23.35	16.6	9.97	2.14

2.3.4.4 Other catalysts

Silica-Alumina combination also works as a catalyst having Lewis and Brønsted acid sites. Lewis acid with electron-accepting sites whereas, Brønsted acid electron sharing sites with an ionizable H^+ atom. Sakata et al., 1997 investigated acidity with different ratios of SiO_2/Al_2O_3. SiO_2/Al_2O_3 (SA = 4.99) has higher acidity than SA-2. SA-2 with lesser acidity produce a higher yield of liquid oil (74.3 wt%), followed by (67.8 wt%) if SA = 1, ZSM-5 has strong acid sites which yield higher liquid product(Sakata et al., 1997).

Cement also works as a catalyst and effects product composition in the pyrolysis process as demonstrated by Obeid et al. 2014 determined product distribution by using the silica sand and product of pyrolysis are 51 wt% of gas, 40 wt% liquid, and 9 wt% wax was obtained whereas the use of cement powder bed produced 82 wt% of liquid and 18 wt% of gas production. The silica band produced C_{10}-C_{22} hydrocarbons but cement bed produced between C_{10}-C_{15} hydrocarbons. This also shows that suitable bed material and catalyst gives the generated pyrolysis liquids to become similar to fuel compounds(Obeid et al., 2014).

Panda and Singh 2011, used kaoline as a catalyst and compared it with silica-alumina catalyst and thermal pyrolysis for polypropylene(Panda & Singh, 2011). The catalyst reduces the resident time for the reaction to finish. Si-Al has slightly better performance than kaolin (Table 2.6).

For the first time, Mesoporous silica SBA-16 is utilized by Choi et al. 2010, for catalytic conversion of plastic waste. SBA-16 catalyst produces the high yields of olefins and gasoline/diesel range oils and found resistance to coke formation. Al-SBA-16 catalyst retains a high potential for catalytic activity for the pyrolysis of polyethylene plastic(Choi et al., 2010).

Table 2.6 Types of catalyst

	Thermal	Kaolin(Panda & Singh, 2011)	Silica-alumina(Choi et al., 2010)
Parameter	Temp 773 K	Catalyst 10 wt% and Temp 723 K	Catalyst 10 wt% and Temp 723 K
Oil yield wt%	82.85	89.5	91
Non condenble gas yield wt%	16.25	9.75	8
Pyro char wt%	0.9	0.75	1

Shape selectivity is an important part of the catalytic process. Often, shape selectivity plays a more important role than acidity. Shape selectivity influences the catalyst's activity and stability against coke formation throughout the process (Marcilly, 2000). So, in all catalysts, FCC is better than the rest of the catalyst. ‘Spent FCC catalyst’ makes it economically favorable while other catalysts are being deactivated during the process due to coke production. Sometimes even if the catalyst is not deactivated, at the end of the reaction it mixes with solid residue and then difficult to separate from residue.

2.3.4.5 Clay catalyst

Catalytic pyrolysis using clay as the main catalyst has been studied widely. Although they are less active than zeolites, they can still decompose the plastics at a higher temperature. Clay behaves as a solid acid catalyst and they were used as a catalyst in the petroleum industry before the discovery of zeolites. Zeolites and silica-alumina catalysts are used instead of zeolites since they are more thermally stable(Chitnis & Sharma, 1997). Since clays, being low-price they are

commercially attractive. Acidity and activity of these catalysts are enhanced by pillaring and acid treatments. These have very extensive use in the organic chemistry industry as a solid acid catalyst. Layered clay forms a two-dimensional porous network, having a microporous dimension larger than zeolites. Pillared clays (Gil et al., 2007)are mainly used as catalytic studies in pyrolysis since they have a network of voids and less flexible than that of their parent expanding clays. In addition, their interlayer space is not changeable during the calcination process. Bronsted and Lewis acidity in the clays comes from hydroxyls and the pillars (Manos et al., 2001).

Manos et al., 2001, compared ultra-stable (US) Y zeolite with clay catalysts. According to the report below 600 K clay, the catalyst is less reactive but with increased temperature, they proved superior to zeolite. Liquid oil yielded 70 wt%, which is 50 wt% more than US-Y zeolite. In addition, the percentage of alkene was more in case of clay catalyst might be due to lower possibilities of hydrogen-transfer secondary reactions because of lower acidity. Coke formation also decreased up to 10 % compare to US-Y zeolite (Manos et al., 2001).

Budsaereechai et al. 2019, conducted the PP, PS, HDPE and LDPE waste pyrolysis using binder-free pelletized bentonite clay at different temperatures and ratio of plastic waste to clay catalyst. It was observed from the results obtained around 85–89 wt% of liquid hydrocarbon yields without catalyst and with catalyst 86–90 wt% of liquid hydrocarbon fuel(Budsaereechai et al., 2019). On details characterization, liquid hydrocarbon produced from clay catalyst contains mostly gasoline range (C5–C9) hydrocarbon for PS pyrolysis and for other plastics, yields aliphatic hydrocarbons suitable for use in diesel engines.

Pyrolysis was performed by A. Marcilla and colleagues in 2005 in the presence of commercial clay (sepiolite) given by industry (Agarwal et al., 2013). The researchers used two distinct particle sizes. Clay catalysts were the primary focus of their research as it pertained to the investigation of the influence on the temperature necessary for the pyrolysis process. Sepiolite brought the temperature down to 23 K for the breakdown of PE and up to 70 K for the degradation of PP when it was exposed to an inert environment. In terms of lowering the temperature of the PP reaction, the sepiolite catalyst performed comparatively better than the FCC and HZSM-5 catalysts (Agarwal et al., 2013).

2.3.4.6 Catalyst tuning

In the case of waste plastic contains moisture, it affects the quality of liquid fuel produced and producing the water in yield in the course of the reaction has been a major challenge. Tailored catalysts have been a good solution to address this problem and upgrading bio-oil quality. There are many reports in investigating new tailored catalysts. The main representative of the mesoporous molecular sieves is MCM-41. They exhibit extremely high and large surface area but, well-defined pore size. Despite, having thermal and chemical stability it has lower acidity that is a major disadvantage of not useful in the petroleum industry. To overcome this problem many laboratories incorporated silicon, aluminum, vanadium, etc. to improve the property of the material.

In the various type of incorporation, Al-MCM-41 combination has been of great importance. Even various types of metals such as Ni, Al, Co, Mo, Fe, and Cu found that the catalytic properties of these materials could be improved(Lewandowska et al., 2002). Beatriz Valle et al. incorporated transition metal as nickel in the HZSM-5 zeolite. This combination increased yields of aromatic compounds and hydrothermal stability of the catalyst(Valle et al., 2010). Often this behavior of metal attributed to the dehydrogenation ability and its moderate acidic behavior.

In the same context, different zeolite catalysts are also being tailored or modified with an additional combination. Q. Zhou et al. 2003, presented their study on a new type of ZSM-5 Zeolite named DeLaZSM-5, prepared by desilication and ion exchange with La^{+3} under microwave irradiation. In this catalyst, the Si/Al ratio is decreased and the BET surface area and pore volume have been increased significantly. The DEGRE of liquid increased and the percentage of gas and solid residue has been decreased respect of the original catalyst. Because of the huge number of weak acidic sites in a liquid, the amount of olefin grew while the amount of plastic oil products dropped (Sjöberg & Dec, 2011). This was due to the fact that the liquid included more hydrogen atoms.

Nishino et al., 2008 employed Ga modified ZSM-5 for the breakdown of polyolefin on a continuous mass flow rate of 10 kg per hour. The product had a liquid content that was more than 50 %, and 80 % of them were aromatics, with the BTX (benzene, toluene, o-xylene, m-xylene, and p-xylene) making up the majority of the aromatics. Modification of ZSM-5 zeolites for catalytic cracking has gained many researchers' attention to the production of light olefins. Keeping the right parameter and loading of the additive amount directly affects the performance

of ZSM-5. Dehydrogenation reactions are brought about by alkaline and exotic metal ores, which induce surface basicity. Transition metals, on the other hand, modify acid distributions, which also brings about dehydrogenation reactions. These dehydrogenation events are the primary factor responsible for the generation of light olefins (Rakopoulos et al., 2007; A. K. Sharma et al., 2020).

To overcome the problems related to brominated high impact polystyrene, C. Ma et al. 2016, studied tuning of HZSM-5 and MCM-41 catalyst with Fe and Ni (Ma et al., 2016). The Br-0HIPS's important end product was hydrocarbon oil, which accounted for 69 % of the feedstock it processed. As a result of these improved catalysts, the yield of wax products has been reduced, which demonstrates a greater level of overall performance. The creation of coke also rises, which may be linked to the intensive secondary cross-linking processes that take place. Liquid product amount in the case of MOM-41 modified catalyst was more or less similar, instead of increasing gas yields, this catalyst performed well in converting the wax product into the oil. FM and FZ catalysts increased yields of double and single ring aromatic compounds significantly. The intensive cross-linking interactions between the vapour intermediates on the surface of the catalysts also improve the yields of multi-ring compounds. NZ increased the yield of C_{16} hydrocarbons whereas FZ increased for C_8 compare to the non-catalytic process. The same trend was observed for MOM-41 modified catalyst but in the case of the HZSM-5 modified percent area were more (Ma et al., 2017).

Nanocrystalline zeolites also have been studied for catalytic degradation of plastics. J.F. Master et al. found greater yields of gaseous products and higher selectivity of products with nanocrystalline HZSM-5 catalyst compared to thermal cracking. Gaseous products are due to the size restriction of nano zeolites (Mastral et al., 2006). Nanocrystalline zeolites with excellent activity and selectivity for gaseous olefins are a viable option for plastic waste reuse (Serrano et al., 2005).

There are few reports which deal with modifications with clays. Next, we will look somewhat in these metals are mainly introduced to have a beneficial effect in the process. Manos et al., 2002, aluminum supported pillared clays for tertiary recycling of polyethylene to hydrocarbon fuel (Manos et al., 2002). The total conversion was above 95 % for pillared clays also the yields to liquid were above 70 wt%. Even the regenerated catalysts are giving 96 % conversion and

67 wt% liquid yield, which is very close to the fresh catalyst. The regenerate- ability and almost the same activity as fresh one is a very good advantage for commercial applications.

The catalytic pyrolysis of polyethylene was performed by De Stefanis et al., 2013, using pillared and reconstructed clays. The selectivity to oil fraction was substantially greater (about 70%) for all of the restructured and pillared clay catalysts examined than for the H-ZSM5 zeolite (50 wt%). Clay catalyst also decreases the temperature required for the reaction to 573 K compare to catalyzed with >873 K. It has lesser activity than zeolite (HZSM-5), but superior for the formation of the liquid products. Higher acidity like zeolites leads to high yields of heavily cracked products, mainly gases, and coke formation (de Stefanis et al., 2013).

Li et al., 2017, used modified pillared clays for catalytic pyrolysis of mixed plastic instead of single plastic waste. They modified pillared clays with different metals such as Fe, Ti, Zr (designated as Fe-PICL, Ti-PICL, Zr-PICL). There was no increase in gas yield using clay catalyst compare to the non-catalytic process. Fe-PICL produced the highest amount of oil product 79.3 % and lowest gas product 18 % in comparison to non-catalytic and other modified clay. In use of another catalyst over the cracking of polymer is suggested which reduces the yield of oil products. All the clay-based catalyst produced a higher yield of C_{13}-C_{19} range hydrocarbon, which is representative of diesel products. Ti-PICL catalyst showed high product selectivity of aromatic compounds in light hydrocarbon range and Fe-PICL showed in heavy hydrocarbon range. On the other hand, the amount of CO_2 is also increased in the catalytic process compare to the non-catalytic process. Fe-PICL was reported for efficiency in regeneration even up to two cycles. These modifications in the clays provide a new field for opportunities and challenges, as they have great potential for commercialization (Li et al., 2017a).

Catalyst characterization and analysis is very important in catalyst development, quality control of product, activity, achieving performance or resolve deactivation problems. The catalyst can be characterized using different techniques such as Fourier transform infrared spectroscopy, X-Ray diffraction analysis, scanning electron microscope (Li et al., 2017b; Y. Zhang et al., 2017), and Transmission Electron Microscope / Energy Dispersive X-ray Spectrometry (F. Chen et al., 2016; Y. Zhang et al., 2015). An X-ray fluorescence equipment may be used to examine basic chemical composition of a catalyst (X. Lin et al., 2015).

The porous (micro-meso) structure of the catalyst has been characterized in the BET surface analyzer by the adsorption-desorption concept. López et al., 2011a, characterized the commercial ZSM-5 zeolite catalyst for its surface area and found to be 412 $m^2 g^{-1}$ with a micropore area of 346 $m^2 g^{-1}$ and pore volume of 0.1 $cm^3 g^{-1}$, which specifies catalyst having the high porosity and active surface area available for process reaction (López, de Marco, Caballero, Adrados, et al., 2011). It was observed, ZSM-5 after the pyrolysis experiment decrease in micropore area (3 $m^2 g^{-1}$), the reasons explained by the authors was the residual pyro-char was deposited on the zeolite surface during the process. Serrano et al., 2012, used Al-MCM-41 for the polyolefinic waste plastics pyrolysis process. The BET surface area of Al-MCM-41 was ~1000 $m^2 g^{-1}$ with a mesoporous size of 2.7 nm compared to an amorphous SiO_2−Al_2O_3 (Serrano et al., 2012). Serrano et al., 2000, prepared the nanocrystalline zeolite for the MPW pyrolysis process and observed the external surface area of 81 $m^2 g^{-1}$ and its activity was higher compared to standard HZSM-5 (Serrano et al., 2000).

To study the crystalline nature of the catalyst, X-ray diffraction was performed by (Li et al., 2017b)at a 2θ angle from 1° to 60° for the pillared clay. Ordering of the clay layers was determined using measured basal spacing d_{001} resulting in 11.9 Å, indicating the interlayer distance increased by pillaring the clay with a procedure (Li et al., 2017b). This was confirmed using the BET surface area analysis technique. The crystal size of the synthesized nanocrystalline zeolite was determined using XRD. The average crystal size was measured to be 75 nm for synthesized nanocrystalline zeolite and compared with standard HZSM-5 with a crystal size of 3 μm (Serrano et al., 2000). This Nano-zeolite was very active and the catalytic degradation of MPW at 340 °C yields the maximum amount of liquid hydrocarbon fuel. Incorporation of aluminum into the zeolite crystals improves the catalyst pore size and enhance the plastic waste degradation (Y. H. Lin & Yang, 2007).

The Brønsted acid or Lewis acid sites of catalysts can be characterized by FTIR PY/2,6-DMPY adsorption method. In this method, Brønsted acidity was identified based on the adsorbed DMPY and if adsorbed by PY indicates the total acidity of the catalyst. Li et al., 2017, performed FTIR PY/2,6-DMPY adsorption method for prepared PILC catalyst and observed that PILC contains both Brönsted and Lewis acid sites, which mainly identify the structure of hydroxyl group of montmorillonite and the metallic oxide pillars, respectively (Li et al., 2017b). Acid strength improves the activity of the catalyst, provided if there are no steric or diffusional limitations. To

understand the catalyst acid strength role in the pyrolysis process Zhao et al., 1996, performed the catalytic cracking of PP in TGA, and observed activity of different acid strength selected catalyst wise HY > H-mordenite > H–L zeolite > Na-mordenite (Zhao et al., 1996). Selectivity of catalyst and acidity if catalyst both determines the activity of catalyst used for the pyrolysis process. To measure the strength of the acid and determine the temperature-programmed desorption (TPD) of NH_3 curves for the prepared catalyst Arabiourrutia et al., 2008 performed calorimetric in combination with thermogravimetric measurements of NH_3 differential adsorption at 423 K. After the catalytic pyrolysis process, HZSM-5 zeolite decrease NH_3 differential adsorption from 140 to 130 kJ (mol of NH_3)$^{-1}$, the same trends were observed while using HY zeolite catalyst (Arabiourrutia et al., 2008). To achieve the high acidity of catalyst, incorporation of aluminum is performed by Lin and Yang, 2007, it enhanced the activity of the catalyst in the degradation of polyolefins (Y. H. Lin & Yang, 2007).

2.4 Product analysis

It is well known that output products of plastic pyrolysis are liquid fuel, solid pyro-char, and gaseous fuel. Liquid product, which is also called as hydrocarbon fuel or plastic oil can be characterized chemically and physically. The liquid fuel and the gaseous fuel were examined by N. Miskolczi et al. in 2004 applying GC-FID and GC-TCD respectively to detect the hydrocarbon in by product. GC made of CarloErba VegaSeries GC 6000 equipped with a fused silica capillary column (Al_2O_3/KCl coating) was used to separate the liquid fuel with a temperature program that starts at 313 K isothermal time of 15 min and starts heating to 633 K at heating of 15 K min^{-1}(Ng et al., 1995). C5-C18 range of hydrocarbons compounds were detected as main components of MPW. Ateş et al. 2013, analyzed the liquid fuel obtained from plastic waste using GC/MS made of Hewlett–Packard HP 7890 gas chromatography coupled to quadrupole detector(Miskolczi et al., 2013b). The temperature program used to separate the liquid fuel was initial oven temperature was to set 318 K held for 2 min and then increased to 563 K at 5 K min^{-1} with an isothermal hold for 10 min. Split less injection was applied. The ion source and detector temperatures were set 503 K and 573 K, respectively. On analysis of the composition, it was observed that C10 to C33 and from C10 to C35 were identified for the Municipal solid waste (MSW) and municipal plastic waste (MPW) pyrolysis oil respectively(Miskolczi et al., 2013b). Pielichowski and Njuguna (2005) used flash pyrolysis with a pyro probe that was linked to various pieces of equipment, including GC–MS, GC-FTIR, and

GC-AED (atomic emission detector), in order to determine the chemical components of the liquid hydrocarbons that were derived from the pyrolysis of MMPW (Pielichowski & Njuguna, 2005). Kumar and Singh 2011, detected the aliphatic hydrocarbons (alkenes and alkanes) in HDPE pyrolysis hydrocarbon fuel with carbon number C9- C24(S. Kumar & Singh, 2011). A SHIMADZU IR-470 made FTIR spectrometer was used to analyze the IR spectra of olefin content in the wavenumber range of 4000-400 cm^{-1}. Miskolczi et al. 2004, identified the vinyl double bonds at 910 and 990 cm^{-1} while vinylidene has internal double bonds at 890 and 956 cm^{-1}.

An elemental analyzer was used in order to accomplish the ultimate examination of the pyro-char (Leco, TruSpec Micro CHNS, USA). Jamradloedluk and Lertsatitthanakorn 2014, conducted experiments on pyro-char produced from MMPW pyrolysis and observed pyro-char contains carbon (81−91wt%), and hydrogen (8−15wt%) in major portion nitrogen (00.1wt%), and sulfur (<0.1wt%) in minor content. It also observed PVC pyrolysis pyro-char product contains chlorine in major content compare to nitrogen and sulfur(Jamradloedluk & Lertsatitthanakorn, 2014).

Simulated distillation is the procedure to quantify the different liquid fuel fractions obtained from the pyrolysis process. The simulated distillation curve was plotted for the hydrocarbon fuel obtained from LDPE/PS waste pyrolysis as per the standard ASTM D 2887-8(Onwudili et al., 2009). Pyrolysis was performed in the temperature range 673–773K and plotted the cumulative yields of the product composition (wt%) of the hydrocarbon fuel against their boiling point ranges 323 K–773 K. The LDPE hydrocarbon fuel obtained at 723 K was close match to kerosene fuel when the plot was compared with diesel and kerosene fuels(Onwudili et al., 2009). Sharma et al. 2014 used high-temperature GC-FID to obtain the boiling point distribution of hydrocarbon plastic crude oil fractions(B. K. Sharma et al., 2014), and experimentally distillation was conducted under 673 K and observed good range of fuels obtained consisting of naphtha, diesel aviation fuel, gasoline, and fuel oil. Detail plot of different fraction fuel were plotted and compared with petroleum fractions.

It was observed that fractions were compatible with petroleum crude oil(B. K. Sharma et al., 2014). This simulated distillation was also conducted with the intention of maintaining the purity of products. It was observed from the analysis of different MMPW pyrolysis, non-condensable

gases composition consisted of H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_2H_2, C_4H_{10}, and C_4H_8 gases (İ. Kayacan & Doğan, 2008) (Duan et al., 2015; Martin et al., 2014; W. J. Yang et al., 2015). Ateşetal.2013, reported the concentrations of CO and CO_2 were 20.43 wt% and 41.52 wt% of MSW pyrolysis at 773 K. Similar results were published by Sharypov et al. 2002, and Duangchan and Samart 2008 (Duangchan & Samart, 2008; Sharypov et al., 2002). Ruoppolo et al. 2012, investigated the non-condensable gases from MMPW pyrolysis and observed the carbon-oxides/hydrocarbons ratio was 1.192 at 873K without catalysts (Ruoppolo et al., 2012). Pielichowski and Njuguna; 2005, studied the evolved gases from the pyrolysis process using GC coupled with a mass-selective detector to understand the complete spectra of chemical composition(Al-Salem et al., 2009).

Plastics are long-lasting and non biodegradable. With an eye toward environmental security and a reduction in non-recoverable conventional fuels, reusing innovation for switching to fuels made from plastic waste has got a lot of attention around the world (Brown et al., 2002; Kessler & White, 2002; Yassin & Hojjati, 2017) . Several scholars and foundations have developed theories and innovations for converting plastic trash to fuel. There have been many patents filed in this area. In various regions of the world, many pilot plants have been established (Brown et al., 2004; Kessler et al., 2003). Numerous investigations over the pyrolysis of certain types or unmixed plastic materials have been conducted. The thermal decomposition behavior of these plastics makes it difficult to convert them into useful fuel in a single reactor. There is a lack of information on the technological elements of plastic waste conversion, and further research is needed to turn plastic waste into fuel (Luzuriaga, Matxain, et al., 2016; Peng et al., 2016; Tesoro, 1988).

Thermochemical conversion technologies are becoming increasingly important for the management of plastic waste. One of the most significant thermochemical conversion techniques for transforming plastic waste into useful products such as liquid oil, gas fuel, and carbon black is pyrolysis (Altuna et al., 2016; Luzuriaga, Martin, et al., 2016). It entails heating material in an inert environment at moderate temperatures of 573–823 K. (nitrogen). It is an endothermic reaction that necessitates a contribution of energy, which is normally provided through the reactor's walls when the feedstock is delivered. Condensable vapours, non-condensable gases, and solid pyro-char (fixed carbon and inorganic compounds (glass, metals, ash, etc.) are

produced as the volatile stuff in input plastic trash decomposes. Pyrolysis produces inorganic chemicals which can be reused in many applications such as chemical recovery or modification, building roads, additives to other plastics, and the third alternative, disposal in landfills, lessens the weight of plastic waste accumulation in the long run (X. Yang et al., 2018; Zako & Takano, 2016). In any event, there are a few points to consider while defining the pyrolysis method and the plastic waste pyrolysis result.

A small number of studies were published on the production and use of specific types of plastic garbage. Hazard 2014., for example, observed hydrocarbon waxes, gums, and coke, as well as light oils, in the liquid result of pyrolysis of high-density polyolefin in the range of temperature 373–753 K (Burger et al., 2016). The results of co-pyrolysis of polypropylene with coal and bottoms of petroleum residue were encouraging, and the plastic waste was repurposed to make condensed coal products. T.Williams and Slaney, 2007 examined the batch method of transforming virgin polymer (PE, PP, PS, and PET) to unrefined liquid oil at 773 K in a Parr micro autoclave yields of 90-95 %, 5-10%, and 1% of liquids, gases, and solid waste, respectively (Benesi & 61, n.d.). Similarly, Chan and Balke (1997) examined the pyrolysis of polypropylene and polyethylene in a steel micro reactor across a temperature range of 523–773 K and discovered that polypropylene conversion was maximum (98 wt %) at 573 K, while HDPE conversion was 92 wt % at 623 K. A wide variety of paraffinic hydrocarbons between C6 and C16 were discovered in the liquid product generated in a microreactor. Because of its good fuel qualities, the liquid can be utilized as a strong fuel (Ganesh et al., 2008a; P. K. Ghodke, 2021b; Kaimal & Vijayabalan, 2015).

Shah et al. (2010) employed a batch reactor to undertake pyrolysis of used plastic at low temperatures. The feedstock utilized was a 3 mm long combination of LDPE and PP. With a non-catalytic pyrolysis process, the usual output of liquid content in the hydrocarbon fuel from plastic waste pyrolysis is 48.6 wt % at 548 K(Porzio et al., 2016) .

Miskolczi et al. (2004) evaluated the utilisation of PP and PE polymers in horizontal tubular reactors at 798 K for the synthesis of hydrocarbon fuels and observed that yields are sensitive on the polymers' feed composition and residence duration (Bujak, 2015).Pinto et al., 1999, used an autoclave to test the same plastics and found that the best conditions for maximal yield were 723 K, 0.14 MPa, and a 30-minute residence period. Aliphatic hydrocarbons, carbon spanning from

C5 to C11, as well as low concentrations of cyclic and branched alkanes, were generated as liquid hydrocarbons (Ganesh et al., 2008a). Ng et al., 1995, evaluated thermal degradation of virgin PE under parametric conditions of residence period of 10 min, pressure of 1.38 – 16.13 MPa range and temperature range of 373 – 873 K. At 743 K, the maximum liquid production was recorded, and the composition analysis of the product revealed that the product included - olefins and branched hydrocarbons (N. Kumar, 2019a; Malkow, 2004b).

In most of the investigations, plastics are converted to liquid product using pyrolysis technology in batch autoclave reactors, stainless steel reactors, and tubular reactors etc. very few studies available on the effect of operating temperatures to convert virgin/domestic plastic into usable alternate fuels (Gray & Ryan, 2018; N. Kumar, 2019a). The effect of temperature on the pyrolysis of municpal mixed plastic wastes in a single reactor was investigated in this study, and the thermal behaviour of MMPW was analyzed.

The thermochemical conversion of plastic waste to fuel presents an opportunity to address the industrial, transportation, and agricultural sectors' energy needs. Segregation, on the other hand, the presence of mixed wastes and the diversity of the materials are significant barriers to the general use of the technology. The processing is the act of it is simplest to deal with single-plastic wastes that have recognized physiochemical characteristics. Nevertheless, collecting single-use plastic trash is a viable option for recycling and reusing. It will not be cost viable to collect money from end-users. (Andersson & Stage, 2018; Moorthy Rajendran et al., 2020a) The random scission process is used in the pyrolysis of polyolefins to break them down. Free radicals are produced, which promote chain reactions that result in the breaking of polymers into a diverse variety of hydrocarbons that exist in both the liquid and gaseous phases of the environment. Several variables are contributing to the development of the process. The residence time, the temperature, and the type of pyrolysis agent employed in the process are the most critical variables to consider. Higher temperatures result in increased yields of hydrogen, methane, acetylene, aromatics, and soot, whereas lower temperatures result in more liquid products (Sakata et al., 1999). The oil product produced by catalytic pyrolysis of high-density polyethylene contained a high production of gasoline range hydrocarbons (C8–C12), with a yield of 97.72 wt. % and an aromatic content of 95.85 wt. %, respectively. According to the results, the liquid products were mostly disseminated in the gasoline fractions (C6–C12) and were

primarily consisted of aliphatic hydrocarbons (alkanes and alkenes). The deterioration over HZSM-5, on the other hand, resulted in light hydrocarbons (C3–C4) reaching 50 wt. % of the total weight and being dominated by aromatic compounds. Oils produced from waste plastics have a wide range of uses, including agriculture industry, automotive industry, and manufacturing industry. Using pyrolysis oil derived from waste plastic as a feedstock for engines in the automotive sector is a huge step forward. (Chintala, Ghodke, et al., 2018; Oyedun et al., 2014).

In comparing waste plastic oil and conventional petroleum products, Additionally, it was discovered that it could be utilised as fuel in CI engines. Because of their outstanding driveability and better thermal efficiency in CI engines. Despite their benefits, they generate large quantities of nitrogen oxides (NOx) and smoke, which will harm human health (P. K. Ghodke, 2021a; Panda et al., 2012). Thermal brake efficiencies were lower than those of diesel fuel under all load conditions, and the temperature of the exhaust gas increased as engine load increased. NOx and CO emissions increase proportionately as the fraction of waste plastic oil in blends increases. In the present state of the art, there has been a considerable lot of variety in engine tailpipe emissions, including all type of pollutants, among other things. When using plastic oils in CI engines, some have noted a decrease in carbon-based pollutants, but others have observed NOx emissions (S. Kumar et al., 2013b)(Chintala, Godkhe, et al., 2018). In the case of waste plastic oil, it is possible that this will result in more considerable heat losses and decreased thermal brake efficiency (Kalargaris et al., 2017; Walendziewski, 2005). EGT was fuelled with neat WPO at a variety of injection timings with increased EGR rates ranging from 10% to 30%. EGT is a temperature indicator for the combustion chamber within the cylinder. The EGT drops as a result of the thermal action of the high specific heat gases contained in the recirculated exhaust gas (Sayin et al., 2009). Using a combination of emulsified bio-solution/palm-biodiesel/diesel, Chen et al. (*Saving Energy and Reducing Pollution by Use of Emulsified Palm-Biodiesel Blends with Bio-Solution Additive | Elsevier Enhanced Reader*, n.d.) proved that the blends benefited the environment by reducing polycyclic aromatic hydrocarbon (PAH) and particulate matter (PM) emissions from diesel engines while conserving Energy and saving money. Previously, it was found that an oxygenated additive might improve nitrogen dioxide (NO_2) emissions and combustion efficiency while decreasing fuel consumption rate, brake-specific fuel consumption, pm emissions, and carbon monoxide (CO) emission (C. Y. Lin &

Wang, 2004). In addition, biodiesel has several drawbacks compared to diesel, such as a greater viscosity, a higher pour point, and a weaker volatile index. As a result, biodiesel's poor cold flow behaviour creates a barrier to biodiesel usage in freezing temperatures. (*Performance and Combustion Characteristics of Biodiesel–Diesel–Methanol Blend Fuelled Engine | Elsevier Enhanced Reader*, n.d.; Singh et al., 2021)

Prommes et al. (Kwanchareon et al., 2007) the phase diagrams of diesel–biodiesel–ethanol blends at various ethanol purity levels and temperatures were analysed, as well as the fuel characteristics and emissions performance of the selected blends in a diesel engine compared to base diesel. They determined that a blend of 80% diesel, 15% biodiesel, and 5% ethanol was the optimal ratio based on the fuel's excellent qualities and low emissions. However, while comparing waste plastic oil to biodiesel, there was a 16 % increase in thermal brake efficiency demonstrated. Additional results showed that when compared with diesel fuel, carbon-containing gases were declined, while oxides of nitrogen were slightly increased, showing that the trend was in the right direction. Senthilkumar et al. (Senthilkumar & Sankaranarayanan, 2016) conducted investigation into the use of Jatropha biodiesel in diesel engines in combination with waste plastic oil. Silica was used as a catalyst in an experiment using waste plastic pyrolysis oil. Diesel engines may run on a mixture of waste plastic pyrolysis oil and diesel at the right ratios. NO_x emissions were found to have risen as exhaust temperatures rose. (Kaimal & Vijayabalan, 2015). Agarwal et al. (Agarwal et al., 2013) In this study, morphological analyses of diesel-fueled HCCI engine loads and EGR rates were varied to test for combustion particulate emissions. Quartz filter paper was shown to accumulate more particulate matter when engine load reduced and exhaust gas recirculation rate increased. When compared to a normal engine, the PCCI engine generates a much lower amount of NOx and smoke pollutants. Post-exhaust gas technologies, such as selective catalytic reduction, may further minimize the amount of HC and CO released into the atmosphere (Bhurat et al., 2021; R. Lin et al., 2021). This is the most critical parameter that controls the combustion characteristics of PCCI since it determines how reactive the charged mixture is and how quickly they ignite. The ignition of PCCI may be affected by adjusting the temperature, pressure, and chemical composition of the fuel in the combustion chamber. Using PCCI ignition, an engine's thermal efficiency may be improved while emissions of nitrogen oxides (NO_x) and soot are reduced (Sjöberg & Dec, 2011). The capacity to adapt to different fuels, on the other hand, is the most crucial criterion for the PCCI

combustion process. Many different types of study have been conducted to determine the effects of various fuel physical and on in-cylinder combustion process yields composite properties. Fuels of many types can be used in our processes provides us with a broad range of options for extending the PCCI's operating range and managing the PCCI's ignition phase (Rakopoulos et al., 2007; A. K. Sharma et al., 2020).

While diesel and internal combustion engines have been heavily scrutinised for their emissions, most of this analysis seems troubled. ICEs can produce critical emissions, which means that the pollution levels coming out of the tailpipe are lower than those in the surrounding air. Since the commercial development of DPFs, we have been aware that they produce high levels of particulate matter. As a result of increasing automobile use, air pollution has recently reached the threshold of a significant worldwide problem(Kurien et al., 2019). Reduced emissions from gasoline-powered automobiles, which now account for the vast majority of vehicles on the road, are the only way to address this problem (Johnson & Joshi, 2018). Due to a rise in automobile use, air pollution has recently become a major global issue. Reducing emissions from gasoline-powered cars, which now account for the majority of new car sales, is critical to finding a solution to this issue (Kishi et al., 1999).

Even though they offer many benefits, they release significant quantities of nitrogen oxides (NOx) and smoke, which harm human health. In consideration of strict pollution rules and the depletion of petroleum-based fuels, it has become imperative to find an alternate fuel source for diesel engines (Dyundi et al., n.d.; D. Kumar et al., 2021). Engine emissions and fuel consumption can be minimized while ensuring adequate engine performance by the use of a fuel injection system (Mani & Nagarajan, 2009). As a result, the current research is primarily concerned with the useful features of MMPW generated oils and liquid hydrocarbon fuel examined in CI engine.

Plastics are made from petroleum products, which are hydrocarbon-based. At the same time, they contain a number of additives that aren't necessarily good for the environment, such as antioxidants, colourants, and stabilisers.(Brems et al., 2012). Char is a solid substance made up of tiny particles that are high in carbon and contain some oxygen and hydrogen(Xu et al., 2020). These particles have a large surface area and porosity, chemically stable, inexpensive, and may be prepared at temperatures between 773- 973 K. (Ahmed & Hameed, 2020) To attain the

desired material properties, plastics often incorporate additives such as, colour pigments, reinforcing fillers, plasticisers, flame retardants, antioxidants and UV stabilisers (around 5 % of total weight). (Beach et al., 2013). However, there has been little research on the use of char in composite manufacturing, and none of these composites used epoxy resin (ER) as a matrix. In aluminium alloy matrix composites, for example, coconut shell char was used.(Moorthy Rajendran et al., 2020b; Murali et al., 1982)

White et al. recently proposed one of the autonomic self-healing systems adapted to fulfil specific objectives in the realm of aeronautic applications.(White et al., 2001) (Krishnakumar et al., 2020). As a result, the mending mechanisms of animated bodies areimitated. High chain mobility permits multiple possible self-healing methods in soft materials with low glass transition temperatures (lower than the material's service temperature). There are substantial limitations in the selection of self-healing methods for load-bearing materials with high stiffness and little chain mobility, resulting in limited chances of success. Hollow fibres and microvascular networks have lately been presented as alternatives to microencapsulated systems.(Patrick et al., 2016)(White et al., 2014). Although several chemistries for vitrimer materials have been investigated, the reported materials are fairly limited in scope, and their mechanical properties are frequently not equivalent to those of commercial resins or conventional engineering polymers. (Brutman et al., 2014)(P et al., 2014).

Epoxy composite materials are created by using epoxy resins in the manufacturing process. Epoxy resins are made up of a matrix and several types of particles that serve as composite (Kang et al. 2001; Verma et al. 2017; Verma et al. 2018a). Talc, calcium carbonate, and synthetic additives like carbon black are used to make these particles (Verma et al. 2018b, c) (Kang et al., 2001; Verma et al., 2017, 2018, 2019). Isosorbide was selected as a natural building block for renewable polymers with high glass transition temperatures due to the abundance of resources it derives from maize, as well as its high stiffness and thermal stability (Tg). The thermal reprocessing of epoxy vitrimers was helped by the relatively high thermal stability of isosorbide. Meanwhile, the dynamic disulfide bond reaction is composed of several mechanisms that are influenced by reaction conditions. Disulfide connections broke mechanically as a result of external stressors, releasing thiol radicals that might swiftly exchange with other disulfide

bonds, resulting in self-healing or reprocessing of crosslinked networks. (Black et al., 2014; Duan et al., 2015; Fenouillot et al., 2010; Martin et al., 2014; W. J. Yang et al., 2015) .

Some bio-based compounds with numerous epoxy groups have been studied as part of the process of developing bio-based vitrimers using this approach as the foundation. A bio-based vitrimer with shape memory, mending characteristics, and the potential to be used as an adhesive was generated by curing sebacic acid poxy with ozonized Kraft lignin. This formed the vitrimer. A vitrimer having properties comparable to those of cured bisphenol in terms of its strength and modulus In order to produce an epoxy, another bio-based triepoxy (TEP) was cured using an anhydride monomer (Liu et al., 2018; S. Zhang et al., 2018) Furthermore, because to the new trend in composite material manufacturing, "Out of autoclave," a significant amount of study has been committed to understanding the nature of thermoplastic composite materials. (Yassin & Hojjati, 2017).

In the further investigation, we employed epoxy resins that were cured at moderate temperatures less than 1473 K to better understand the influence of the inorganic filler. We used tertiary amines as curing catalysts to do this. Anionic polymerization occurs when Lewis bases, such as tertiary amines, are present. Due to the lengthy cure cycles requirement and the low heat-distortion point of the resultant resins, anionic initiator polymerization of epoxy resins has not yet received widespread commercial use. However, the most recent discoveries, which are described in this paper, provide strong potential for reducing earlier concerns and boosting adoption of this class of catalytic curing agents in the future. Only a small amount of literature exists in the subject of diepoxide (or polyepoxide) resins on the use of anionic initiators as curing agents. However, in recent years, these curative agents have become more popular among worldwide researchers working on aeronautical functional applications.(Brown et al., 2002, 2004; Kessler et al., 2003; Kessler & White, 2002; Krishnakumar et al., 2020; White et al., 2001). Peng et al. employed a similar process to create (Graphene oxide) rGO/epoxy polymer nanocomposites with good rGO nanosheet dispersion, which they found to be quite beneficial. The GO was reduced by suspending it in an epoxy resin (triglycidyl paraaminophenol) for 5 minutes at 473 K, followed by curing the epoxy resin with the addition of 3,5-dimethylthio-2,4-toluenediamine and curing the epoxy resin. (Peng et al., 2016) .

The exchangeable link concept can also be used to create materials that are hard at room temperature yet flexible but insoluble at higher temperatures. hydroxy groups and ester linkages are found in widely used epoxy-anhydride resins. (Tesoro, 1988). Within that work, theyinvestigateda reliable method for creating self-healing epoxy vitrimer nanocomposites that are encouraged by graphene oxide without the need of a catalyst (Krishnakumar et al., 2020) (Luzuriaga, Martin, et al., 2016; Luzuriaga, Matxain, et al., 2016).

In an effort to enhance the performance of an epoxy vitrimer, Altuna et al. conducted research on the curing of the material with carboxylic acids using imidazole as a catalyst. After 1 hour of heating at 433 K, the BERs of esterification and transesterification were utilised to analyse the different properties of the epoxy vitrimer's reconfigurable forms. In the samples, shape fixities and shape recovery ratios were 99 % accurate. During partial stress relaxation, the characteristics of vitrimers can be identified to a limited extent.(Altuna et al., 2016).

Zako et al. devised a method for incorporating small thermoplastic adhesive particles into glass/epoxy composite laminates (50m). The epoxy resin matrix was cured at a temperature of 373-383 K. When damaged composites were heated to 393 K for 10 minutes on a hot plate, the thermoplastic particles implanted in them melted. The percentage of curing was documented in the subsequent three-point bend test based on the measurement of flexural strength of the repaired specimen, and the load-displacement curve revealed that stiffness was recovered in the repaired specimen.(Zako & Takano, 2016).

Thermal activation is some of the most prominent approaches for developing self-healing characteristics in biological systems. As a result, raising the heat conductivities of polymers would assist in the enhancement of the self-healing efficiency of the polymers (Burger et al., 2016; X. Yang et al., 2018).(Krishnakumar et al., 2020)

To create a low-temperature self-healing material, activated carbon pyrochar derived from municipal mixed plastic waste pyrolysis was combined with an epoxy vitrimer system as part of an effort to create more environmentally friendly composites. As a result, a composite vitrimer with aromatic disulfide crosslink-assisted self-healing has been developed. For the purpose of enhancing the chemical and mechanical characteristics of epoxy vitrimer composites, a number of different aromatic disulfide concentrations are also used. The thermomechanical and self-healing properties of plastic pyrochar-derived activated carbon epoxy vitrimer composites have

yet to be thoroughly explored. The issues highlighted in this study have been dealt with succinctly.

CHAPTER 3 : PYROLYSIS OF MIXED MUNICIPAL PLASTIC WASTE(MMWP)

3.1 Scope and Outline of the Present work

- To produce liquid, gaseous fuels and char through fast pyrolysis of plastic wastes and improvement in yield pattern by using catalysts.
- To develop a cheaper catalyst for pyrolysis process and its testing at larger scale.
- To design, fabricate and test a pilot scale demonstrable pyrolyzer for rural areas
- To evaluate and confirm the potential of plastic waste pyrolysis oil as a fuel option for IC engine application

3.2 Research gap

- Availability of a more affordable catalyst for the pyrolysis process.
- A pyrolyzer that can be demonstrated on a pilot scale.
- Evaluating the viability of utilizing pyrolysis oil derived from plastic waste as a potential fuel alternative for internal combustion engine (IC engine) applications.

3.3 Objectives

Based on the above mentioned research gaps following are the main objectives of the research work

- To design and develop a pilot scale demonstrable pyrolyzer for rural areas.
- To optimize plant operating parameters and work on cheaper catalysts to improve yield pattern.
- To produce liquid and gaseous fuels as well as pyro char through fast pyrolysis of plastic wastes.
- To evaluate performance of IC engine fueled with plastic waste pyrolysis oil.

CHAPTER 4 : PREPARATION OF LIQUID HYDROCARBON FUEL FROM PLASTIC WASTE

4.1 Production of hydrocarbon fuels from mixed municipal plastic waste

Plastic waste is increasing everyday as a consequence of an ever-increasing population, modernisation and industry industry. Because of their varied chemical compositions and thermal characteristics, these plastic wastes make the production of hydrocarbon fuels a challenging endeavour. Pyrolysis of MMPW was performed at temperatures ranging from 473 to 973 K in order to solve these limitations. Reactor tests was performed to determine the best operating parameters for maximum hydrocarbon fuel output. The experiments were carried out with the assistance of a fixed-bed tubular reactor, which was responsible for the production of hydrocarbon fuels. A 72.4 wt % yield of liquid fuel was achieved using mixed plastic wastes under the optimal operating parameters specified. ASTM procedures were used to evaluate the fuel's viscosity, density, fire and flash points as well as pour and calorific values, and the results were motivating.

4.2 Feedstock Materials and characterization methods

4.2.1 Municipal mixed plastic waste

The plastic waste was gathered from several locations of university, including food court waste, hotel garbage, classroom waste, office waste, sports activity area, library. The mixed plastic particles that was collected was shredded into little pieces and sieved to get the particle size between 10 and 15 mm. The particles were then cleaned and dried for the purpose of investigation and testing.

4.2.2 Catalyst materials

Samples of different rocks were identified and taken from the Garhwal Himalayas region of Uttarakhand, India to be used as catalyst for pyrolysis process. The in-depth investigation was performed out so that their properties and behaviour as an acidic mineral clay with a large surface area could be evaluated. Out of various samples, one sample named as CAT-1 was found to be higly effective and choosen as catalyst. Before being put to use in the pyrolysis process, the catalyst underwent calcination at a temperature of 973 K. The influence of the catalyst (CAT-1) on the breaking down of the plastic waste to produce the highest possible yield of products was investigated by using a catalyst concentration of 10 % by weight.

4.3 **Experimental test setup**

The Centre for Alternative Energy Research (UPES) has developed a lab-scale pyrolysis reactor. Production flow process of plastic to alternate fuel is illustrated in Fig. 4.1. It shows the flow process of plastic waste to usable alternate fuel, plastic waste obtained from the university campus was processed from cleaning to conversion into fuel. Pyrolysis reactor was designed to sustain the high temperatures and corrosive chemicals. Cylindrical tube of 300 mm height and 54 mm internal diameter cylindrical quartz column was designed such that preheated feed gas (Nitrogen) can be facilitated at an adequate distance from the inlet of quartz cylindrical column (Fig. 4.2). Inside the reactor, induced heating was being provided by a heating coil, and a programmable temperature controller was linked so that the temperature could be kept at the required level. Reactor outlet was connected to water cooling jackets to condense the volatile from the pyrolysis of feedstock.

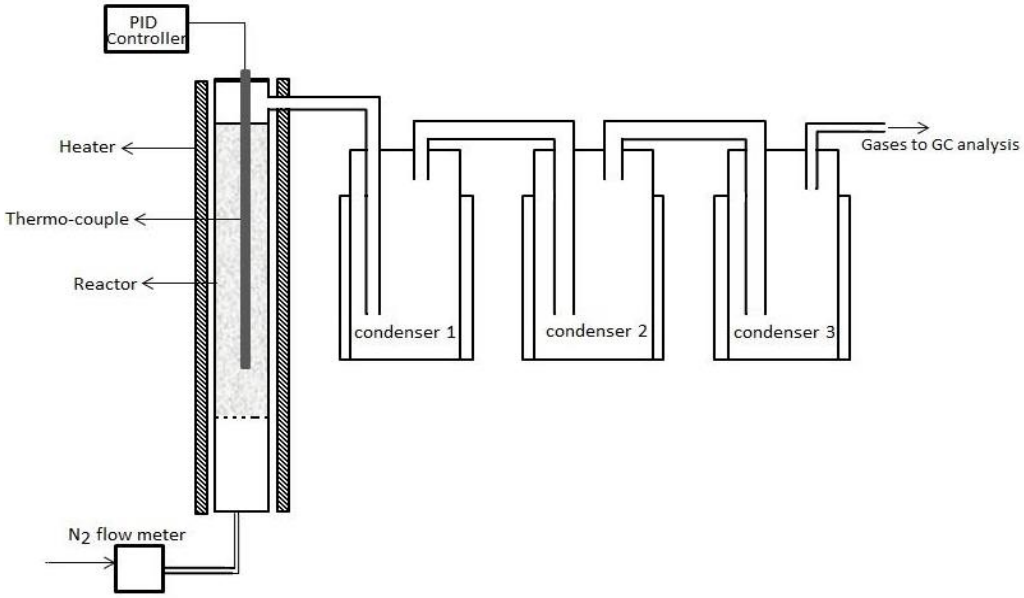

Figure 4.1 Three-stage condensing system for liquid hydrocarbons production through pyrolysis

Experiments were carried out in non-isothermal conditions with a heating rate of 10 ^{0}C per minute from the surrounding ambient temperature up to the required temperature. This was followed by 30 minutes of isothermal conditions in order to achieve a consistent temperature throughout the reactor and finish the reaction. Nitrogen was first used to purge the reactor at a rate of 500 ml per

minute in order to maintain the reactor's state of inertness.The reactor's lower molecular condensable volatiles are collected in a subsequent condenser (Fig. 4.2).

The process parameter like temperature, residence time, heating rate, and catalyst % were optimized in this lab scale reactor and given in table 4.1

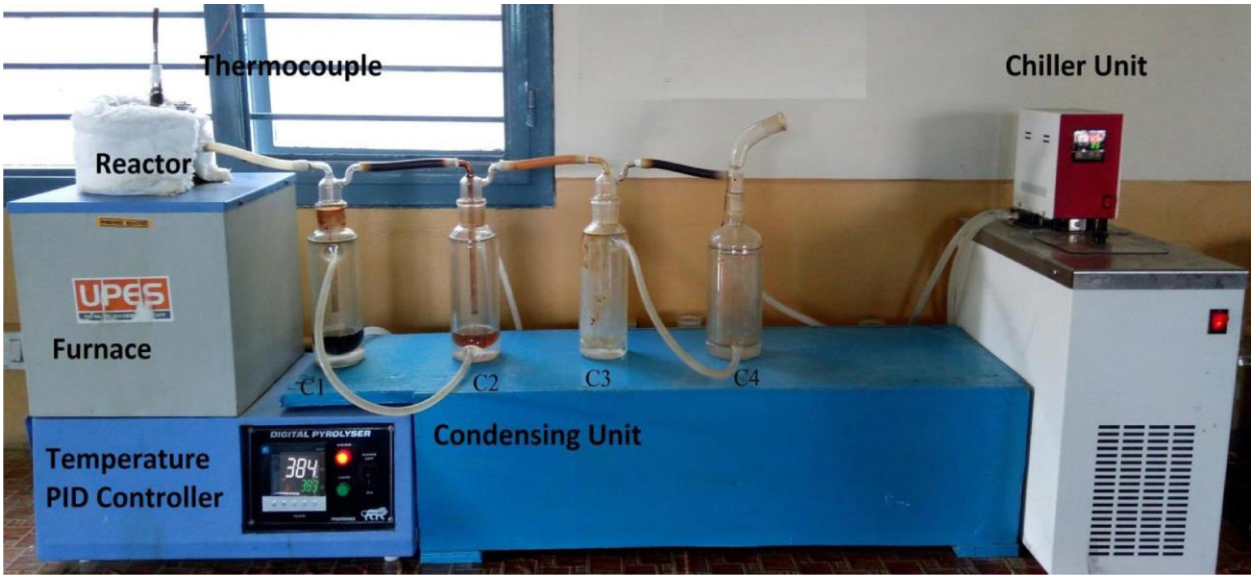

Figure 4.2 Lab scale pyrolysis Reactor

Table 4.1 Plant process parameter optimization.

Process Parameter	Optimium value
Temperature	723 K
Residence time	30 minutes
Heating rate	10 ^{0}C per minute
Catalyst %	10%

After optimising the parameters, a pilot scale reactor was design and fabricated. The pilot scale reactor having capacity of 5 kg. the reactor and condenser are made using stainless steel because of the reactor operating temperature of around 723 K.

Fig 4.3 is the illustration of a pilot-scale pyrolysis reactor for conversion of municipal mixed plastic waste to hydrocarbon fuel. This pilot-scale pyrolysis reactor has four major components: a reactor, a condenser, a control panel, and a chiller. First, the plastic waste is dried in sunlight

for moisture reduction, then fed into the shredder to get particle of size 10 mm to 20 mm to increase the contact area and afterward feed into the reactor.

Figure 4.3 Reactor in series with condensation for the pyrolysis-based production of hydrocarbon fuel.

The temperature and length of time in residence may both be controlled by using the control panel. The first step in the procedure involves flushing the reactor with nitrogen to get rid of any oxygen that may be present in the reactor. Following the completion of the purge, the feed are then introduced into the reactor, where they undergo a reaction that results in the formation of a liquid product that can be condensed and gases that cannot be condensed. In the bladder, we were able to capture some of the gases that did not condense.

4.4 Result and Discussion

4.4.1 Investigation of MMPW feed

Properties of all the plastic feedstock are depicted in Table 4.2. The performance was evaluated according to the standards in order to provide a proximate study of the combustion qualities. The ultimate analysis was performed in an elemental analyzer (vario MICRO CHNS), and oxygen concentration was calculated based on the difference. The high heating value was determined using a bomb calorimeter.

Table 4.2 Characteristic properties of Municipal mixed plastic waste feedstocks (dry basis)

Properties	MMPW feedstock

Volatile matter (wt%)	93.45
Fixed carbon (wt%)	5.34
Ash (wt%)	1.21
Carbon (wt%)	83.23
Hydrogen (wt%)	12.45
Nitrogen (wt%)	2.71
Sulfur (wt%)	0.41
Oxygen (By difference)	1.21
Heating value (MJ/kg)	42.04

4.4.1.1 FTIR spectrometric analysis

Figure 4.4 displays the FTIR spectrum of MMPW. FTIR spectra may be used to identify the fillers, binders, additives, etc. in MMPW by comparing them to the stretching frequencies of the hydrocarbon mixture.

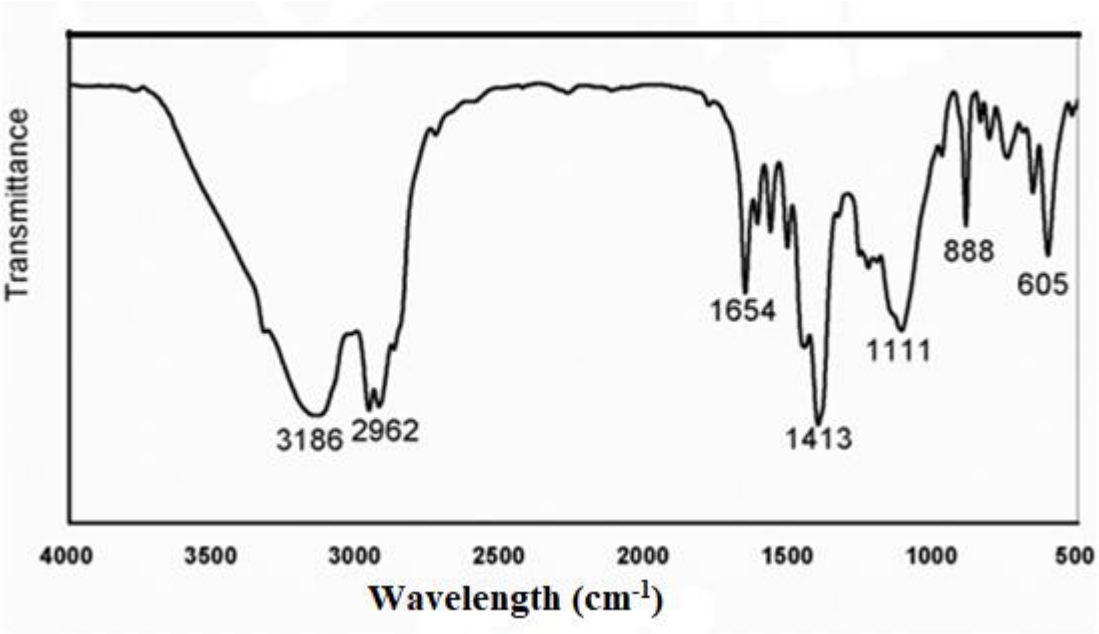

Figure 4.4 MMPW Fourier Transformed Infrared Spectra.

Hydrocarbon compounds are present when =C-H, -C-H, and C-C stretching frequencies fall between 2900 and 3000 cm^{-1} (Figure 4.3). Hydrocarbon compounds with closed and densely packed structures and long-chain hydrocarbons with similar packing densities may be responsible for this quality. Above 3000 cm^{-1}, there is a little shift in the wave numbers. Spectra

were drawn to show the frequency ranges of =C-H stretching, -C-H stretching, C=C stretching, and -C-H bending. In the region of 2600-2900 cm^{-1}, MMPW additionally exhibits the presence of oxygen-containing groups (O-H). Table 4.2 provides specifics on the strength, mode of vibration (bending & stretching), and behaviour of the various functional groups of hydrocarbons in MMPW.

Table 4.3 MMPW FTIR analysis results.

Wavenumber(cm^{-1})	**Functional Group**	**Remarks**
3186	Alkene	=C-H stretch, CH_3, CH_2 & CH (strong)
2962	Alkane	-C-H stretch, CH_3, CH_2 & CH (strong)
1654	Alkene	C = C stretch
1413	Alkane	-C–H bending, C = C bending.
1111	Carboxylic Acids & Derivatives	O-C bending, C-O-H medium stretching
Below 900	Alkane, alkene, alkynes	=C–H stretching and fingerprint region

4.4.2 Charactrization of CAT-1

The detailed analysis was carried out to assess its characteristics acidity and behavior as mineral clay and acidity.

The catalyst, CAT-1 was characterized for mineral content by X-ray fluorescence, phase identification of crystalline material by X-ray powder diffraction. The acidity of CAT-1 was measured using the titration method as per Benesi 1957 (Benesi & 61, n.d.; P. K. Ghodke, 2021b).

Table 4.4 Acid Properties of CAT-1

SNo	**Acid Property**	**Value**	**Details**
1	Maximum Acidity of Acid Sites	Reasonable	Enhances hydrocarbon production yield at lower temperatures

2	Catalyst Mass Used	15 g	Consistent mass used in acidity experiments
3	Indicator	Anthraquinone	Used to determine end-point of color change
4	Acid Number (pKa Range)	pKa < 8.1	Indicates the range of strongest acid sites
5	Total Acidity	~0.05 meq amines/g catalyst	Measured up to pKa 4.0
6	Application	Polymer Breakdown	Effective for breaking down MMPW polymers

The acidity of CAT-1 mineral was determined and found that maximum acidity of the acid sites is a reasonable requirement for enhancing the yields of the targeted hydrocarbon production at a lower temperature. 15 g of catalyst was consistently used to carry out the acidity experiment. Anthraquinone was the indicator used to identify the end-point of color change to quantify the acidity of the CAT-1 catalyst. The acid number (pKa range of strongest sites) of CAT-1 <−8.1 and total acidity to pKa 4.0 was approximately 0.05 meq amines/g catalyst (Benesi & 61, n.d.; P. K. Ghodke, 2021b).The findings indicated that mineral clays CAT-1 are useful for breaking down the MMPW polymers.

The mineral composition and its influence on catalytic processes were evaluated by thorough XRF analysis of the catalyst. XRF analysis of the inorganic content of CAT-1 revealed sodium, iron, magnesium, aluminium, silicon and trace amounts of manganese, calcium, titanium, potassium and phosphorus. Table 4.5 displayed the specific metal oxides that made CAT-1. The acidic nature of the catalyst that caltaysis the cracking process of the feed as CAT-1 is composed of about 48 parts aluminium oxide and 30 parts silica oxide.

Table 4.5 Chemical composition of CAT-1.

Inorganic element proportions	**Wt%**
Al_2O_3	48

TiO_2	1
CaO	2
SiO_2	30
K_2O	1
P_2O_5	2
Fe_2O_3	4
Na_2O	7
MgO	3
MnO	2

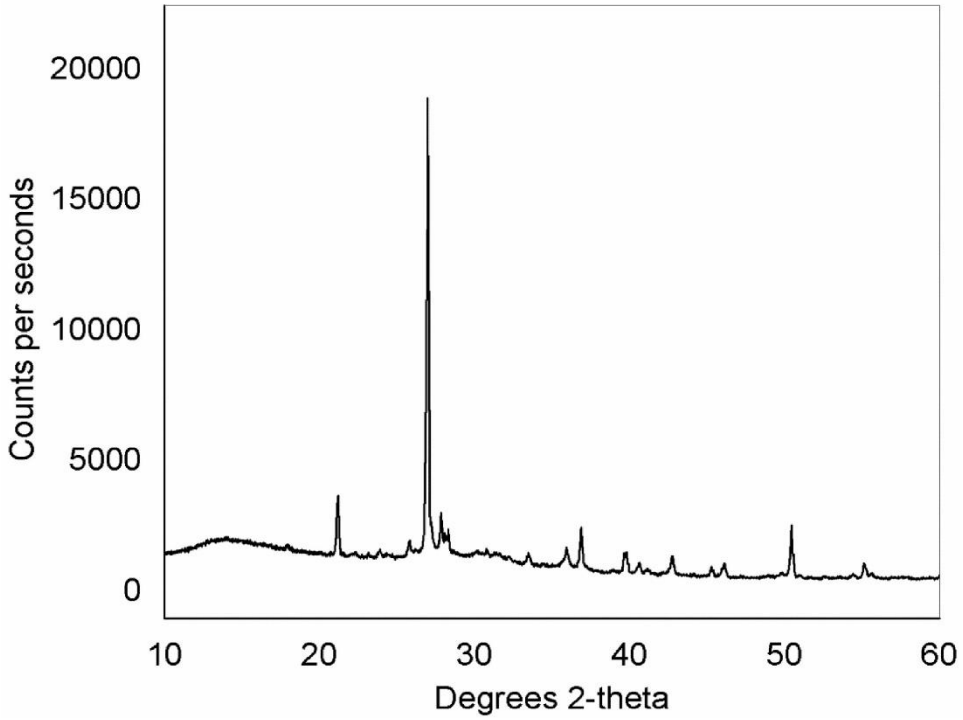

Figure 4.5 shows results for XRD pattern of CAT-1.

The XRD pattern in Figure 4.5 shows a strong reflection at an angle of 2θ around 27°, which is characteristic of CAT-1 in the [0 0 1] orientation. This well-defined peak within the 27–30° range confirms the crystalline nature of CAT-1. Additionally, this reflection aligns with typical silicon dioxide (SiO_2) peaks, particularly in the quartz phase, which commonly exhibits a peak near 26.6–27°.

4.4.2.1 FTIR of CAT-1

Functional categories of the CAT-1 were plotted against the FITR spectrum (Figure 4.5). The figure 4.5 shows that the CAT-1 has a high concentration of the soild hydroxides frequency at 3452 cm^{-1}. The broad peak around 1000 cm^{-1} typically indicates the presence of Si-O-Si stretching vibrations in the material. This stretching mode occurs in the range of 1000-1200 cm^{-1} in the infrared spectrum of materials containing silicon-oxygen bonds, such as silicates or silicones.

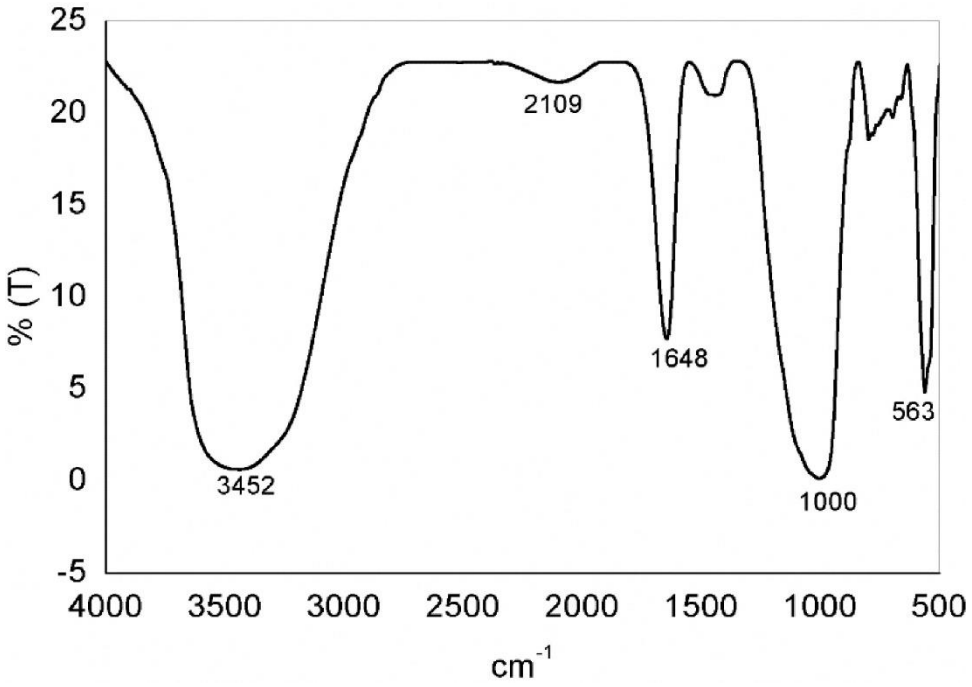

Figure 4.6 shows the CAT-1 catalyst's FT-IR spectrum analysis findings.

Table 4.6 FTIR analysis of CAT-1.

Wavenumber (cm^{-1})	**Functional Group**	**Remarks**
3452	Soild hydroxyl group	OH stretching
1700-1000	solid hydroxyl group bendind	OH deformation
563	Silica stretches	Si

4.4.3 Analysis of liquid hydrocarbon

The MMPW pyrolysis process was analyzed for product distribution with temperature change and the effect of the catalyst on the yield of liquid product. The yield distribution of pyro-char, hydrocarbon fuel, and non-condensable syngas from thermal pyrolysis and catalytic pyrolysis of MMPW is shown in Figure 4.7 & 4.8. With the aim of optimizing the production of liquid hydrocarbon fuel, a series of experiments were conducted at varying temperatures with and without a catalyst. The figure shows that the yield of the liquid product increases with temperature up to 773 K, when it begins to decline owing to the creation of non-condensable gases. The mass balance of the pyrolysis process was quantified and plotted in Figure 4.7. However, with catalyst the maximum liquid product obtained at 723 K with different yields of other products. The maximal decomposition temperature of MMPW is shown in figures 4.7 & 4.8 to be about 723 K. The maximum yield of liquid product was about 62.5 wt% without catalyst and 74.8 wt% with CAT-1 catalyst, that gives an increment of 19.68% in the yield , which is quiet appreciable when its come to commercial production. From the obtained graph it is clear the 723K is the optimum temperature when liquid fuel is required. However, for getting large amount of pyrochar the reaction has to be carried out at low temperature of 473K and good yield can be obtained without the use of catalyst.

The formation of gaseous products is favoured at high temperature i.s 973K that too without catalyst. So, the used catalyst favours the decomposition of MMWP into liquid product and the maximum yield of hydrocarbon liquid product from catalytic pyrolysis was obtained with 10 wt% CAT-1 catalyst (Figure 4.8).

The liquid hydrocarbons obtained were subject to various physio-chemical charactization to evaluate kinematic viscosity, density, flash point, pour point, and moisture analysis; the results of these tests are listed in Table 4.7. For comparison purposes, the standard value of conventional fuel (Diesel) is also provided. To verify the findings, each analysis was performed in triplicate in accordance with the specified criteria. The sample were also subjected to ultimate and proximate analysis, FTIR & GCMS and get an information regarding their composition

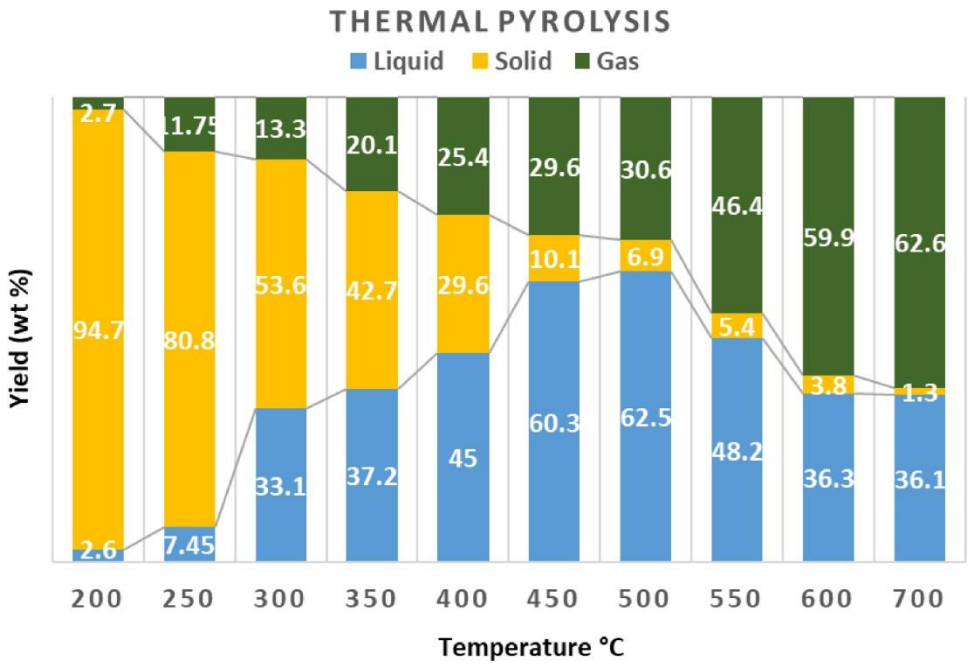

Figure 4.7 Distribution pattern of pyro-char, liquid hydrocarbon and non-condensable syngas from thermal pyrolysis of MMPW

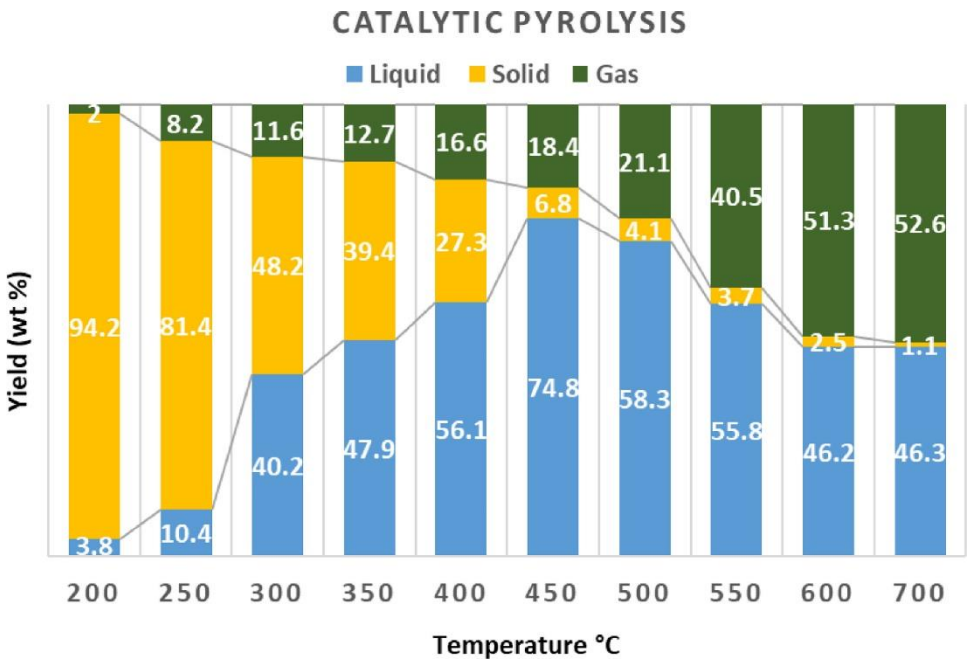

Figure 4.8 Distribution pattern of pyro-char, liquid hydrocarbon , and non-condensable syngas from thermal catalytic (CAT-1) pyrolysis of MMPW

Table 4.7 Fuel properties of MMPW

Parameter	MMPW	Gasoline	Diesel
Appearance	Dark Brown	No color	Pale yellow
Moisture (% v/v) (ASTM D95)	2.4	0.4-0.5	0.1-0.3
Density kg/m^3 (ASTM-1298)	860	780	807
Kinematic viscosity (cSt) (ASTM D445)	2.34	1.17	1.9–4.1
Gross heat of combustion (MJ/kg) (ASTM D240 – 17)	42.58	42.5	43
API gravity (ASTM D287)	39.6	54.2	39.6
Conradson carbon residue (% wt) (ASTM D189)	0.4	0.14	0.35
Flash Point (°C) (ASTM D93)	35	42	52
Pour point (°C) (ASTM D97)	18	-	6
Aniline Point (°C)	60	71	77.5
Ash (%wt) (ASTM D482)	0.013	0.001	0.01

4.4.3.1 FTIR of liquid hydrocarbon from MMPW

Figure 4.9 shows the FTIR of an liquid hydrocarbon derived from the pyrolysis of MMPW. The FTIR wavelength include C-H bonds and C=C and =C-H bonds; as a result, these spectra are virtually identical to those of polymer. At a frequency of 3449 cm^{-1} with =C-H, stretching vibration was detected, indicating the existence of alkenes. Similarly, an appearance of olefin with C=C vibrational bonding is found at 1718.84 cm^{-1}, while the existence of C=C bending is discovered at 1638.02 cm^{-1}. At wavelengths of 2942 cm^{-1} and 2824 cm^{-1}, alkanes with C-H

stretching vibration have been shown. Additionally, alkanes with a C-H bending bond have been detected at a wavelength of 1385 cm^{-1}.

In Table 4.8, FTIR spectra have been summarised so that the existence of hydrocarbon bonds with varied configurations, such as scissor, vibrational, and bending stretching, may be understood more easily. Since FTIR analysis can only offer a basic notion of whether or not functional groups are present, GC-MS technique was used to assess the final chemical structure. The next section presents the results of a GC-MS study on the detection of transitions between functional groups.

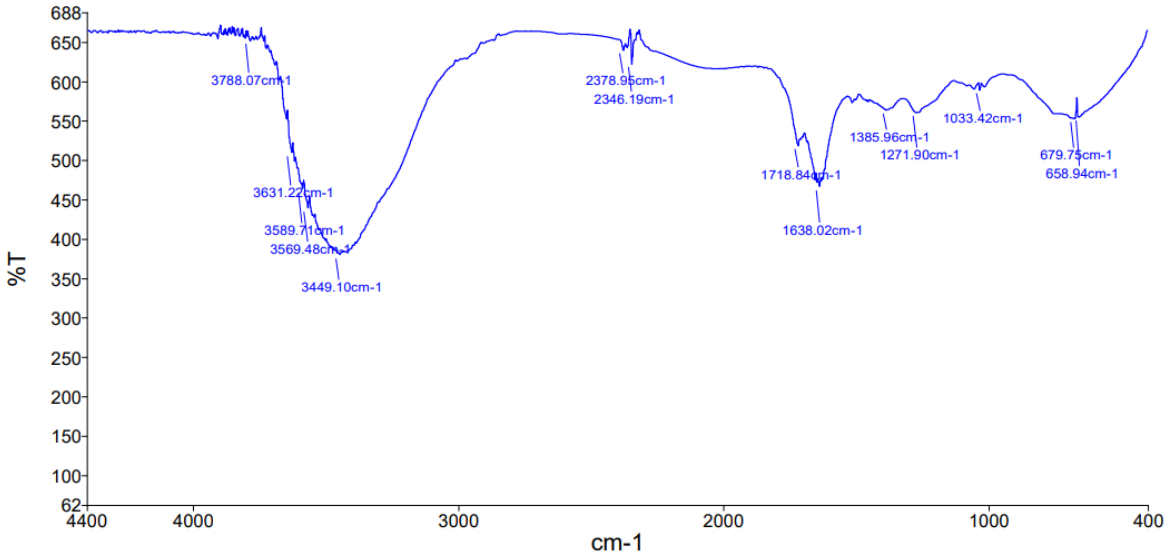

Figure 4.9 FTIR analysis of liquid hydrocarbon from MMPW

Table 4.8 FTIR analysis of liquid hydrocarbon.

Wavenumber(cm^{-1})	**Functional Group**	**Remark**
3449, 3631	Alkene	=C-H stretch, CH_3, CH_2 & CH (strong)
2942, 2824	Alkane	-C-H stretch, CH_3, CH_2 & CH (strong)
1718, 1638	Olefin, Alkene	C = C stretch

Wavenumber(cm^{-1})	Functional Group	Remark
1385, 1271	Alkane, alkene	-C-H bending, C = C bending.
1033, 908	Carboxylic Acids & Derivatives	O-C bending, C–O–H medium stretching
Below 900	Alkynes	=C–H stretching

4.4.3.2 GC-MS characterization of liquid hydrocarbon generated from MMPW

Gas chromatography was used to evaluate the chemical make-up of the liquid hydrocarbons produced during MMPW catalytic pyrolysis, a mass spectrometer was used to identify the mass components, as shown in Table 4.9. The mass spectrometric measurement resulted in a determined area percentage, which was then used to normalise the overall composition of hydrocarbons to 100 wt%. Hydrocarbon composition may be evaluated for use in heating and power production. Aliphatic (alkane, alkene, and alkyl) carbon, which spans C9–C17, made up the bulk of the created hydrocarbon fuels.

Table 4.8 shows that straight-chain molecules replaced almost all aliphatic hydrocarbon products. Many hydrocarbons undergo random scission during pyrolysis, producing a wide variety of hydrocarbon pieces. After the link is broken, degradation causes a stable C=C bond to develop between the surviving C-C bonds in the poly-alkene composition. Knoweldge of the chemical make-up of liquid hydrocarbon may shed light on its possible heating and power generation uses. Hydrocarbons make up the bulk of liquid hydrocarbon fuel, with a little amount of oxygen added as an additive. Most oil is made up of aliphatic hydrocarbons, which have carbon chains that are C9 to C17 long.

The hydrocarbon chain of compounds is the primary component of plastic oil. Pentadecane is a chemical utilised as a plasticizer in the paint production business that was found to have an unusual oxygenated compound. The majority of the liquid plastic fuel's components are found in the lower hydrocarbon groups, with 1-tridecene playing a particularly large role. The primary components of the liquid plastic fuel are 1-decene and 1-hexadecene, both of which are present in high concentrations. The chemical consists of a negligible amount of nonane and 1-nonadecene. The results show that fuel derived from plastic waste has high combustion

characteristics and contains hydrocarbons similar to those found in diesel. Therefore, liquid hydrocarbon fuel might be utilised to generate both heat and power.

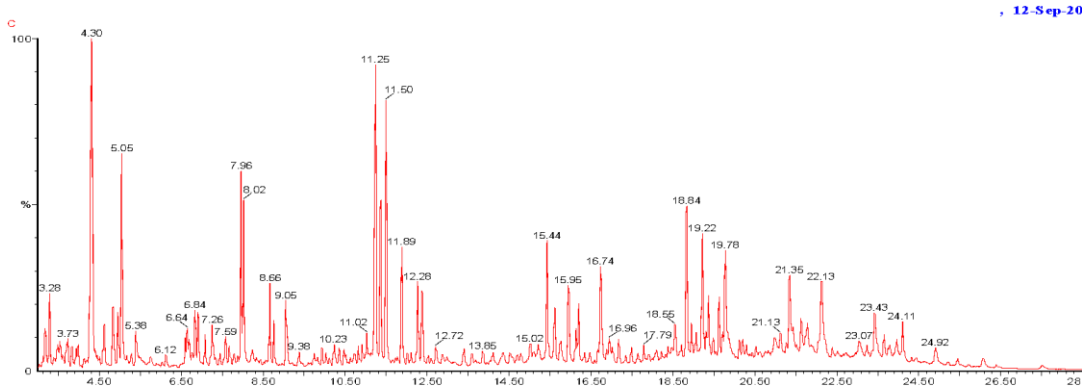

Figure 4.10 GC-MS of plasto fuel generated from MMPW.

Table 4.9 Chemical Composition of liquid Hydrocarbon obtained from mixed plastic waste.

Retention Time (min)	Compound Name	Molecular formula	Wt (%)
3.262	1-Nonene	C_9H_{18}	3.16
3.707	Nonane	C_9H_{20}	1.9
4.305	1-Decene	$C_{10}H_{20}$	11.49
6.836	Decane	$C_{10}H_{22}$	3.42
7.968	1-Undecene	$C_{11}H_{22}$	5.6
8.628	Dodecane	$C_{12}H_{26}$	4.69
11.034	1-Tridecene	$C_{13}H_{26}$	3.58
11.264	Tridecane	$C_{13}H_{28}$	8.23
11.883	1-Tetradecene	$C_{14}H_{28}$	5.86
15.441	Tetradecane	$C_{14}H_{30}$	5.83

16.761	1-Pentadecene	$C_{15}H_{30}$	5.08
17.74	Pentadecane	$C_{15}H_{32}$	8
18.826	1-Hexadecene	$C_{16}H_{32}$	10.3
19.806	1-Heptadecene	$C_{17}H_{34}$	8.33
21.357	Hexadecane	$C_{16}H_{34}$	7.71
23.463	Heptadecane	$C_{17}H_{36}$	4.41
24.123	1-Nonadecene	$C_{19}H_{38}$	2.08

4.5 Summary

Pyrolysis is a well-known process for transforming municipal mixed plastic trash into useful fuel. Liquid Hydro - carbon fuel generated from MMPW with a high heating value and a high concentration of aliphatic hydrocarbons might be utilised as a substitute to conventional fuel. The features of pyrolysis of municipal mixed plastic waste accessible at university revealed that it is a possible hydrocarbon fuel that can be used to generate heat and electricity.

CHAPTER 5 : EFFECT OF COMBUSTION ON PLASTIC WASTE FOR LIQUID HYDROCARBON FUEL PRODUCTION

Municipal mixed plastic waste (MMPW) recycling is an innovative way to turn environmental waste into energy fuels. In the present study, a thermochemical process was applied to MMPW to depolymerize to produce hydrocarbon fuels named liquid hydrocarbon fuel. The obtained liquid hydrocarbon fuel was blended with conventional diesel to test the PCCI-mode single-cylinder, four-stroke, direct-injection diesel engine performance. The PCCI combustion mixture was tested with 15 % and 30% fuel vapor, to ensure homogeneity with and without exhaust gas recirculation. The modified engine findings were compared to a standard conventional engine. At higher loads, PCCI combustion decreases emissions such as carbon monoxide and nitrogen oxides. While the brake thermal efficiency was marginally reduced at all engine loads, using the blends. Results showed that with and without 10% exhaust gas recirculation, the increase in air mix reduces NOx emissions, however in the case of smoke emissions an opposite trend has been observed. Additionally, a blend of liquid hydrocarbon fuels reduced unburned hydrocarbon (HC) and CO emissions at higher loads. In conclusion, it was observed that liquid hydrocarbon fuels blended with conventional diesel performed better than diesel fuel.

5.1 Properties of liquid hydrocarbon fuel produced from MMPW Waste

A lab-scale pyrolysis setup was developed at UPES. The production flow process of plastic waste to alternate fuel was illustrated as shown in Figure 5.1. (P. K. Ghodke, 2021b).

Table 5.1 Fuel properties determined in based on ASTM standards.

Fuel properties	**Liquid hydrocarbon fuel**
Appearance	Dark brown
Moisture (% v/v) (ASTM D95)	2.4
Density ($kg/m^{3)}$ (ASTM-1298)	816
Kinematic Viscosity @ 40°C (cSt)	2.34

(ASTM-D445)	
Gross heat of combustion (MJ/kg) (ASTM D240-17)	42.58
API gravity @ 60 °F (ASTM D287)	39.6
Conradson carbon residue (% wt) (ASTM D189)	0.4
Cetane number (ASTM-D613)	52.7
Ash (% wt) (ASTM D482)	0.013
Flashpoint (°C) (ASTM-D93)	35
Pour point (°C) (ASTM D97)	18
Diesel index	35.34

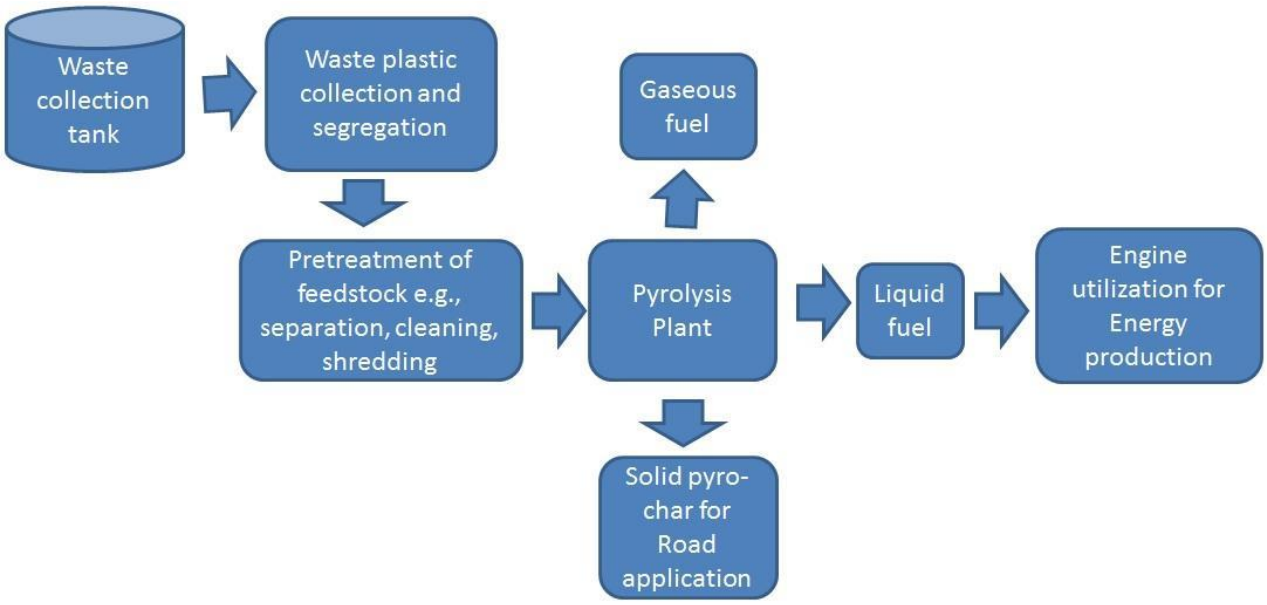

Figure 5.1 Schematic flow process diagram of domestic plastic waste to alternate fuel

5.2 Engine test setup and experiment methodology

A PCCI engine was put through its paces under a variety of load conditions while utilizing two distinct diesel-blended liquid hydrocarbon fuel vapors

1. 15% liquid hydrocarbon fuel blended with 85% Diesel,

2. 30% liquid hydrocarbon fuel blended with 70% Diesel,

10% exhaust gas recirculation (EGR) and without EGR. First, we prepared liquid hydrocarbon fuel blended with diesel at thecomposition of 15:85 and 30:70 then poured into a fuel tank and connected with common rail injections into the intake manifold through fuel pump.

Figure 5.2 and 5.3 shows a CI engine adapted to function in PCCI mode coupled to a water-cooled eddy current dynamometer for the experiments. Its eddy current dynamometer was used to measure the engine load and change. Table 5.2 lists engine specs. A direct injectionA 3.7 kW single cylinder diesel engine (compression ignition: CI engine) @ 1500 rpm. diesel engine (compression ignition: CI engine) with 3.7 kW at 1500 rpm and engine loads of 20%, 40%, 60%, 80%, and 100% was tested. We collected performance, pollution, and ignition data to assess the engine's performance. Single-cylinder engines may be easier to inspect. Complexity grows with engine cylinder count.

The fuel injection timing was maintained at 23^{o} BTDC throughout the testing, and the exhaust gas temperature was measured between the exhaust gas manifold and before the EGR.

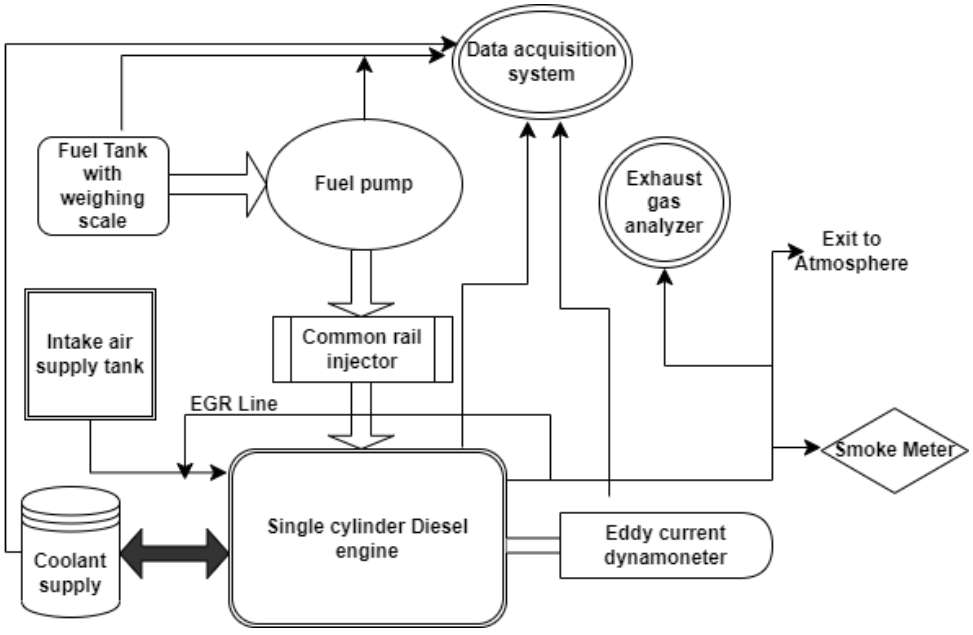

Figure 5.2 Engine experimental test setup schematic Diagram

In addition, to monitor any temperature increases that may occur within the engine, there are four temperature sensors, two of which are located at the intake of cooling water and the other

two at the exhaust. The quantifiable properties of liquid hydrocarbon fuel that were examined per ASTM standards are listed in Table 5.1. In order to make room for the water-cooled EGR, the intake manifold had to be redesigned.

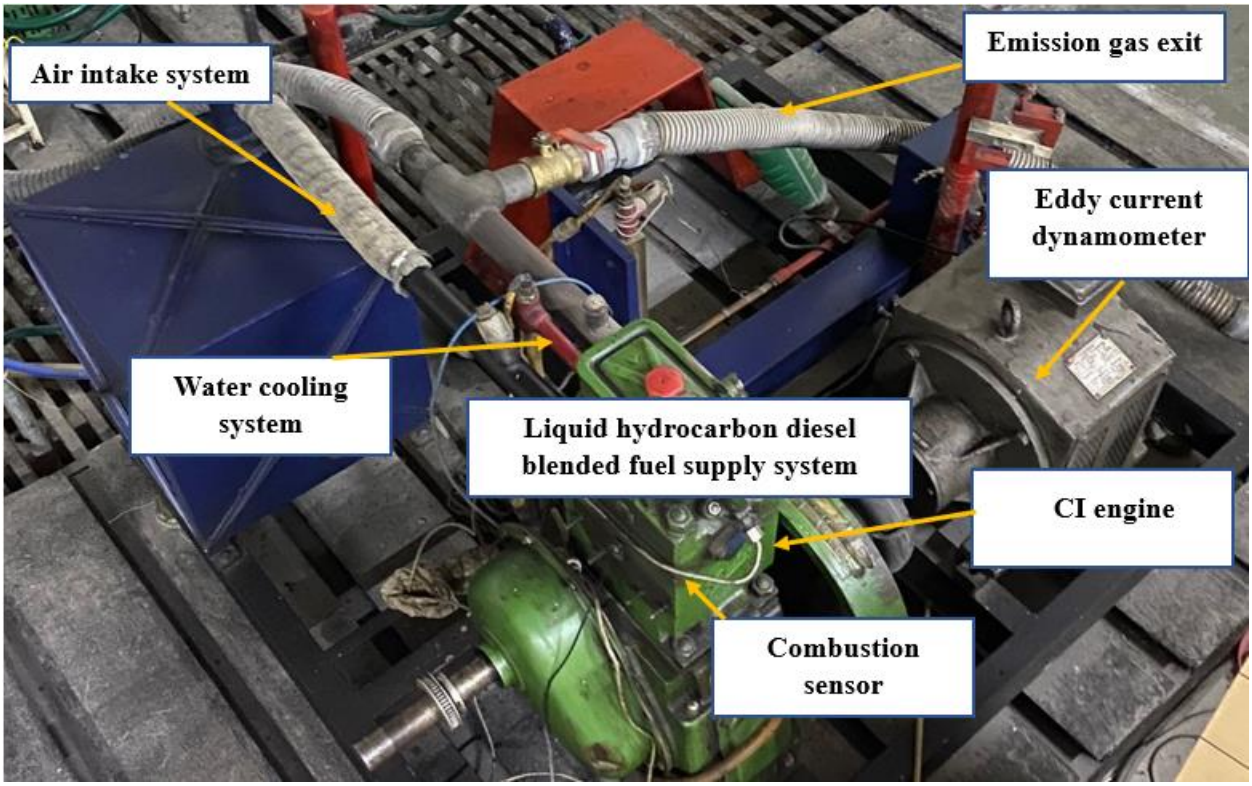

Figure 5.3 Engine experimental test setup

Table 5.2 Technical parameters for the diesel engine under test.

Parameter	**Specifications**
Engine type	Compression ignition
Engine cooling type	Water-cooled
Number of cylinders	1
Stroke/Bore	110 mm/87.5 mm
Specific fuel consumption	265 g/kWh
Maximum output power	@ 1500 rpm, 3.7 kW
Storke volume	0.533 L
Compression ratio	16.5:1

Throughout, the engine RPM was held constant. Therefore, the only factor at play was the amount of work being done by the engine. Thus, the EGR flow rate can be kept constant at 10% via mechanical means, no variations in engine load. Exhaust gas temperature variations were monitored using temperature sensors included within the data collecting system, which were also connected to the exhaust pipe. The mass basis was used for the purpose of determining the engine's fuel consumption. The rate of fuel flow was adjusted so that it corresponded with the load that was physically estimated. The input flow rate for diesel blended liquid hydrocarbon fuel was manually determined for every varying load of the engine. The flow rate value was measured with the help of a digital scale and a timer, and then it was transformed to the same mass flow rate flow. The procedure was repeated for each engine load and vapour percentage that was required. The governor of the engine adjusts minor differences. After making any adjustments, we let the engine rest for two to three minutes before compiling the final data.

The exhaust gas analyzer with NDIR technology was used to monitor engine tailpipe pollutants such as hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides. To gather data from the exhaust, a smoke metre has been mounted for the engine. Measurement accuracy and uncertainty of instruments have been present in Table 5.3.

5.3 The effect of using liquid hydrocarbon fuels on the engine performance

The following results were obtained from tests conducted on the four possible permutations defining PCCI operation:

30% fuel vapor (diesel blended with 30% liquid hydrocarbon fuel) with EGR

30% fuel vapor (diesel blended with 30% liquid hydrocarbon fuel) without EGR

15% fuel vapor (diesel blended with 15% liquid hydrocarbon fuel) with EGR

15% fuel vapor (diesel blended with 15% liquid hydrocarbon fuel) without EGR

It was found that running the conventional engine in PCCI mode was possible by introducing diesel vapor from outside the engine into the air intake manifold. It was feasible to use the PCCI engine in four different configurations. One possible comparison to a standard engine might be the engine's performance, combustion, and emissions. There was no variation in engine load, and the engine's speed was maintained at a steady 1500 rpm throughout the process. In order to fairly evaluate the relative merits of PCCI with and without EGR.

Table 5.3 Measurement accuracy and uncertainty.

Parameter	Measuring range	Accuracy	Uncertainty (%)
Exhaust gas analyser HC emission	< 2000 ppm volume ≥2000 ppm volume	± 10 ppm ± 4% of value	3.09
CO emission	< 0.7% volume ≥0.7% volume	± 0.03% ± 3% of value	3.92
NOx emission	< 1000 ppm volume ≥1000 ppm volume	± 5 ppm ± 5% of the value	2.692
Smoke emission	0–100% opacity	± 1% of value	2.512
Brake thermal efficiency			0.25
The volume flow rate of air	0–300 m^3 /h	± 2% of the flow	1.7
Eddy current dynamometer	Maximum Power: 20 kW Maximum Torque: 50 Nm	± 1 rpm ± 0.25 Nm	
Data acquisition system	Pressure range: 0–90 bar Temperature range: 30–1000 °C	± 1°C	0.12
Weighing balance	Maximum weight: 5 kg	± 0.01 g	

5.3.1 Brake thermal efficiency

The brake thermal efficiency was measured at varying loads. It was measured at different fuel vapor percentages, with and without exhaust gas recirculation, as shown in Figure 5.4. The results showed that, in the absence of EGR, it was declined by 2.50% with 15% fuel vapor and by 3.25% with 30% fuel vapor. Similarly, it was decreased by 8-10% with EGR as the fuel vapor increased and the engine was operating at maximum load. The main reason for decreasing the efficiency was that it dilutes the oxygen in the charge stream to lower NOx emissions.

Other reasons observed are that external mixing with fuel vapor, Air-Fuel homogeneity, combustion conditions, and charged mixture quality. The diesel blended liquid hydrocarbon fuel vapor, EGR, and air induction into the combustion chamber are only allowed through the intake manifold. Increasing the fuel vapor induction rate to 30%, reduces charge generation airflow and BTE for optimal combustion. 30% diesel blended liquid hydrocarbon fuel vapor with EGR induction drastically restrict air intake, resulting in insufficient charge for combustion and significant brake power losses. The intake manifolds absorbed fuel vapor from the outside, which may have condensed due to the temperature difference between intake air fluids and diesel vapor with liquid hydrocarbon fuel. Since PCCI combustion uses less fuel to charge, brake thermal efficiency decreases (Ganesh et al., 2008a).

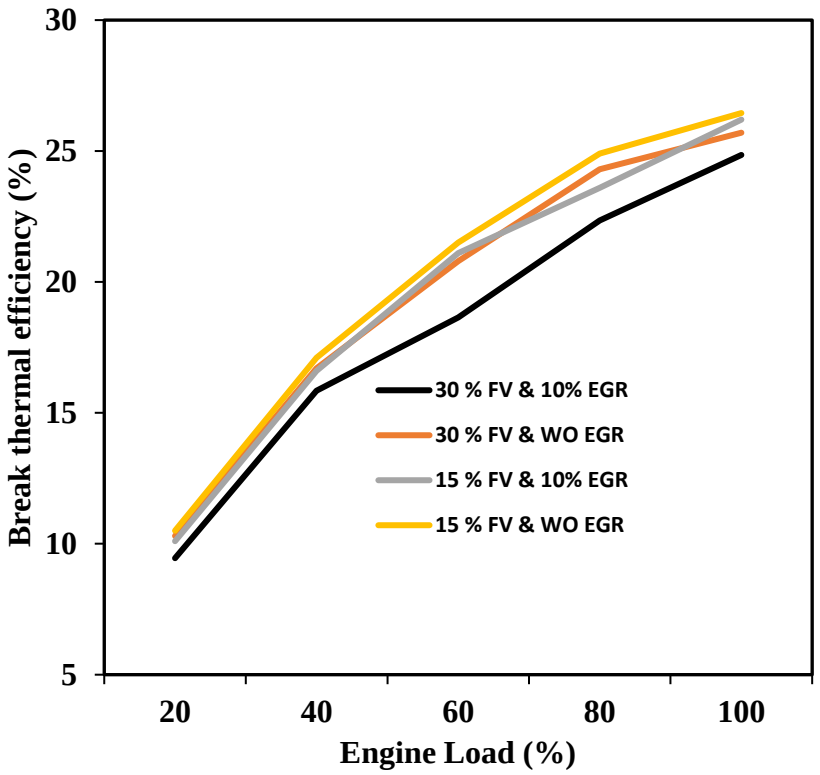

Figure 5.4 Brake thermal efficiency variation concerning engine load

5.3.2 Specific fuel combustion

As can be seen in Figure 5.5, the test engine had a specific fuel consumption (SFC) that was measured with liquid hydrocarbon fuel blended diesel. As an illustration, the fuel consumption of the test engine, which utilized 30% fuel vapor (liquid hydrocarbon fuel blended diesel fuel) with

EGR, decreased from 426 g/kWh at 20% load to 308 g/kWh at 100% load. Simultaneously, the fuel consumption of the test engine, which utilized 15% fuel vapor with EGR, decreased from 435 g/kWh at 20% load to 320 g/kWh when operating at full load.

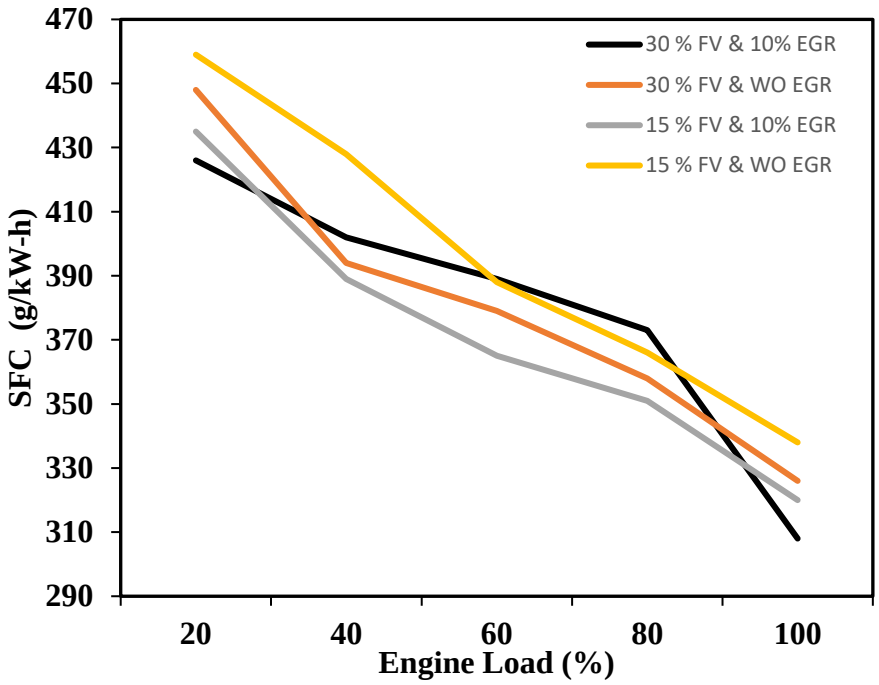

Figure 5.5 Specific fuel consumption variation concerning engine load

5.3.3 Exhaust gas temperature

The variations in exhaust gas temperature (EGT) with varying engine loads (i.e.,20%, 40%, 60%, 80%, and 100%) are shown in Figure 5.6. The main observations are that the combustion rate, temperature, and pressure increase when the engine does more work or operated at higher loads. As a direct consequence, the exhaust gas temperature increases whenever the engine load increases. While operating at full engine load and in PCCI mode with 15% fuel vapor and no EGR, the engine reached its maximum EGT temperature of 580 K. The main reasons identified are the interaction between the temperature of the cylinder and the geometry.

When utilising EGR as the major benchmark for comparison, EGT lowers by 9% for 15% fuel vapour induction and 23% for 30% fuel vapour induction, and by 29% and 32%, respectively, when using EGR as the primary standard for comparison. The lean A-F charge, which causes a cooler combustion temperature, was crucial in reducing EGT in PCCI mode. The intake air's phase change, caused by its temperature, prohibits it from participating in

combustion. As EGR dilutes the charge, the outcome is a low charge density (Ganesh et al., 2008b).

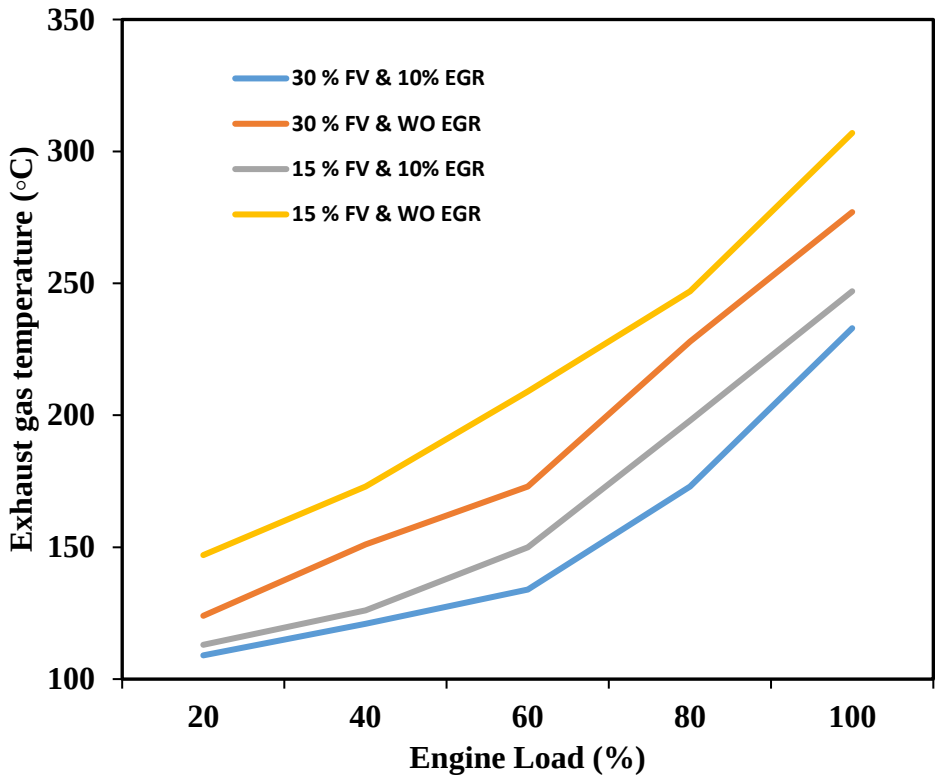

Figure 5.6 Exhaust gas temperature variation concerning engine load

5.3.4 Volumetric efficiency

The exhaust gas recirculation (EGR) and fuel vapor induction systems are both activated during experimentation. Figure 5.7 illustrates the range of volumetric efficiencies an engine can achieve under various load conditions. According to the observation, there is a decrease in volumetric efficiency with an increase in EGR. While a conventional engine operates in its suction stroke, the intake manifold is only open to air circulation, which is not in the case of PCCI conditions. Following the compression stroke, fuel is delivered into the combustion chamber while the charge is formed. Due to the intake, air that fills the manifold has high volumetric efficiency, but due to the area's size, it only has a small charge mixing span. The combustion process does not use the intake air entirely due to the shorter mixing period.

As a result, a sizable amount of air is wasted throughout the process. The intake airflow rate in the manifold is obstructed due to the increased occupancy brought on by recirculated exhaust gas

and the volume in the manifold that is filled with fuel vapor while in the PCCI, which lowers volumetric efficiency. Pre-mixing, on the other hand, starts with the suction stroke and continues until the combustion stroke begins. In contrast to the traditional method, which results in excess air and raises NOx emissions, this allows for a longer time for producing a homogeneous charge and fully utilizing the available air. It has been shown that at 30% fuel vapour induction, with and without EGR, volumetric efficiency declines by 10% and 23%, respectively. Furthermore, it was shown that when the amount of fuel vapor induction is 15% and 30%, the volumetric efficiency decreases by 9 % and 16 %. Because of this, the impact of EGR is substantially more significant than the impact of gasoline vapor on the engine's drop in volumetric efficiency.

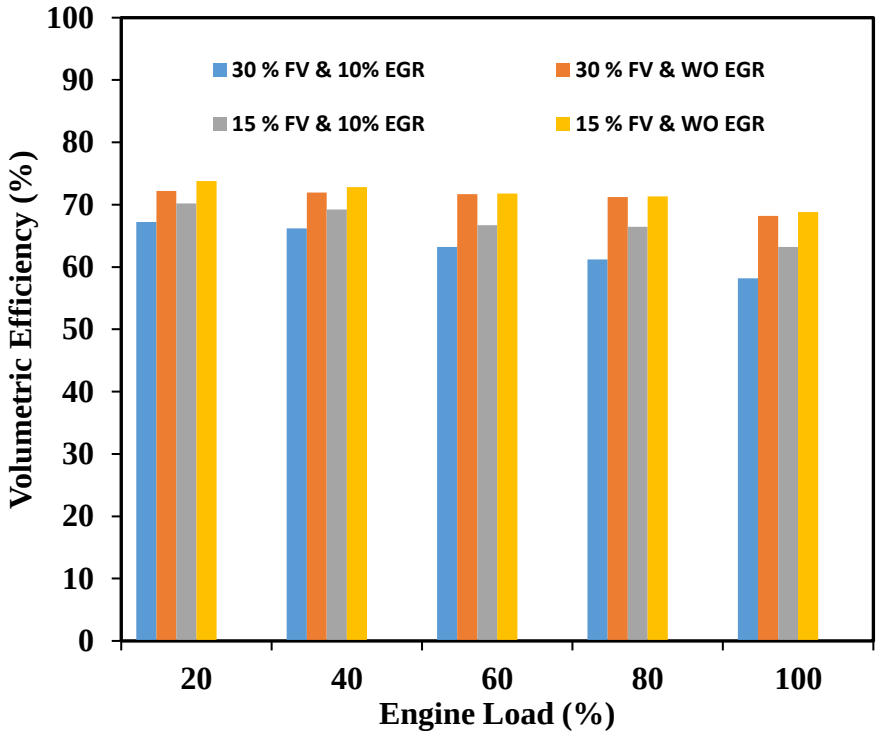

Figure 5.7 Volumetric efficiency variation concerning engine load

5.4 The effect of using liquid hydrocarbon fuels on the engine Emissions

5.4.1 Hydrocarbon emissions

Diesel vapor causes fluctuations in the air-vapor ratio and inefficient combustion because it promotes homogeneity but decreases volumetric efficiency. As engine load rises, air-vapor ratios achieve ideal combustion conditions. In general, when engine loads rose, HC emissions followed declining patterns. A high fuel vapor-to-intake air ratio and improper combustion, which

increases HC and CO, are caused by the EGR cutting off more air than is necessary when the engine is running at low engine loads.

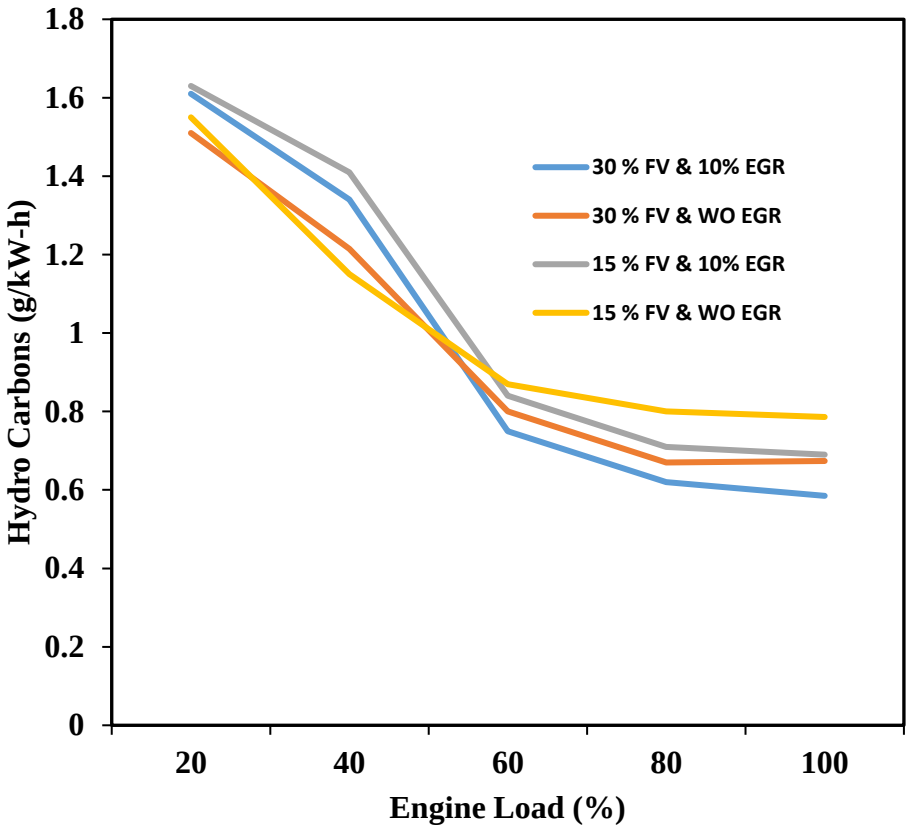

Figure 5.8 Hydrocarbon emission variation concerning engine load

In conventional engines, lean mixture generation results in early lean flame blowout zone development and considerable HC emissions at low engine loads (N. Kumar, 2019a). Figures 5.8 depicts the variation in HC emissions across all engine loads. The patterns show that both emissions, which are highest at low load, are caused by incomplete combustion. When compared to a conventional engine operating at a low engine load, the use of 15 % diesel-blended liquid hydrocarbon fuel vapors with 10 % EGR induction results in a increase of 1.63 g/kW.h in HC emissions, whereas the use of 15 % fuel vapour without EGR induction results in an decrease of 1.55 g/kW.h in these emissions. However, increases in hydrocarbon (HC) emissions of 0.58 g/kW.h and 0.67 g/kW.h are caused by the presence of 30 % diesel-blended liquid hydrocarbon fuel vapors with 10 % EGR induction and the absence of EGR induction, respectively.

5.4.2 Carbon monoxide emissions

According to shown in the study, lean mixture production in a conventional engine is what causes the early development of the lean flame blowout zone, which is responsible for considerable CO emissions even when the engine is not under a heavy load (N. Kumar, 2019b). Figures 5.9 depict the fluctuation in CO emissions at constant engine speed under various engine loads. It is brought on by incomplete combustion, which generates both pollutants, while an engine runs at a low load. When the engine runs at a low load, 15% diesel blended liquid hydrocarbon fuel with 10% EGR observed higher CO emissions by 6.4 g/kWh whereas at high load its reduced by 0.94 g/kWh. When the engine runs at a low load, 30% diesel blended liquid hydrocarbon fuel with 10% EGR observed higher CO emissions by 6.75 g/kWh whereas at high load its reduced by 1.16 g/kWh.CO emissions have been observed to be higher by 6.4 g/kWh when the engine is operating at low load on 15 % diesel blended liquid hydrocarbon fuel with 10 % EGR, but seem to be reduced by 0.94 g/kWh when the engine is operating at high load. CO emissions have been reported to be 6.75 g/kWh higher when the engine is operating at low load on a mix of 30% diesel and liquid hydrocarbon fuel with 10% EGR, but 1.16 g/kWh lower when the engine is operating at high load.

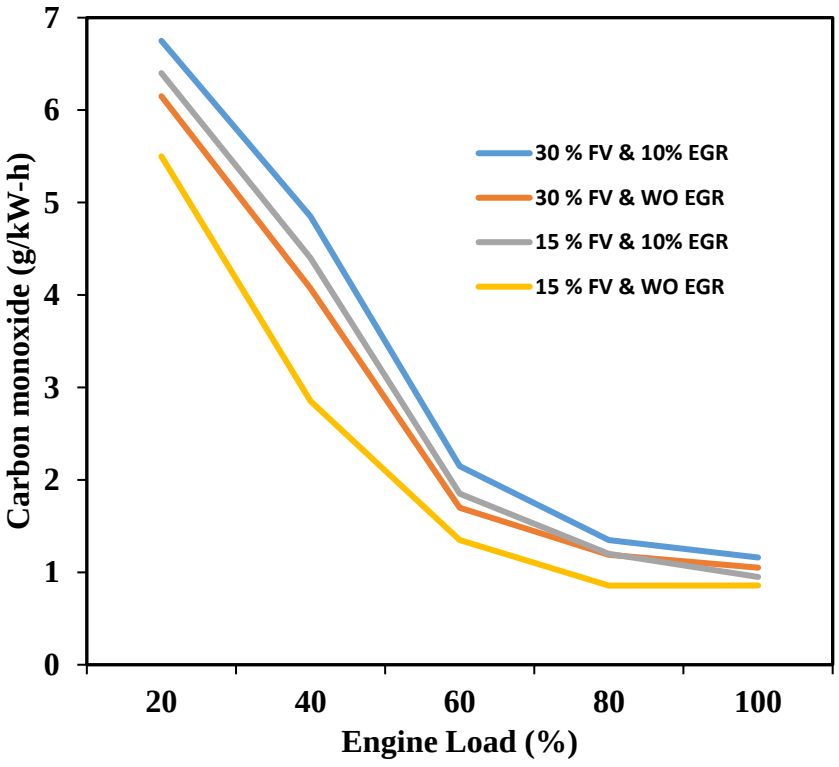

Figure 5.9 Carbon monoxide emission variation concerning engine load

5.4.3 NOx emissions

As seen in Figure 5.10 illustrates how NOx emissions steadily decreased for 30% and 15% of FV with and without EGR test periods as engine load increased from 20 to 100%. The conventional engine loses velocity due to fuel atomization and insufficient mixing, which restricts charge output. When diesel and air are combined, NOx forms at the point of contact (Gray & Ryan, 2018). In contrast to conventional induction, which produces distinct layers, fuel vapor induction at a low load generates a uniform charge. During partial PCCI, diesel fuel injection diminishes due to vapor induction. Vapor induction, the primary cause of heterogeneity, has increased, lowering the air available for fuel injection.

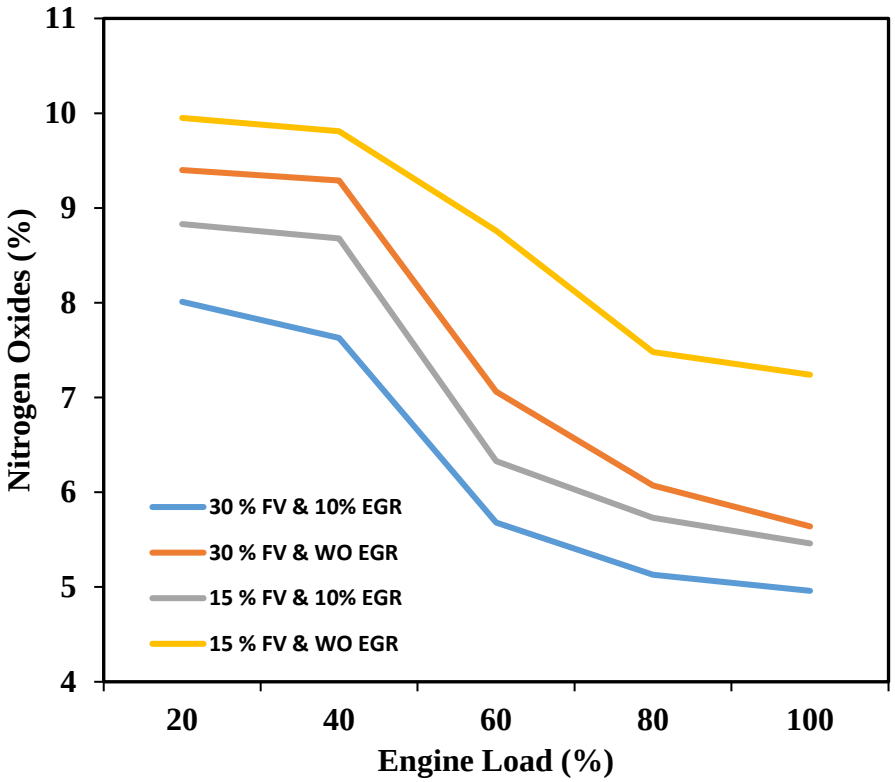

Figure 5.10 NOx emission variation concerning engine load

Additionally, raising the vapor percentage offsets the loss of direct injection and reduces NOx emissions; however, injecting fuel in an environment with insufficient air may result in increased HC and CO emissions. With 15% diesel blended liquid hydrocarbon fuel vapour induction without EGR, the decreased NOx emissions from low to high engine load was 27%, and with

30% fuel vapor induction, it was 40%. EGR combined with fuel vapor induction can further reduce NOx emissions for 30% at low engine load and 38% at high engine load by respectively, for 15% and 30% diesel-blended liquid hydrocarbon fuel vapors induction. When the engine operates under light load conditions, the fuel-air ratio that produces the most effective utilization of fuel and air in conventional engines is attained. A brief burst of combustion occurs in the combustion chamber, where the fuel pockets have developed, as the compression process proceeds. More than 425 K are reached as a result(Bhurat et al., 2021) .

The partial PCCI engine provides a longer premixing interval for air and fuel vapor than the regular PCCI engine, leading to a more uniform charge generation. It helps stop nitrogen from reacting since there are less free radicals. The exhaust gas recirculation (EGR) system helps enhance engine performance by lowering the amount of oxygen present in the combustion chamber.

5.4.4 Smoke emission

During the experiment, an increase in smoke opacity was seen in the exhaust stream. It is the result of using EGR and producing a rich combination of the air-fuel mixture. With increasing load, A-F ratio decreases while Smoke emissions increase. For all engine loads, Figure 5.11 shows an increase in smoke opacity. The engine produces more smoke under larger loads due to the denser mixture, which also causes a buildup of emissions like HC, CO in the exhaust.

The smoke is opaque due to the lack of air to ignite the fuel. Smoke was reduced by 24% and 29% for 15% and 30% fuel vapour, respectively, when EGR is used in conjunction with a light engine load. When the engine was operated at a high load with a 15% and 30% fuel vapor mix, the visible smoke decreased by 18 % and 23 %, respectively. Compared to a traditional engine, the premixing of a uniform air-vapor mixture lowers opacity by preventing the creation of rich mixture pockets. Some places may not have enough oxygen to oxidize the rich mixture's fuel completely. Because there is less soot in the exhaust than there would be with better combustion, the smoke is less opaque. Its because carbon monoxide and hydrocarbons tend to increase the richness of the total mixture. 10% EGR did not reduce smoke opacity in part-load operation by recycling unburned hydrocarbons or eliminating essential O_2 from the actual air fuel combination.

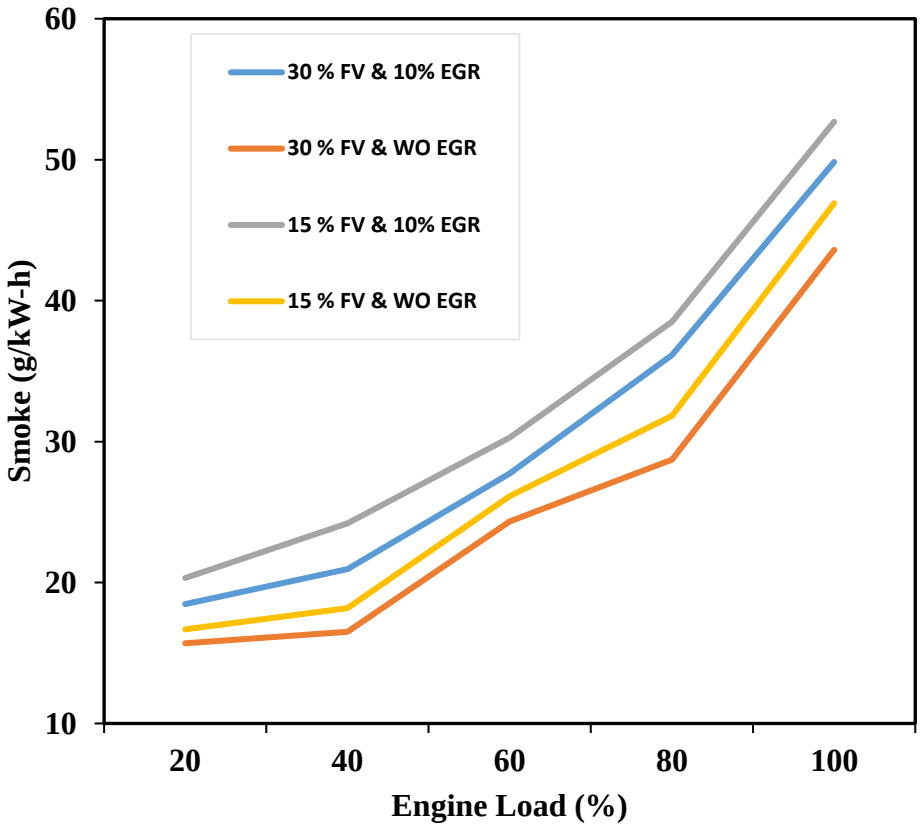

Figure 5.11 Smoke emission variation concerning engine load

5.5 Summary

The result recommended employing retrofitting technologies, such as air mixture homogeneity, which lowered NOx, smoke, HC, and CO emissions from standard diesel engines using a mixture of liquid hydrocarbon fuel. The external mixture production strategy can be used cost-effectively with a standard engine with only minor intake manifold changes. Cooled EGR controlled up to 10% of PCCI combustion. The PCCI engine's EGR postponed combustion. PCCI engines have low-pressure, early burnout. The study found that under intermediate and higher loads, the test engine's brake thermal efficiency using liquid hydrocarbon fuels decreased. At all load activities, the engine's efficiency with liquid hydrocarbon fuels was almost as good as diesel fuel. Liquid hydrocarbon fuels, which omitted nitrogen oxides, created more carbon-based pollutants at intermediate and higher loads than diesel fuel. Activities with lower loads revealed minimal variation in the pollutants. High loads resulted in lower in-cylinder combustion chamber temperatures, which decreased nitrogen oxide emissions.

Diesel PCCI combustion engine at 30% and 15% diesel-blended liquid hydrocarbon fuel vapors induction may perform better with exhaust gas recirculation. At the full load (100%), HC, CO, NOx, and smoke emissions were 0.585 g/kW.h, 1.16 g/kW.h, 4.96 g/kW.h, and 50 %, respectively with 30% fuel vapor and 10 % EGR. At the full load (100%), HC, CO, NOx, and smoke emissions were 0.692 g/kW.h, 0.95 g/kW.h, 5.46 g/kW.h, and 53 %, respectively with 15% fuel vapor and 10% EGR. So as per findings 30 % liquid hydrocarbon fuel blended with diesel shows more efficient for especially HC, NOx, and smoke emissions reductions compare with 15 % liquid hydrocarbon fuel blended with diesel. While NOx and smoke emissions dropped, HC and CO emissions rise, supporting earlier findings. The PCCI engine releases less NOx and smoke, per a recent study. Comparing PCCI's operation to conventional diesel and engine operation using liquid hydrocarbon fuels, we can see that it was functioning with improved performance and emissions. Engine performance and emissions were enhanced using liquid hydrocarbon fuel from municipal mixed plastic waste recovery and recycling—technologies used after exhaust gas emissions, such as selective catalytic reduction, can lower HC and CO emissions. In the future, diesel engines might be replaced by PCCI technology with less than 10% EGR and SCR technology.

CHAPTER 6 : A NOVEL APPOROACH TO USE RESIDUE AS SELF HEALING MATERIAL

6.1 Development of self-healing epoxy vitrimer composites with activated carbon pyrochar derived from municipal mixed plastic waste pyrolysis

A ecological vitrimer is being developed by using activated carbon pyrochar obtained from municipal mixed plastic waste pyrolysis into an epoxy composite. Durable vitrimeric materials may be created by adding pyrochar to polymeric composites. Due to their ductility, reusability, and recyclability, virimeric materials have become popular and reliable materials. As a result, the self-healing temperature of composite vitrimers is lower via disulfide exchanges than that of virgin epoxy vitrimers. Additionally, compressive studies have been utilised to study self-healing capacities and modulus variations have been used to highlight changes in the healing efficiency of the materials.

6.2 Materials

As already discussed, a lab-scale pyrolysis setup was developed @ UPES. The production flow process of plastic waste to alternate fuel was illustrated as shown in Figure 4.1. Plastic waste obtained from the university campus was processed from cleaning to conversion into fuel (P. K. Ghodke, 2021b). From Sigma-Aldrich, we obtained the following components for the epoxy resins: DETA, BADGE and AFD. This study describes the preparation of the activated carbon (AC) pyrochar produced from municipal mixed plastic waste pyrolysis(Krishnakumar et al., 2021).

Calculation for epoxy and amine hardener ratio:

$$\text{Parts by weight of amine to be used with 100 parts by weight of BADGE resin (phr)} = \left(\frac{\text{amine hardener molecular weight / number of hydrogens per molecule}}{\text{BADGE equivalent weight}}\right) * 100\%$$

BADGE resin has an equivalent weight of 176 g/mole (as stated by the manufacturer), and an active hydrogen in 2-AFD is four.=> $\left(\frac{248/4}{176}\right) * 100\% = 35.6\%$

To cure 100 g of BADGE resin, 35.6 g of AFD is required.

6.3 Preparation of epoxy nanocomposite

300 mg of synthesis AC, was dissolved in 20 ml of solvent, and after that, it was ultrasonically agitated for half an hour. After instantly pouring the AC solution, the BADE resin was subjected to vigorous stirring in order to ensure that it was completely dissolved. (EP- x %; x: 0,0.1,0.2,0.5,1), where 'x' refers to the quantity of AC that was added to the combination of epoxy resin and hardener in terms of wt %. The mixture was also heated to 353 K and vacuum degassed until the ethanol was completely gone. The 2-aminophenyl disulfide (APD) hardener was then introduced, and the combination was kept at the appropriate temperature for fifteen minutes while being stirred. The degassed liquid was then poured into a silicon mould and baked at 423 K for five hours in order to fix the colour. Bisphenol a diglicidyl ether resin-based standard specimen was produced, with diethylenetriamine (DETA) functioning like a curing agent. This was done in order to investigate the effect that APD has on the process of self-healing. In order to investigate the effects of activated carbon, nanocomposites made of reference clean epoxy (R-epoxy) and epoxy with activated carbon infused into it (R-Epoxy-1 %) were constructed (Hummers & Offeman, n.d.; Krishnakumar et al., 2020; Nia et al., 2014; C. Park et al., 2019; Rana et al., 2016).

6.4 Material characterization Methods

In order to detect the activated carbon, the D8 ADVANCE ECO – Bruker was used to conduct an X-Ray Diffraction spectroscopy analysis. Epoxy's activated carbon was studied with the use of the spectroscopic UV-Visimeter (LAMDA 35, Perkin Elmer). The curing process was studied by FT-IR spectra analysis. The effects of activated carbon dispersion in epoxy matrix were investigated using an HR-TEM, JEM 2100F, from JEOL. Both DSC tests and TA-Q400em Variation in Measurements investigations were used in order to ascertain the temperature at which the glass transition occurs. The Perkin Elmer DSC-7 has been performed with a temperature range of 303 to 493 K, a flow rate of 19.8 ml/min of nitrogen purge gas. Rectangular specimens (15mm x 5mm x 0.5mm) were tested at 3 point bending test in the TA-Q400em to determine their mechanical characteristics.

The flexural test, also known as the bend or three-point bending test, is essential for evaluating the mechanical properties and healing efficiency of self-healing materials. This test assesses the material's ability to recover its mechanical properties after deformation. It involves applying a

load to a beam-shaped specimen at two support points, while a third point applies a load to the center. The material's response, including the load-displacement curve, indicates its stiffness, strength, and ductility. After an initial test, the specimen can be damaged and then allowed to heal under specific conditions. The flexural test is repeated on the healed specimen to assess its recovery of mechanical properties, providing crucial insights into the material's self-healing performance and potential applications.

All mechanical characteristics tests were carried out at temperatures ranging from 313 to 393 K, with heating rates of 10 °C per minute, a nitrogen purge gas flow of 50 ml per minute, and a force of 0.02 Newton. To straighten the specimen in the stress relaxation experiment, a preloaded force of $1*10^{-3}$ N was applied. After determining the temperature and strain, testing consisted of applying 1% strain at the proper temperature and measuring the relaxation modulus with respect to time. Stress-strain experiments were conducted in strain ramp mode with a force of 0.02 N and strain was measured at an isothermal temperature of 313 K.

6.5 Material characterization

The use of ultraviolet (UV) spectroscopy allowed for the determination of whether or not an epoxy vitrimer compound included AC. The material was characterised by employing a finely ground matrix that was effectively dispersed in ethanol by means of ultrasonication. The presence of activated carbon in epoxy composite was revealed by the absorbance peak at 237 nm. In Figure 6.1, the obtained UV data for epoxy, activated carbon, and epoxy-AC composites were plotted together.

The x-ray diffraction spectroscopy (XRD) analysis of the activated carbon synthesised from pyrochar (Figure 6.2) shows that the peak at 27.23° marks their formation. where the lack of distinct peaks indicated the amorphous nature Because of the hexagonal shape resembling a graphite flake peak found at 27.23°, Activater carbon might be termed as assemblages of imperfect graphene.

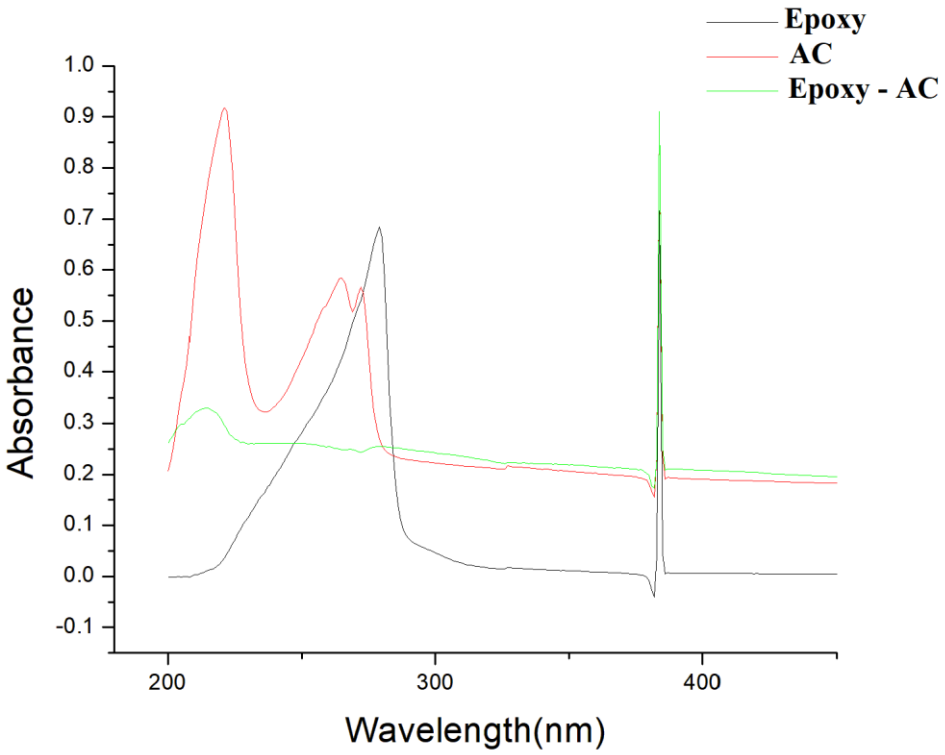

Figure 6.1 Epoxy, activated carbon, and the epoxy-activated carbon composite each have their characteristic UV spectrum.

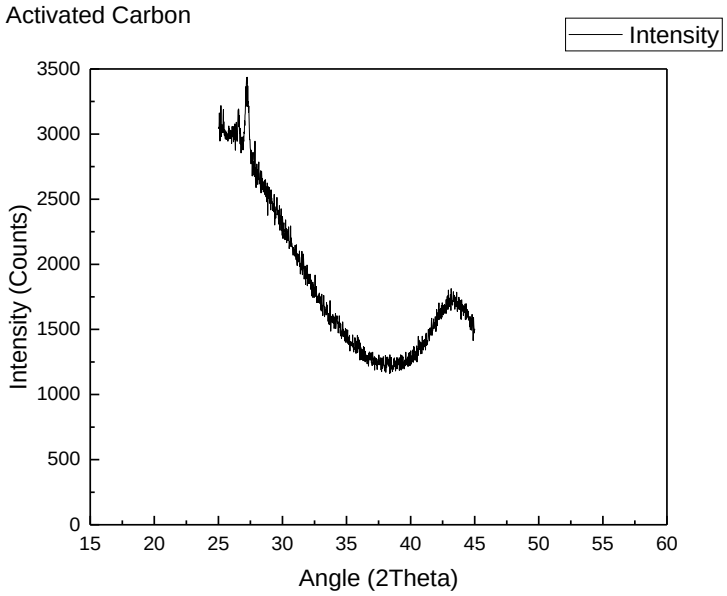

Figure 6.2 XRD spectrum for activated carbon

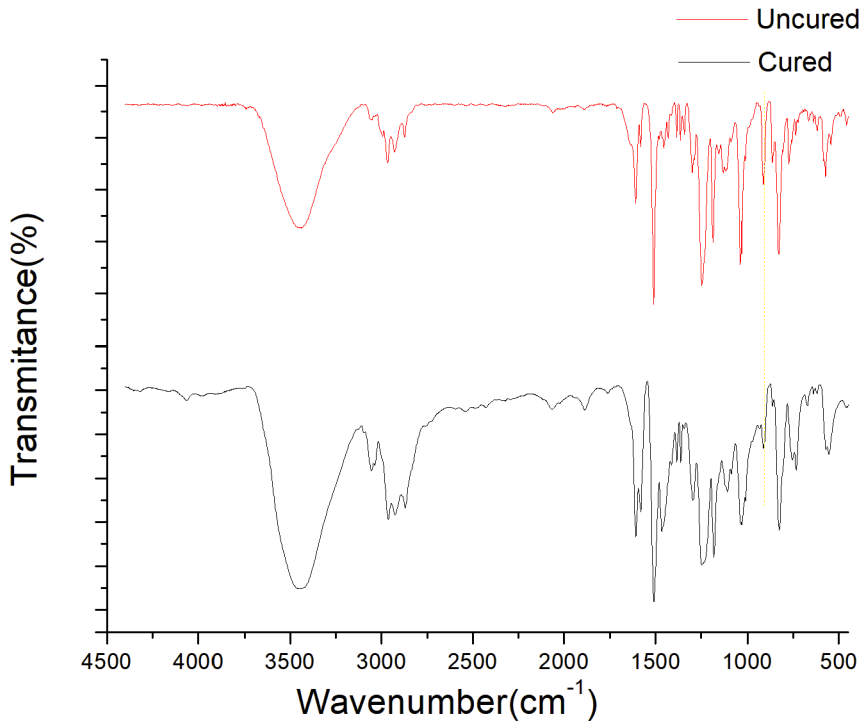

Figure 6.3 FTIR spectrum for cured and uncured epoxy composite

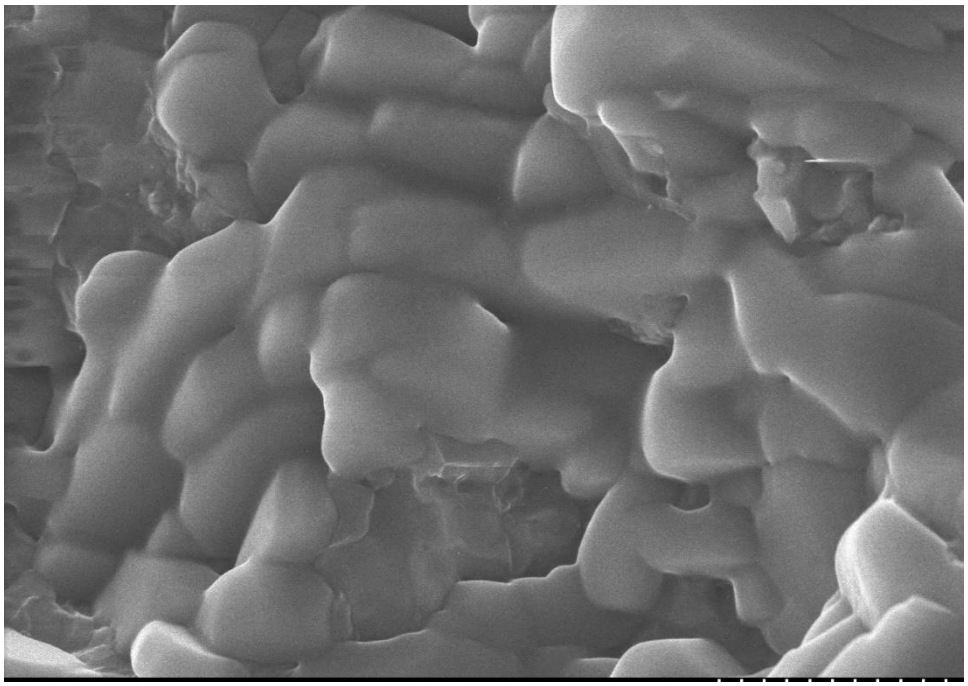

Figure 6.4 SEM images for pyrochar carbon

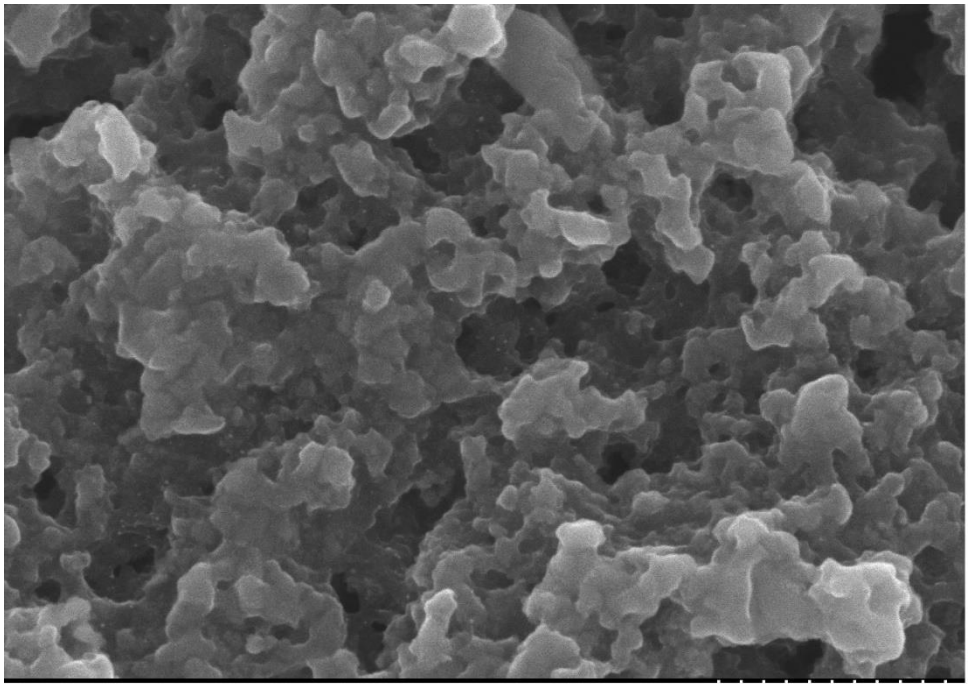

Figure 6.5 SEM images for activated carbon

The curing and uncuring of epoxy vitrimer composites were determined using FT-IR analysis. The disappearance of the oxirane rings of the oxirane ring (917 cm^{-1}) was noticed, which indicated that the epoxy had completed its curing process (Figure 6.3). The curing of the epoxy was monitored using FT-IR analysis at intervals of one hour, and it was discovered that the curing process was completed after 5 hours of observation. Chemically activated carbon, comprising graphite and π electron-connected graphene layers, demonstrates notable porosity, enhancing its surface area despite altering the graphene layer structure. Scanning electron microscopy (SEM) analysis reveals pores on the surface of pyrochar produced from municipal mixed plastic waste pyrolysis and chemically activated carbon (Figure 6.4 & 6.5). Activation with phosphoric acid highlights these pores, which are of low volume but crucial for increasing the surface area available for chemical reactions. This property is beneficial for achieving progressive chain exchanges.

6.6 Mechanical and thermo-mechanical Properties

A thermomechanical analyzer was used to determine the Tg and dynamic mechanical performance of activated carbon-epoxy vitrimer composites. The thermal characteristics of pristine epoxy composites have been investigated. The TA Q-400em is effective in finding Tg from temperature influenced aspect variations.

Table 6.1 Glass transition temperature of epoxy composites

Material	**T_g (TMA)(^{o}c)**
EP-pristine	83
EP-0.1%	62
EP-0.2%	58
EP-0.5%	56
EP-1%	53

Table 6.1 displays the Tg values for virgin epoxy vitrimer, activated carbon-epoxy vitrimer composites, and activated carbon-epoxy vitrimer composites with varying percentages of activated carbon filler. EP-1 % exhibited the lowest Tg of all of the epoxy samples that were investigated.

In addition, the absence of reactivity between epoxy and activated carbon promotes chain mobility, which in turn makes it possible for there to be a greater amount of free space between the particles and the matrix. As a consequence of this, chains that are close to the interface may move through the free volume with relative ease, which increases mobility and decreases Tg [263]. To improve chain mobility and achieve low-temperature self-healing capabilities, the free volume space that exists between the matrix and the particles [264] may have resulted in a lower glass transition temperature for all composites. However, the study reported that adding 1 wt% activated carbon filler increases Tg somewhat, perhaps owing to amalgamation of activated carbon in the epoxy matrix (Krishnakumar et al., 2020; Robert F. Landel, 1994).

The decreased Tg facilitates self-healing at modest temperatures as well as shape memory in materials. As a result, more study was conducted on composites containing up to 1% activated carbon in the matrix. The variations that take place in the physical behavior of vitrimer epoxy as a result of using cured pristine and activated carbon epoxy are outlined in Table 6.2. The viscoelasticity of pristine epoxy vitrimer and activated carbon-epoxy vitrimer composites was investigated at different temperatures (Figures 6.6 and 6.7). In the high activated carbon sample,

the storage modulus (52.2 GPa) (EP-1%). Figure 6.6 shows a steady rise in storage modulus with nanofiller, and Table 6.2 shows the achieved values.

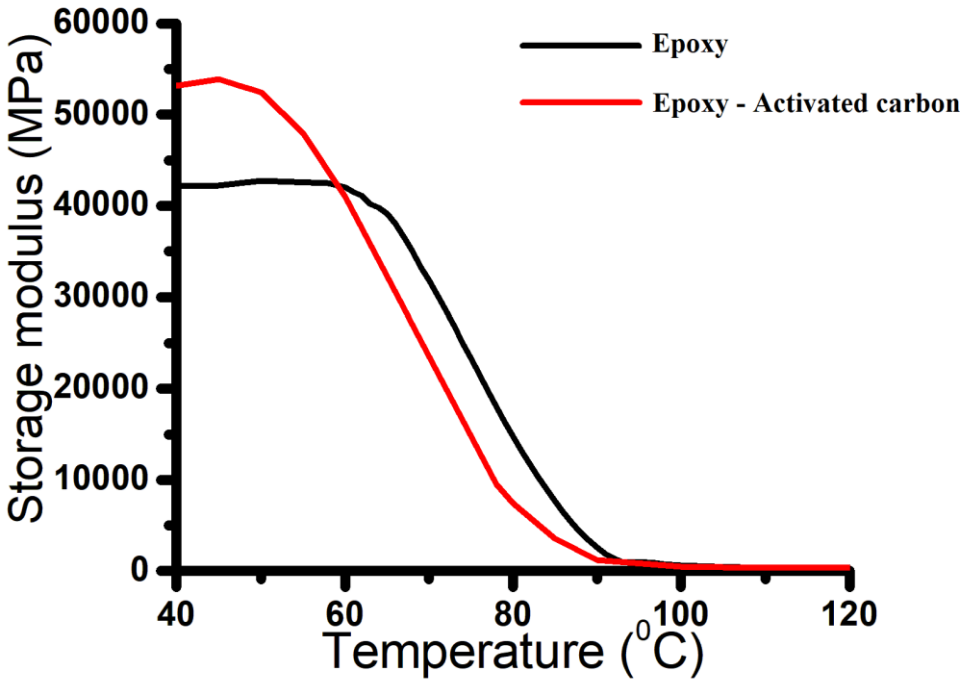

Figure 6.6 Storage modulus for epoxy vitrimer

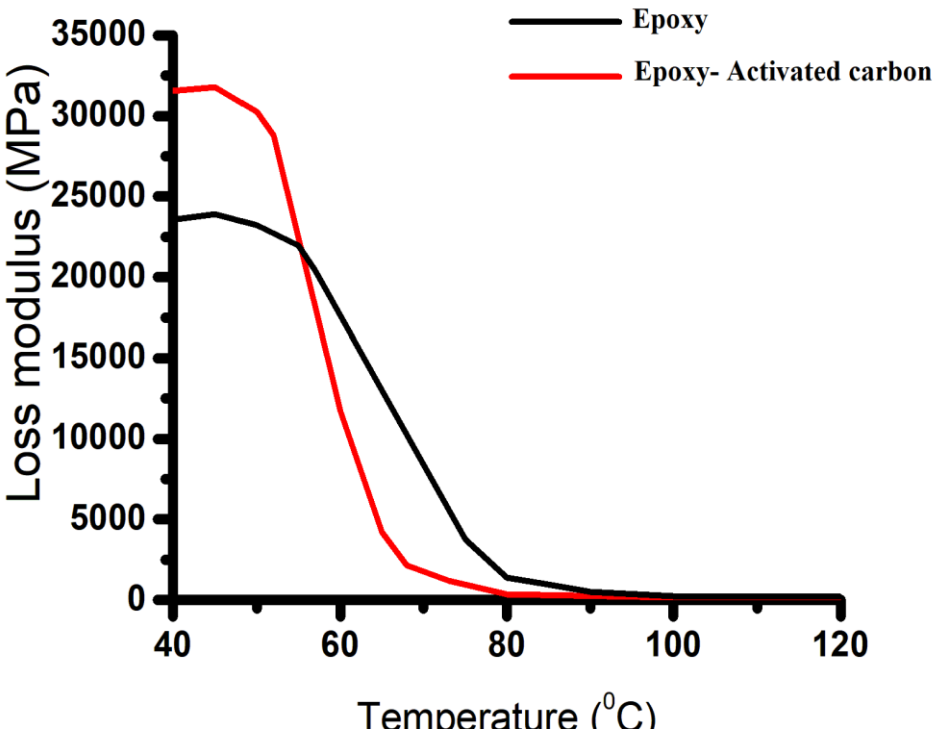

Figure 6.7 Loss modulus for epoxy vitrimer

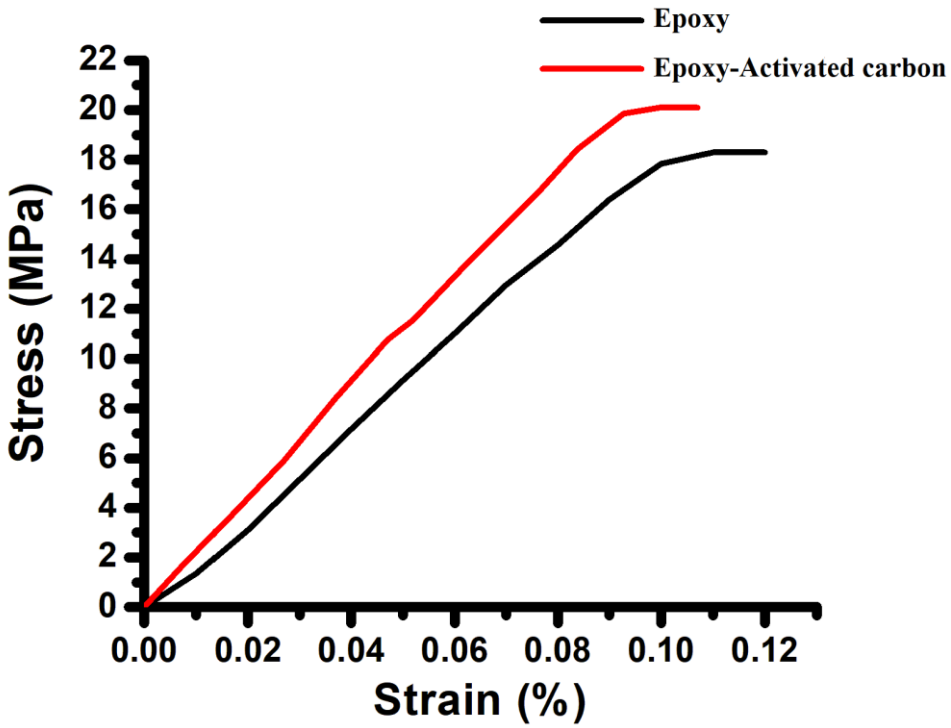

Figure 6.8 Stress-strain curve for epoxy vitrimer

The wavy structure of activated carbon may aid effective intercalate interlocking with polymer matrix, thereby increasing modulus [52]. The loss modulus (E") (Figure 6.8) also shows the material's viscoelasticity (E'>E"). The shoulder peak (Figure 6.6) represents the rubbery area of the vitrimer materials following Tg. The glass transition temperature (Tg) of the epoxy vitrimer was decreased by adding 1% activated carbon to EP-1. With the addition of fillers, Tg decreases, resulting in a low-temperature rubbery zone in vitrimeric composites. (Robert F. Landel, 1994)
As a result, the solid to rubbery phase shift temperature was completely dependent on material viscoelasticity (storage and loss modulus). (Guadagno et al., 2011).
The stress-strain relationship of developed vitrimer composites was determined using three-point bending tests at 313 K. According to Fig. 6.8, EP-1 % has a greater flexural strength than EP-Pristine and (Table 6.2). By combining activated carbon with epoxy composites gain stiffness and bending resistance while reducing strain-at-break. (Bortz et al., 2012). The use of activated carbon fillers enhanced the flexural modulus from 0–9.4%

The pure epoxy sample has a lower flexural modulus than EP-1%. The variation in flexural mechanical properties that is caused by nanocomposite depicted in figure 6.7. Table 6.2 contains a comparison of the flexural parameters (strength and strain on breakdown) of standard epoxy matrices and vitrimer epoxy matrices (Ebnesajjad & Landrock, 2015).

Table 6.2 Mechanical properties epoxy AC nanocomposites

Epoxy material	**Storage modulus (GPa)**	**Flexural strength (MPa)**	**Flexural strain%**	**Flexural modulus (GPa)**
EP-P	42.3	19.4	0.05	32.5
EP-1%	53.5	19.2	0.11	15.7

6.7 Dynamic properties

6.7.1 Stress relaxation

By performing stress relaxation analysis on the epoxy composites, which is designed to determine the relaxation modulus of malleable materials, it has been verified that they exhibit vitrimer behaviour. (Ogden & Guan, 2018). In this study, an EP-pristine stress relaxation

investigation was carried out, and the resulting time-dependent relaxation modulus was plotted in accordance with the data received from their temperature measurements. The high relaxation rates reported in the material are suggestive of a fast dislufide exchange in the substance. Because of the relationship between temperature and relaxation time, a shorter relaxation period corresponds to a quicker disulfide exchange rate. The temperatures of 330 K, 343 K, and 353 K used in the experiments resulted in relaxation durations of 112.8 s, 40.8 s, and 34s, respectively. The obtained findings indicate that there is a quick exchange response after Tg and that the imposed tension is rapidly relaxed. By using an Arrhenius equation (1), the acquired data were displayed, which allowed for the calculation of a low activation energy (Jousseaume et al., 2002)

$\tau^* = \tau_0 \exp (E_a/RT)$ (1)

$Ea = 59/KJ\ mol^{-1}$

Some hypotheses attribute this by the availability of activated carbon, that has a lower epoxy vitrimer crosslinking density and higher viscosity. The growth of surface area between the matrix and filler, on the other hand, was revealed to be the most essential factor in the lowering of the glass transition temperature (Sun et al., 2004).Generally, when viscosity exceeds 10^{12} Pa.s, it is necessary to consider the temperature of material topology transition shift. (Dyre, 2006). Using Maxwell's and Arrhenius' equations, the projected topological freezing transition temperature (Tv) was calculated to be 19°C as a result of this typical study.

6.7.2 Self-healing

In order to study the self-healing behaviour of the produced samples, a temperature value of 348 K was used. The findings indicate that the samples had considerable self-healing effects. This had been anticipated as self-healing will be associated with lower temperature, which will be beneficial in lowering the Tg, where the S-S bonds will be able to reorganise more quickly at the lower Tg. As a result of the inclusion of the filler, the self-healing capability has been enhanced, which is beneficial in accelerating and restricting the transit of disulfide groups. Self-healing at a low temperature has been achieved for the EP-1 % sample, which was effective in bringing the Tg down to a lower value. A razor blade was used to split the test specimen in half, and the parts were instantly assembled at 348 K for 5 minutes with the use of a tweezer to assess their bond strength(Olowojoba et al., 2017). The effectiveness of the healed samples was determined using flexural testing, and the stress-strain correlations of the healed samples were presented in Figure 6.9 for two different healed samples.

Table 6.3 After healing, the flexural modulus varies.

Sample EP-x%	Before healing (GPa)	After healing (GPa)	
		1st	2nd
EP-pristine	34.2	28.7	20.9
EP-1	39.8	34.6	32.3

No changes in flexural strength were seen after healing, however the flexural modulus was significantly reduced as a result of the higher strain, by the data in Table 6.2. Specifically, this decrease establishes the upper limit for crosslinked chains and is related to the drop in crosslink density. (Florea et al., 2015; Guadagno et al., 2018). After healing, EP-pristine and EP-1 % returned to 72% and 83% of their flexural modulus, respectively, and the second healing cycle demonstrated a 60% and 75% increase in flexural modulus, respectively (Figure 6.9). So, the reported values proved to be useful in determining the healing efficiency that had prevailed, and it was identified that carbon pyrochar generated from municipal mixed plastic waste pyrolysis was good in achieving effective healing.

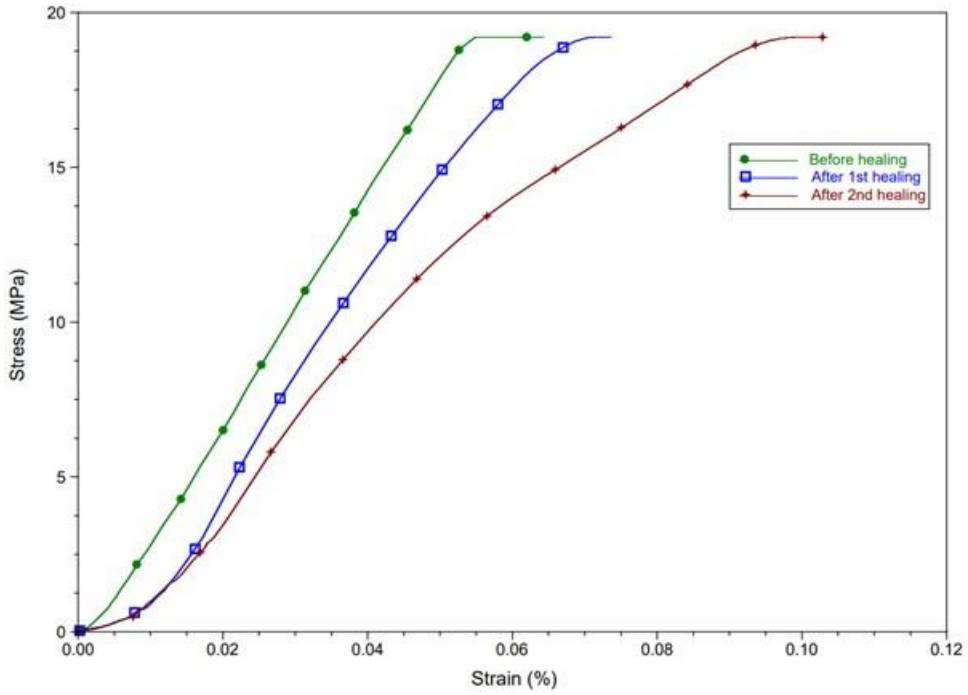

Figure 6.9 EP-pristine healing represented stress-strain curve.

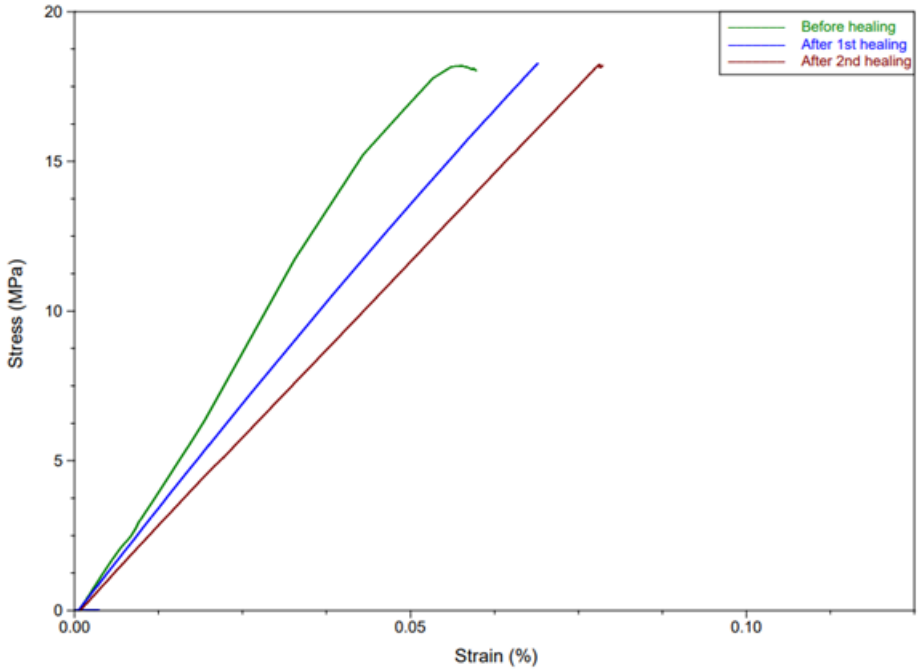

Figure 6.10 EP-1% healing represented stress-strain curve.

6.8 Summary

This study suggests that activated carbon could be used as a filler in an epoxy vitrimer composites. Chain exchanges were possible due to the enormous surface area of activated carbon in the AC-epoxy vitrimer composites. Self-healing was observed in virgin epoxy vitrimer at 80°C for 5 minutes; however, when activated carbon was added, the material self-healed at 348 K for 5 minutes. When the EP-1 % composite (which includes 1 wt% AC) is compared to virgin epoxy vitrimers, the EP-1 % composite has 17 % stronger flexural strength and modulus, as well as a 16.9 % rise in modulus. In flexural experiments, vitrimer composites containing 1 wt% AC (EP-1) demonstrated an 83 % and 75 % recovery efficiency after two repeated healings. Composite vitrimer research will be important in the future to see environmentally friendly vitrimer composite materials for practical applications.

CHAPTER 7 : CONCLUSION

In this work, four objectives were framed, as discussed in the initial sections, with Objective II:

To optimize plant operating parameters and work on cheaper catalysts to improve yield pattern. Pyrolysis is a well-known process for transforming municipal mixed plastic trash into useful fuel. The Centre for Alternative Energy Research (UPES) has developed a lab-scale pyrolysis reactor. The experiments were carried out with the assistance of a fixed-bed tubular reactor, which was responsible for the production of hydrocarbon fuels. The process parameter like temperature, residence time, heating rate, and catalyst % were optimized in this lab scale reactor. After optimising the parameters, a pilot scale reactor was design and fabricated.

The same was addressed in Objective I: **To design and develop a pilot scale demonstrable pyrolyzer for rural areas.** The pilot scale reactor having capacity of 5 kg. the reactor and condenser are made using stainless steel because of the reactor operating temperature of around 723 K. A 72.4 wt % yield of liquid fuel was achieved using mixed plastic wastes under the optimal operating parameters specified.

In Objective III: **To produce liquid and gaseous fuels as well as pyro char through fast pyrolysis of plastic wastes.** In fast pyrolysis of Mixed Municipal plastic waste conversion into liquid hydro carbon fuel, non condensed gas, pyro char. Hydro - carbon fuel generated from MMPW has high heating value and high concentration of aliphatic hydrocarbons that supports its application as a substitute to conventional fuel. The features of pyrolysis of municipal mixed plastic waste accessible at university revealed that it is a possible hydrocarbon fuel that can be used to generate heat and electricity.

In the next section of this work, i.e. Objective IV:**To evaluate performance of IC engine fueled with plastic waste pyrolysis oil.**The result obtained from the engine performance of 30% liquid hydrocarbon blended diesel recommends employing retrofitting technologies, such as air mixture homogeneity, which lowered NOx, smoke and HC emissions from standard diesel engines using a mixture of liquid hydrocarbon fuel. The external mixture production strategy can be used cost-effectively with a standard engine with only minor intake manifold changes. Cooled EGR controlled up to 10% of PCCI combustion. The PCCI engine's EGR postponed combustion. PCCI

engines have low-pressure, early burnout. The study found that under intermediate and higher loads, the test engine's brake thermal efficiency using liquid hydrocarbon fuels decreased.

At all load activities, the engine's efficiency with liquid hydrocarbon fuels was almost as good as diesel fuel. Liquid hydrocarbon fuels, which omitted nitrogen oxides, created more carbon-based pollutants at intermediate and higher loads than diesel fuel. Activities with lower loads revealed minimal variation in the pollutants. High loads resulted in lower in-cylinder combustion chamber temperatures, which decreased nitrogen oxide emissions.

Diesel PCCI combustion engine at 30% and 15% diesel-blended liquid hydrocarbon fuel vapors induction may perform better with exhaust gas recirculation. At the full load (100%), HC, CO, NOx, and smoke emissions were 0.585 g/kW.h, 1.16 g/kW.h, 4.96 g/kW.h, and 50 %, respectively with 30% fuel vapor and 10 % EGR. At the full load (100%), HC, CO, NOx, and smoke emissions were 0.692 g/kW.h, 0.95 g/kW.h, 5.46 g/kW.h, and 53 %, respectively with 15% fuel vapor and 10% EGR. So as per findings 30 % liquid hydrocarbon fuel blended with diesel shows more efficient for especially HC, NOx, and smoke emissions reductions compare with 15 % liquid hydrocarbon fuel blended with diesel. While NOx and smoke emissions dropped, HC and CO emissions rise, supporting earlier findings. The PCCI engine releases less NOx and smoke, per a recent study. Comparing PCCI's operation to conventional diesel and engine operation using liquid hydrocarbon fuels, we can see that it was functioning with improved performance and emissions. Engine performance and emissions were enhanced using liquid hydrocarbon fuel from municipal mixed plastic waste recovery and recycling technologies used after exhaust gas emissions, such as selective catalytic reduction, can lower HC and CO emissions. In the future, diesel engines might be replaced by PCCI technology with less than 10% EGR and SCR technology.

Additionally, activated carbon could be used as a filler in an epoxy vitrimer composites. Chain exchanges were possible due to the enormous surface area of activated carbon in the AC-epoxy vitrimer composites. Self-healing was observed in virgin epoxy vitrimer at 80°C for 5 minutes; however, when activated carbon was added, the material self-healed at 348 K for 5 minutes. When the EP-1 % composite (which includes 1 wt% AC) is compared to virgin epoxy vitrimers, the EP-1 % composite has 17 % stronger flexural strength and modulus, as well as a 16.9 % rise in modulus. In flexural experiments, vitrimer composites containing 1 wt% AC (EP-1) demonstrated an 83 % and 75 % recovery efficiency after two repeated healings. Composite

vitrimer research will be important in the future to see environmentally friendly vitrimer composite materials for practical applications.

7.1 Future work/scope

- Evaluate the feasibility of using non-condensed gas, a byproduct of plastic waste pyrolysis, as fuel for gas engines.
- To conduct a detailed economic, environmental analysis and investigate the correlation between fracture energy and the results of the wedge-split fracture test in composite self-healing materials for industrial scale.
- Explore techniques to upgrade the pyrolysis products, such as upgrading the liquid fraction to produce higher-quality fuels or chemicals.
- Conduct a detailed economic analysis to assess the feasibility of large-scale waste plastic pyrolysis plants, considering factors such as capital costs, operational costs, and revenue from product sales.
- Evaluate the environmental impact of waste plastic pyrolysis, including emissions, energy consumption, and waste generation, to ensure it is a sustainable waste management solution.
- Explore the integration of waste plastic pyrolysis with other processes, such as co-pyrolysis with biomass or waste tires, to improve overall process efficiency and product diversity.

REFERENCE

Abbas-Abadi, M. S., Haghighi, M. N., Yeganeh, H., & McDonald, A. G. (2014). Evaluation of pyrolysis process parameters on polypropylene degradation products. *Journal of Analytical and Applied Pyrolysis*, *109*, 272–277. https://doi.org/10.1016/J.JAAP.2014.05.023

Adelawon, B. O., Latinwo, G. K., Eboibi, B. E., Agbede, O. O., & Agarry, S. E. (2022). Comparison of the slow, fast, and flash pyrolysis of recycled maize-cob biomass waste, box-benhken process optimization and characterization studies for the thermal fast pyrolysis production of bio-energy. *Chemical Engineering Communications*, *209*(9), 1246–1276. https://doi.org/10.1080/00986445.2021.1957851

Adrados, A., de Marco, I., Caballero, B. M., López, A., Laresgoiti, M. F., & Torres, A. (2012). Pyrolysis of plastic packaging waste: A comparison of plastic residuals from material recovery facilities with simulated plastic waste. *Waste Management*, *32*(5), 826–832. https://doi.org/10.1016/J.WASMAN.2011.06.016

Agarwal, A. K., Singh, A. P., Lukose, J., & Gupta, T. (2013). Characterization of exhaust particulates from diesel fueled homogenous charge compression ignition combustion engine. *Journal of Aerosol Science*, *58*, 71–85. https://doi.org/10.1016/J.JAEROSCI.2012.12.005

Ahmed, M. J., & Hameed, B. H. (2020). Insight into the co-pyrolysis of different blended feedstocks to biochar for the adsorption of organic and inorganic pollutants: A review. *Journal of Cleaner Production*, *265*, 121762. https://doi.org/10.1016/J.JCLEPRO.2020.121762

Aishwarya, K. N., & Sindhu, N. (2016). Microwave Assisted Pyrolysis of Plastic Waste. *Procedia Technology*, *25*, 990–997. https://doi.org/10.1016/J.PROTCY.2016.08.197

Akubo, K., Nahil, M. A., & Williams, P. T. (2019). Aromatic fuel oils produced from the pyrolysis-catalysis of polyethylene plastic with metal-impregnated zeolite catalysts. *Journal of the Energy Institute*, *92*(1), 195–202. https://doi.org/10.1016/J.JOEI.2017.10.009

Almeida, D., & De Fátima Marques, M. (2016). Thermal and catalytic pyrolysis of plastic waste. *Polímeros*, *26*(1), 44–51. https://doi.org/10.1590/0104-1428.2100

Alper, K., Tekin, K., & Karagöz, S. (2015). Pyrolysis of agricultural residues for bio-oil production. *Clean Technologies and Environmental Policy*, *17*(1), 211–223. https://doi.org/10.1007/s10098-014-0778-8

Al-Salem, S. M., Lettieri, P., & Baeyens, J. (2009). The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals. *Progress in Energy and Combustion Science*, *36*, 103–129. https://doi.org/10.1016/j.pecs.2009.09.001

Altuna, F. I., Hoppe, C. E., & Williams, R. J. J. (2016). Shape memory epoxy vitrimers based on DGEBA crosslinked with dicarboxylic acids and their blends with citric acid. *RSC Advances*, *6*(91), 88647–88655. https://doi.org/10.1039/C6RA18010H

Andersson, C., & Stage, J. (2018). *Direct and indirect effects of waste management policies on household waste behaviour: The case of Sweden*. https://doi.org/10.1016/j.wasman.2018.03.038

Anene, A. F., Fredriksen, S. B., Sætre, K. A., & Tokheim, L. A. (2018). Experimental Study of Thermal and Catalytic Pyrolysis of Plastic Waste Components. *Sustainability 2018, Vol. 10, Page 3979*, *10*(11), 3979. https://doi.org/10.3390/SU10113979

Annual Report 2020-21 on Implementation of Plastic Waste Management Rules, 2016 Central Pollution Control Board. (n.d.).

Arabiourrutia, M., Olazar, M., Aguado, R., López, G., Baron, A., & Bilbao, J. (2008). HZSM-5 and HY Zeolite Catalyst Performance in the Pyrolysis of Tires in a Conical Spouted Bed Reactor. *Industrial and Engineering Chemistry Research*, *47*(20), 7600–7609. https://doi.org/10.1021/IE800376D

Artetxe, M., Lopez, G., Amutio, M., Elordi, G., Bilbao, J., & Olazar, M. (2013). Cracking of high density polyethylene pyrolysis waxes on HZSM-5 catalysts of different acidity. *Industrial and Engineering Chemistry Research*, *52*(31), 10637–10645. https://doi.org/10.1021/IE4014869/ASSET/IMAGES/MEDIUM/IE-2013-014869_0009.GIF

Bagri, R., & Williams, P. T. (2002). Catalytic pyrolysis of polyethylene. *Journal of Analytical and Applied Pyrolysis*, *63*(1), 29–41. https://doi.org/10.1016/S0165-2370(01)00139-5

Beach, E. S., Weeks, B. R., Stern, R., & Anastas, P. T. (2013). Plastics additives and green chemistry. *Pure and Applied Chemistry*, *85*(8), 1611–1624. https://doi.org/10.1351/PAC-CON-12-08-08

Benesi, H. A., & 61, V. (n.d.). *ACJDITY OF CATALYST SURFACES. 11. AMINE TITRATION USING HAMMETT INDICATORS*.

Bhurat, S., Pandey, S., Chintala, V., Jaiswal, M., & Kumar, A. (2021). Investigation of partially pre-mixed charge compression ignition engine characteristics implemented with toroidal combustion chamber and exhaust gas recirculation. *Https://Doi.Org/10.1080/15567036.2021.1909675*. https://doi.org/10.1080/15567036.2021.1909675

Bimbela, F., Ábrego, J., Gonzalo, A., Sánchez, J. L., & Arauzo, J. (2014). *Biomass pyrolysis liquids. Fundamentals, technologies and new strategies.*

Black, S. P., Sanders, J. K. M., & Stefankiewicz, A. R. (2014). Disulfide exchange: exposing supramolecular reactivity through dynamic covalent chemistry. *Chemical Society Reviews*, *43*(6), 1861–1872. https://doi.org/10.1039/C3CS60326A

Bortz, D. R., Heras, E. G., & Martin-Gullon, I. (2012). *Impressive Fatigue Life and Fracture Toughness Improvements in Graphene Oxide/Epoxy Composites*. *45*, 238–245. https://doi.org/10.1021/ma201563k

Brajendra K.Sharma, Bryan R.Moser, Karl E.Vermillion, Kenneth M.Doll, N. R., Sharma, B. K., Moser, B. R., Vermillion, K. E., Doll, K. M., Rajagopalan, N., Brajendra K.Sharma, Bryan R.Moser, Karl E.Vermillion, Kenneth M.Doll, N. R., Sharma, B. K., Moser, B. R., Vermillion, K. E., Doll, K. M., & Rajagopalan, N. (2014). Production, characterization and fuel properties of alternative diesel fuel from pyrolysis of waste plastic grocery bags. *Fuel Processing Technology*, *122*, 79–90. https://doi.org/10.1016/j.fuproc.2014.01.019

Brems, A., Baeyens, J., & Dewil, R. (2012). Recycling and recovery of post-cet alonsumer plastic solid waste in a European context. *Thermal Science*, *16*(3), 669–685. https://doi.org/10.2298/TSCI120111121B

Brown, E. N., Sottos, N. R., & White, S. R. (2002). Fracture testing of a self-healing polymer composite. *Experimental Mechanics 2002 42:4*, *42*(4), 372–379. https://doi.org/10.1007/BF02412141

Brown, E. N., White, S. R., & Sottos, N. R. (2004). Microcapsule induced toughening in a self-healing polymer composite. *Journal of Materials Science 2004 39:5*, *39*(5), 1703–1710. https://doi.org/10.1023/B:JMSC.0000016173.73733.DC

Brutman, J. P., Delgado, P. A., & Hillmyer, M. A. (2014). *Polylactide Vitrimers*. https://doi.org/10.1021/mz500269w

Buckley, T. J. (1991). Calculation of higher heating values of biomass materials and waste components from elemental analyses. *Resources, Conservation and Recycling*, *5*(4), 329–341. https://doi.org/10.1016/0921-3449(91)90011-C

Budsaereechai, S., Hunt, A. J., & Ngernyen, Y. (2019). Catalytic pyrolysis of plastic waste for the production of liquid fuels for engines. *RSC Advances*, *9*(10), 5844–5857. https://doi.org/10.1039/C8RA10058F

Bujak, J. W. (2015). Thermal utilization (treatment) of plastic waste. *Energy*, *90*, 1468–1477. https://doi.org/10.1016/J.ENERGY.2015.06.106

Burger, N., Laachachi, A., Ferriol, M., Lutz, M., Toniazzo, V., & Ruch, D. (2016). Review of thermal conductivity in composites: Mechanisms, parameters and theory. *Progress in Polymer Science*, *61*, 1–28. https://doi.org/10.1016/J.PROGPOLYMSCI.2016.05.001

Chen, D., Yin, L., Wang, H., & He, P. (2015a). Pyrolysis technologies for municipal solid waste: A review. *Waste Management*, *37*(12), 116–136. https://doi.org/10.1016/j.wasman.2015.01.022

Chen, D., Yin, L., Wang, H., & He, P. (2015b). Pyrolysis technologies for municipal solid waste: A review. *Waste Management*, *37*(12), 116–136. https://doi.org/10.1016/j.wasman.2015.01.022

Chen, F., Wu, C., Dong, L., Vassallo, A., Williams, P. T., & Huang, J. (2016). Characteristics and catalytic properties of Ni/CaAlOx catalyst for hydrogen-enriched syngas production

from pyrolysis-steam reforming of biomass sawdust. *Applied Catalysis B: Environmental*, *183*, 168–175. https://doi.org/10.1016/J.APCATB.2015.10.028

Chin, B. L. F., Yusup, S., Al Shoaibi, A., Kannan, P., Srinivasakannan, C., & Sulaiman, S. A. (2014). Kinetic studies of co-pyrolysis of rubber seed shell with high density polyethylene. *Energy Conversion and Management*, *87*, 746–753. https://doi.org/10.1016/J.ENCONMAN.2014.07.043

Chintala, V., Ghodke, P., Phadtare, S., Tadpatrikar, M., Pandey, J. K. K., Kumar, S., Ghodke, P., Phadtare, S., Tadpatrikar, M., Pandey, J. K. K., & Kumar, S. (2018). A comparative assessment of single cylinder diesel engine characteristics with plasto-oils derived from municipal mixed plastic waste. *Energy Conversion and Management*, *166*(April), 579–589. https://doi.org/10.1016/j.enconman.2018.04.068

Chintala, V., Godkhe, P., Phadtare, S., Tadpatrikar, M., Pandey, J. K., & Kumar, S. (2018). A comparative assessment of single cylinder diesel engine characteristics with plasto-oils derived from municipal mixed plastic waste. *Energy Conversion and Management*, *166*, 579–589. https://doi.org/10.1016/J.ENCONMAN.2018.04.068

Chitnis, S. R., & Sharma, M. M. (1997). Industrial applications of acid-treated clays as catalysts. *Reactive and Functional Polymers*, *32*(1), 93–115. https://doi.org/10.1016/S1381-5148(96)00074-0

Choi, S. J., Park, Y. K., Jeong, K. E., Kim, T. W., Chae, H. J., Park, S. H., Jeon, J. K., & Kim, S. S. (2010). Catalytic degradation of polyethylene over SBA-16. *Korean Journal of Chemical Engineering 2010 27:5*, *27*(5), 1446–1451. https://doi.org/10.1007/S11814-010-0281-9

Dahlbo, H., Poliakova, V., Mylläri, V., Sahimaa, O., & Anderson, R. (2018). Recycling potential of post-consumer plastic packaging waste in Finland. *Waste Management*, *71*, 52–61. https://doi.org/10.1016/J.WASMAN.2017.10.033

Dayana Anuar Sharuddin, S., Abnisa, F., Mohd Ashri Wan Daud, W., & Kheireddine Aroua, M. (n.d.). *A review on pyrolysis of plastic wastes*. https://doi.org/10.1016/j.enconman.2016.02.037

de Marco, I., Caballero, B. M., López, A., Laresgoiti, M. F., Torres, A., & Chomón, M. J. (2009). Pyrolysis of the rejects of a waste packaging separation and classification plant. *Journal of Analytical and Applied Pyrolysis*, *85*(1–2), 384–391. https://doi.org/10.1016/J.JAAP.2008.09.002

de Stefanis, A., Cafarelli, P., Gallese, F., Borsella, E., Nana, A., & Perez, G. (2013). Catalytic pyrolysis of polyethylene: A comparison between pillared and restructured clays. *Journal of Analytical and Applied Pyrolysis*, *104*, 479–484. https://doi.org/10.1016/J.JAAP.2013.05.023

Degnan, T. F. (2000). Applications of zeolites in petroleum refining. *Topics in Catalysis 2000 13:4*, *13*(4), 349–356. https://doi.org/10.1023/A:1009054905137

Demirbas, A. (2004). Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons. *Journal of Analytical and Applied Pyrolysis*, *72*(1), 97–102. https://doi.org/10.1016/J.JAAP.2004.03.001

Diaz Silvarrey, L. S., & Phan, A. N. (2016). Kinetic study of municipal plastic waste. *International Journal of Hydrogen Energy*, *41*(37), 16352–16364. https://doi.org/10.1016/J.IJHYDENE.2016.05.202

Donaj, P. J., Kaminsky, W., Buzeto, F., & Yang, W. (2012). Pyrolysis of polyolefins for increasing the yield of monomers' recovery. *Waste Management*, *32*(5), 840–846. https://doi.org/10.1016/J.WASMAN.2011.10.009

Duan, R.-T., He, Q.-X., Dong, X., Li, D.-F., Wang, X.-L., & Wang, Y.-Z. (2015). Renewable Sugar-Based Diols with Different Rigid Structure: Comparable Investigation on Improving Poly(butylene succinate) Performance. *ACS Sustainable Chemistry and Engineering*, *4*(1), 350–362. https://doi.org/10.1021/ACSSUSCHEMENG.5B01335

Duangchan, A., & Samart, C. (2008). Tertiary recycling of PVC-containing plastic waste by copyrolysis with cattle manure. *Waste Management*, *28*(11), 2415–2421. https://doi.org/10.1016/J.WASMAN.2007.12.010

Dyre, J. C. (2006). *Colloquium: The glass transition and elastic models of glass-forming liquids*. https://doi.org/10.1103/RevModPhys.78.953

Dyundi, S., Matolia, S., Singla, A., Kumar, D., Sharma, A., Bhurat, S., & Upadhyay, A. K. (n.d.). *Review on Biodiesel Production and Emission Characteristic of Non-Edible Vegetable Oil*. https://doi.org/10.1088/1757-899X/691/1/012024

Ebnesajjad, S., & Landrock, A. H. (2015). Characteristics of Adhesive Materials. *Adhesives Technology Handbook*, 84–159. https://doi.org/10.1016/B978-0-323-35595-7.00005-X

Elordi, G., Olazar, M., Lopez, G., Amutio, M., Artetxe, M., Aguado, R., & Bilbao, J. (2009). Catalytic pyrolysis of HDPE in continuous mode over zeolite catalysts in a conical spouted bed reactor. *Journal of Analytical and Applied Pyrolysis*, *85*(1–2), 345–351. https://doi.org/10.1016/J.JAAP.2008.10.015

Encinar, J. M., & González, J. F. (2008). *Pyrolysis of synthetic polymers and plastic wastes. Kinetic study*. https://doi.org/10.1016/j.fuproc.2007.12.011

Escola, J. M., Aguado, J., Serrano, D. P., García, A., Peral, A., Briones, L., Calvo, R., & Fernandez, E. (2011). Catalytic hydroreforming of the polyethylene thermal cracking oil over Ni supported hierarchical zeolites and mesostructured aluminosilicates. *Applied Catalysis B: Environmental*, *106*(3–4), 405–415. https://doi.org/10.1016/J.APCATB.2011.05.048

Fenouillot, F., Rousseau, A., Colomines, G., Saint-Loup, R., & Pascault, J. P. (2010). Polymers from renewable 1,4:3,6-dianhydrohexitols (isosorbide, isomannide and isoidide): A review.

Progress in Polymer Science (Oxford), *35*(5), 578–622. https://doi.org/10.1016/J.PROGPOLYMSCI.2009.10.001

Florea, N. M., Lungu, A., Badica, P., Craciun, L., Enculescu, M., Ghita, D. G., Ionescu, C., Zgirian, R. G., & Iovu, H. (2015). Novel nanocomposites based on epoxy resin/epoxy-functionalized polydimethylsiloxane reinforced with POSS. *Composites Part B: Engineering*, *75*, 226–234. https://doi.org/10.1016/J.COMPOSITESB.2015.01.043

Fogler, H., & Fogler, S. (1999). *Elements of chemical reaction engineering*. https://books.google.com/books?hl=en&lr=&id=tEZ1yPBnxBkC&oi=fnd&pg=PR17&ots=mc4ANS5wHv&sig=7UGUxBKUoiMT2PiX4LswU1fRN0U

Ganesh, D., Nagarajan, G., & Mohamed Ibrahim, M. (2008a). Study of performance, combustion and emission characteristics of diesel homogeneous charge compression ignition (HCCI) combustion with external mixture formation. *Fuel*, *87*(17–18), 3497–3503. https://doi.org/10.1016/J.FUEL.2008.06.010

Ganesh, D., Nagarajan, G., & Mohamed Ibrahim, M. (2008b). Study of performance, combustion and emission characteristics of diesel homogeneous charge compression ignition (HCCI) combustion with external mixture formation. *Fuel*, *87*(17–18), 3497–3503. https://doi.org/10.1016/J.FUEL.2008.06.010

Gerasimov, G., & Volkov, E. (2015). Modeling study of oil shale pyrolysis in rotary drum reactor by solid heat carrier. *Fuel Processing Technology*, *139*, 108–116. https://doi.org/10.1016/J.FUPROC.2015.08.001

Ghodke, P. K. (2021a). High-quality hydrocarbon fuel production from municipal mixed plastic waste using a locally available low-cost catalyst. *Fuel Communications*, *8*, 100022.

Ghodke, P. K. (2021b). High-quality hydrocarbon fuel production from municipal mixed plastic waste using a locally available low-cost catalyst. *Fuel Communications*, *8*, 100022. https://doi.org/10.1016/J.JFUECO.2021.100022

Ghodke, P., & Mandapati, R. N. (2018). *Investigation of particle level kinetic modeling for babul wood pyrolysis*. https://doi.org/10.1016/j.fuel.2018.09.084

Gil, A., Gandía, L. M., & Vicente, M. A. (2007). Recent Advances in the Synthesis and Catalytic Applications of Pillared Clays. *Https://Doi.Org/10.1081/CR-100100261*, *42*(1–2), 145–212. https://doi.org/10.1081/CR-100100261

Gray, A. W., & Ryan, T. W. (2018). *Homogeneous Charge Compression Ignition (HCCI) of Diesel Fuel*.

Guadagno, L., de Vivo, B., di Bartolomeo, A., Lamberti, P., Sorrentino, A., Tucci, V., Vertuccio, L., & Vittoria, V. (2011). Effect of functionalization on the thermo-mechanical and electrical behavior of multi-wall carbon nanotube/epoxy composites. *Carbon*, *49*(6), 1919–1930. https://doi.org/10.1016/J.CARBON.2011.01.017

Guadagno, L., Vertuccio, L., Naddeo, C., Calabrese, E., Barra, G., Raimondo, M., Sorrentino, A., Binder, W. H., Michael, P., & Rana, S. (2018). Development of aeronautical epoxy nanocomposites having an integrated selfhealing ability. *MATEC Web of Conferences*, *233*. https://doi.org/10.1051/MATECCONF/201823300021

Hummers, W. S., & Offeman, R. E. (n.d.). *339 PREPARATION OF GRAPHITIC OXIDE Preparation of Graphitic Oxide*.

Igathinathane, C., Shankar Tumuluru, J., Sokhansanj, S., Bi, X., Lim, C. J., Melin, S., & Mohammad, E. (n.d.). *Simple and inexpensive method of wood pellets macro-porosity measurement*. https://doi.org/10.1016/j.biortech.2010.03.034

Ivanova, S. R., Gumerova, E. F., Minsker, K. S., Zaikov, G. E., & Berlin, A. A. (1990). Selective catalytic degradation of polyolefins. *Progress in Polymer Science*, *15*(2), 193–215. https://doi.org/10.1016/0079-6700(90)90028-Y

Jamradloedluk, J., & Lertsatitthanakorn, C. (2014). Characterization and Utilization of Char Derived from Fast Pyrolysis of Plastic Wastes. *Procedia Engineering*, *69*, 1437–1442. https://doi.org/10.1016/J.PROENG.2014.03.139

Jiang, J. (2006). Study on out heating pyrolysis technology of municipal solid waste. In *Wuhan: Huazhong University of Science and Technology*.

Johnson, T., & Joshi, A. (2018). *Review of Vehicle Engine Efficiency and Emissions*. https://doi.org/10.4271/2018-01-0329

Jousseaume, B., Laporte, C., Toupance, T., & Bernard, J. M. (2002). Efficient bismuth catalysts for transcarbamoylation. *Tetrahedron Letters*, *43*(36), 6305–6307. https://doi.org/10.1016/S0040-4039(02)01391-6

Jung, S. H., Cho, M. H., Kang, B. S., & Kim, J. S. (2010). Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor. *Fuel Processing Technology*, *91*(3), 277–284. https://doi.org/10.1016/J.FUPROC.2009.10.009

Kaimal, V. K., & Vijayabalan, P. (2015). A detailed study of combustion characteristics of a DI diesel engine using waste plastic oil and its blends. *Energy Conversion and Management*, *105*, 951–956. https://doi.org/10.1016/j.enconman.2015.08.043

Kalargaris, I., Tian, G., & Gu, S. (2017). Combustion, performance and emission analysis of a DI diesel engine using plastic pyrolysis oil. *Fuel Processing Technology*, *157*. https://doi.org/10.1016/j.fuproc.2016.11.016

Kaminsky, W., & Kim, J. S. (1999). Pyrolysis of mixed plastics into aromatics. *Journal of Analytical and Applied Pyrolysis*, *51*(1–2), 127–134. https://doi.org/10.1016/S0165-2370(99)00012-1

Kaminsky, W., & Zorriqueta, I. J. N. (2007). Catalytical and thermal pyrolysis of polyolefins. *Journal of Analytical and Applied Pyrolysis*, *79*(1–2), 368–374. https://doi.org/10.1016/J.JAAP.2006.11.005

Kang, S., Hong, S. il, Choe, C. R., Park, M., Rim, S., & Kim, J. (2001). Preparation and characterization of epoxy composites filled with functionalized nanosilica particles obtained via sol–gel process. *Polymer*, *42*(3), 879–887. https://doi.org/10.1016/S0032-3861(00)00392-X

Kayacan, I., & Doğan, Ö. M. (2008). Pyrolysis of low and high density polyethylene. Part I: Non-isothermal pyrolysis kinetics. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, *30*(5), 385–391. https://doi.org/10.1080/15567030701457079

Kayacan, İ., & Doğan, Ö. M. (2008). Pyrolysis of Low and High Density Polyethylene. Part I: Non-isothermal Pyrolysis Kinetics. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, *30*(5), 385–391. https://doi.org/10.1080/15567030701457079

Kessler, M. R., Sottos, N. R., & White, S. R. (2003). Self-healing structural composite materials. *Composites Part A: Applied Science and Manufacturing*, *34*(8), 743–753. https://doi.org/10.1016/S1359-835X(03)00138-6

Kessler, M. R., & White, S. R. (2002). *Cure Kinetics of the Ring-Opening Metathesis Polymerization of Dicyclopentadiene*. https://doi.org/10.1002/pola.10317

Khuenkaeo, N., & Tippayawong, N. (2020). Production and characterization of bio-oil and biochar from ablative pyrolysis of lignocellulosic biomass residues. *Chemical Engineering Communications*, *207*(2), 153–160. https://doi.org/10.1080/00986445.2019.1574769

Kiliç, M., Pütün, E., & Pütün, A. E. (2014). Optimization of Euphorbia rigida fast pyrolysis conditions by using response surface methodology. *Journal of Analytical and Applied Pyrolysis*, *110*(1), 163–171. https://doi.org/10.1016/j.jaap.2014.08.018

Kishi, N., Kikuchi, S., Suzuki, N., & Hayashi, T. (1999). *Technology for Reducing Exhaust Gas Emissions in Zero Level Emission Vehicles(ZLEV)*.

Krishnakumar, B., Bose, D., Singh, M., Sanka, R. V. S. P., Gurunadh, V. V. S. S., Singhal, S., Parthasarthy, V., Guadagno, L., Vijayan P, P., Thomas, S., & Rana, S. (2021). Sugarcane Bagasse-Derived Activated Carbon- (AC-) Epoxy Vitrimer Biocomposite: Thermomechanical and Self-Healing Performance. *International Journal of Polymer Science*, *2021*. https://doi.org/10.1155/2021/5561755

Krishnakumar, B., Prasanna Sanka, R. V. S., Binder, W. H., Park, C., Jung, J., Parthasarthy, V., Rana, S., & Yun, G. J. (2020). Catalyst free self-healable vitrimer/graphene oxide nanocomposites. *Composites Part B: Engineering*, *184*(October 2019), 107647. https://doi.org/10.1016/j.compositesb.2019.107647

Kumar, D., Kumar, A., Singla, A., & Dewan, R. (2021). Production and tribological characterization of castor based biodiesel. *Materials Today: Proceedings*, *46*, 10942–10949. https://doi.org/10.1016/J.MATPR.2021.02.009

Kumar, N. (2019a). Study of oxygenated ecofuel applications in CI engine, gas turbine, and jet engine. *Advanced Biofuels: Applications, Technologies and Environmental Sustainability*, 405–441. https://doi.org/10.1016/B978-0-08-102791-2.00016-7

Kumar, N. (2019b). Study of oxygenated ecofuel applications in CI engine, gas turbine, and jet engine. *Advanced Biofuels: Applications, Technologies and Environmental Sustainability*, 405–441. https://doi.org/10.1016/B978-0-08-102791-2.00016-7

Kumar, S., Prakash, R., Murugan, S., & Singh, R. K. (2013a). *Performance and emission analysis of blends of waste plastic oil obtained by catalytic pyrolysis of waste HDPE with diesel in a CI engine*. https://doi.org/10.1016/j.enconman.2013.05.028

Kumar, S., Prakash, R., Murugan, S., & Singh, R. K. K. (2013b). Performance and emission analysis of blends of waste plastic oil obtained by catalytic pyrolysis of waste HDPE with diesel in a CI engine. *Energy Conversion and Management*, *74*, 323–331. https://doi.org/https://doi.org/10.1016/j.enconman.2013.05.028

Kumar, S., & Singh, R. K. (2011). Recovery of hydrocarbon liquid from waste high density polyethylene by thermal pyrolysis. *Brazilian Journal of Chemical Engineering*, *28*(4), 659–667. https://doi.org/10.1590/S0104-66322011000400011

Kunwar, B., Cheng, H. N., Chandrashekaran, S. R., & Sharma, B. K. (2015). *Plastics to fuel: a review*. https://doi.org/10.1016/j.rser.2015.10.015

Kurien, C., Srivastava, A. K., Kumar, D., Kurien, C., Srivastava, A. K., & Kumar, D. (2019). Geometric Design Validation of Oxidation Catalysis System in Composite Regeneration Emission Control System. *International Journal of Vehicle Structures and Systems*, *11*(1), 83–87. https://doi.org/10.4273/IJVSS.11.1.16

Kwanchareon, P., Luengnaruemitchai, A., & Jai-In, S. (2007). Solubility of a diesel-biodiesel-ethanol blend, its fuel properties, and its emission characteristics from diesel engine. *Fuel*, *86*(7–8), 1053–1061. https://doi.org/10.1016/J.FUEL.2006.09.034

Lewandowska, A., Monteverdi, S., Bettahar, M., & Ziolek, M. (2002). MCM-41 mesoporous molecular sieves supported nickel—physico-chemical properties and catalytic activity in hydrogenation of benzene. *Journal of Molecular Catalysis A: Chemical*, *188*(1–2), 85–95. https://doi.org/10.1016/S1381-1169(02)00339-4

Li, K., Lei, J., Yuan, G., Weerachanchai, P., Wang, J. Y., Zhao, J., & Yang, Y. (2017a). Fe-, Ti-, Zr- and Al-pillared clays for efficient catalytic pyrolysis of mixed plastics. *Chemical Engineering Journal*, *317*, 800–809. https://doi.org/10.1016/J.CEJ.2017.02.113

Li, K., Lei, J., Yuan, G., Weerachanchai, P., Wang, J. Y., Zhao, J., & Yang, Y. (2017b). Fe-, Ti-, Zr- and Al-pillared clays for efficient catalytic pyrolysis of mixed plastics. *Chemical Engineering Journal*, *317*, 800–809. https://doi.org/10.1016/J.CEJ.2017.02.113

Lin, C. Y., & Wang, K. H. (2004). Effects of a combustion improver on diesel engine performance and emission characteristics when using three-phase emulsions as an alternative fuel. *Energy and Fuels*, *18*(2), 477–484. https://doi.org/10.1021/EF0300848

Lin, R., O'Shea, R., Deng, C., Wu, B., & Murphy, J. D. (2021). A perspective on the efficacy of green gas production via integration of technologies in novel cascading circular bio-systems. *Renewable and Sustainable Energy Reviews*, *150*. https://doi.org/10.1016/J.RSER.2021.111427

Lin, X., Zhang, Z., Sun, J., Guo, W., & Wang, Q. (2015). Effects of phosphorus-modified HZSM-5 on distribution of hydrocarbon compounds from wood–plastic composite pyrolysis using Py-GC/MS. *Journal of Analytical and Applied Pyrolysis*, *116*, 223–230. https://doi.org/10.1016/J.JAAP.2015.09.007

Lin, Y. H., & Yang, M. H. (2007). Chemical catalysed recycling of waste polymers: Catalytic conversion of polypropylene into fuels and chemicals over spent FCC catalyst in a fluidised-bed reactor. *Polymer Degradation and Stability*, *92*(5), 813–821. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2007.01.028

Lin, Y. H., & Yen, H. Y. (2005). Fluidised bed pyrolysis of polypropylene over cracking catalysts for producing hydrocarbons. *Polymer Degradation and Stability*, *89*(1), 101–108. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2005.01.006

Lin, Y.-H. H., & Yen, H.-Y. Y. (2005). Fluidised bed pyrolysis of polypropylene over cracking catalysts for producing hydrocarbons. *Polymer Degradation and Stability*, *89*(1), 101–108. https://doi.org/10.1016/j.polymdegradstab.2005.01.006

Liu, T., Hao, C., Zhang, S., Yang, X., Wang, L., Han, J., Li, Y., Xin, J., & Zhang, J. (2018). A Self-Healable High Glass Transition Temperature Bioepoxy Material Based on Vitrimer Chemistry. *Macromolecules*, *51*(15), 5577–5585. https://doi.org/10.1021/ACS.MACROMOL.8B01010

López, A., de Marco, I., Caballero, B. M., Adrados, A., & Laresgoiti, M. F. (2011). Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes. *Waste Management*, *31*(8), 1852–1858. https://doi.org/10.1016/J.WASMAN.2011.04.004

López, A., de Marco, I., Caballero, B. M., Laresgoiti, M. F., & Adrados, A. (2011). Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor. *Chemical Engineering Journal*, *173*(1), 62–71. https://doi.org/10.1016/J.CEJ.2011.07.037

Lopez, G., Artetxe, M., Amutio, M., Bilbao, J., & Olazar, M. (2017). *Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review*. https://doi.org/10.1016/j.rser.2017.01.142

Ludlow-Palafox, C., & Chase, H. A. (2001). Microwave-Induced Pyrolysis of Plastic Wastes. *Industrial and Engineering Chemistry Research*, *40*(22), 4749–4756. https://doi.org/10.1021/IE010202J

Luzuriaga, A. R. de, Martin, R., Markaide, N., Rekondo, A., Cabañero, G., Rodríguez, J., & Odriozola, I. (2016). Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites. *Materials Horizons*, *3*(3), 241–247. https://doi.org/10.1039/C6MH00029K

Luzuriaga, A. R. de, Matxain, J. M., Ruipérez, F., Martin, R., Asua, J. M., Cabañero, G., & Odriozola, I. (2016). Transient mechanochromism in epoxy vitrimer composites containing aromatic disulfide crosslinks. *Journal of Materials Chemistry C*, *4*(26), 6220–6223. https://doi.org/10.1039/C6TC02383E

Ma, C., Yu, J., Wang, B., Song, Z., Zhou, F., Xiang, J., Hu, S., & Sun, L. (2016). Influence of Zeolites and Mesoporous Catalysts on Catalytic Pyrolysis of Brominated Acrylonitrile–Butadiene–Styrene (Br-ABS). *Energy and Fuels*, *30*(6), 4635–4643. https://doi.org/10.1021/ACS.ENERGYFUELS.6B00460

Ma, C., Yu, J., Yan, Q., Song, Z., Wang, K., Wang, B., & Sun, L. (2017). Pyrolysis-catalytic upgrading of brominated high impact polystyrene over Fe and Ni modified catalysts: Influence of HZSM-5 and MCM-41 catalysts. *Polymer Degradation and Stability*, *146*, 1–12. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2017.09.005

Mahadevan, R., Shakya, R., Neupane, S., & Adhikari, S. (2015). Physical and chemical properties and accelerated aging test of bio-oil produced from in situ catalytic pyrolysis in a bench-scale fluidized-bed reactor. *Energy and Fuels*, *29*(2), 841–848. https://doi.org/10.1021/EF502353M/SUPPL_FILE/EF502353M_SI_001.PDF

Malkow, T. (2004a). Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal. *Waste Management*, *24*(1), 53–79. https://doi.org/10.1016/S0956-053X(03)00038-2

Malkow, T. (2004b). Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal. *Waste Management*, *24*(1), 53–79. https://doi.org/10.1016/S0956-053X(03)00038-2

Mani, M., & Nagarajan, G. (2009). Influence of injection timing on performance, emission and combustion characteristics of a DI diesel engine running on waste plastic oil. *Energy*, *34*(10), 1617–1623. https://doi.org/10.1016/J.ENERGY.2009.07.010

Manos, G., Yusof, I. Y., Gangas, N. H., & Papayannakos, N. (2002). Tertiary Recycling of Polyethylene to Hydrocarbon Fuel by Catalytic Cracking over Aluminum Pillared Clays. *Energy and Fuels*, *16*(2), 485–489. https://doi.org/10.1021/EF0102364

Manos, G., Yusof, I. Y., Papayannakos, N., & Gangas, N. H. (2001). Catalytic Cracking of Polyethylene over Clay Catalysts. Comparison with an Ultrastable Y Zeolite. *Industrial and Engineering Chemistry Research*, *40*(10), 2220–2225. https://doi.org/10.1021/IE001048O

Marcilla, A., Hernández, M. del R., & García, Á. N. (2007). Study of the polymer–catalyst contact effectivity and the heating rate influence on the HDPE pyrolysis. *Journal of Analytical and Applied Pyrolysis*, *79*(1–2), 424–432. https://doi.org/10.1016/J.JAAP.2006.10.017

Marcilly, C. R. (2000). Where and how shape selectivity of molecular sieves operates in refining and petrochemistry catalytic processes. *Topics in Catalysis 2000 13:4*, *13*(4), 357–366. https://doi.org/10.1023/A:1009007021975

Martin, R., Rekondo, A., Luzuriaga, A. R. de, Cabañero, G., Grande, H. J., & Odriozola, I. (2014). The processability of a poly(urea-urethane) elastomer reversibly crosslinked with aromatic disulfide bridges. *Journal of Materials Chemistry A*, *2*(16), 5710–5715. https://doi.org/10.1039/C3TA14927G

Mastral, J. F., Berrueco, C., Gea, M., & Ceamanos, J. (2006). Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite. *Polymer Degradation and Stability*, *91*(12), 3330–3338. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2006.06.009

Miskolczi, N., Ateş, F., & Borsodi, N. (2013a). Comparison of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part II: Contaminants, char and pyrolysis oil properties. *Bioresource Technology*, *144*, 370–379. https://doi.org/10.1016/j.biortech.2013.06.109

Miskolczi, N., Ateş, F., & Borsodi, N. (2013b). Comparison of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part II: Contaminants, char and pyrolysis oil properties. *Bioresource Technology*, *144*, 370–379. https://doi.org/10.1016/j.biortech.2013.06.109

Moorthy Rajendran, K., Chintala, V., Sharma, A., Pal, S., Pandey, J. K., & Ghodke, P. (2020a). Review of catalyst materials in achieving the liquid hydrocarbon fuels from municipal mixed plastic waste (MMPW). *Materials Today Communications*, *24*(February), 100982. https://doi.org/10.1016/j.mtcomm.2020.100982

Moorthy Rajendran, K., Chintala, V., Sharma, A., Pal, S., Pandey, J. K., & Ghodke, P. (2020b). Review of catalyst materials in achieving the liquid hydrocarbon fuels from municipal mixed plastic waste (MMPW). *Materials Today Communications*, *24*, 100982. https://doi.org/10.1016/J.MTCOMM.2020.100982

Murali, T. P., Prasad, S. v., Surappa, M. K., Rohatgi, P. K., & Gopinath, K. (1982). Friction and wear behaviour of aluminium alloy coconut shell char particulate composites. *Wear*, *80*(2), 149–158. https://doi.org/10.1016/0043-1648(82)90214-9

Murata, K., Sato, K., & Sakata, Y. (2004). Effect of pressure on thermal degradation of polyethylene. *Journal of Analytical and Applied Pyrolysis*, *71*(2), 569–589. https://doi.org/10.1016/J.JAAP.2003.08.010

Ng, S. H., Seoud, H., Stanciulescu, M., & Sugimoto, Y. (1995). Conversion of Polyethylene to Transportation Fuels through Pyrolysis and Catalytic Cracking. *Energy and Fuels*, *9*(5), 735–742. https://doi.org/10.1021/EF00053A002/ASSET/EF00053A002.FP.PNG_V03

Nia, A. S., Rana, S., Döhler, D., Noirfalise, X., Belfiore, A., & Binder, W. H. (2014). Click chemistry promoted by graphene supported copper nanomaterials. *Chemical Communications*, *50*(97), 15374–15377. https://doi.org/10.1039/C4CC07774A

Obeid, F., Zeaiter, J., Al-Muhtaseb, A. H., & Bouhadir, K. (2014). Thermo-catalytic pyrolysis of waste polyethylene bottles in a packed bed reactor with different bed materials and catalysts. *Energy Conversion and Management*, *85*, 1–6. https://doi.org/10.1016/J.ENCONMAN.2014.05.075

Ogden, W. A., & Guan, Z. (2018). Recyclable, Strong, and Highly Malleable Thermosets Based on Boroxine Networks. *Journal of the American Chemical Society*, *140*(20), 6217–6220. https://doi.org/10.1021/JACS.8B03257/SUPPL_FILE/JA8B03257_SI_001.PDF

Olowojoba, G. B., Kopsidas, S., Eslava, S., Gutierrez, E. S., Kinloch, A. J., Mattevi, C., Rocha, V. G., & Taylor, A. C. (2017). A facile way to produce epoxy nanocomposites having excellent thermal conductivity with low contents of reduced graphene oxide. *Journal of Materials Science 2017 52:12*, *52*(12), 7323–7344. https://doi.org/10.1007/S10853-017-0969-X

Onwudili, J. A., Insura, N., & Williams, P. T. (2009). Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time. *Journal of Analytical and Applied Pyrolysis*, *86*(2), 293–303. https://doi.org/10.1016/J.JAAP.2009.07.008

Overview of Plastic Waste Management. (2013).

Oyedun, A. O., Gebreegziabher, T., Ng, D. K. S., & Hui, C. W. (2014). Mixed-waste pyrolysis of biomass and plastics waste - A modelling approach to reduce energy usage. *Energy*, *75*, 127–135. https://doi.org/10.1016/j.energy.2014.05.063

P, T., K, Y., RK, S., Y, J., HJ, Q., & W, Z. (2014). Heat- or water-driven malleability in a highly recyclable covalent network polymer. *Advanced Materials (Deerfield Beach, Fla.)*, *26*(23), 3938–3942. https://doi.org/10.1002/ADMA.201400317

Panda, A. K., & Singh, R. K. (2011). Catalytic performances of kaoline and silica alumina in the thermal degradation of polypropylene. *Journal of Fuel Chemistry and Technology*, *39*(3), 198–202. https://doi.org/10.1016/S1872-5813(11)60017-0

Panda, A. K., Singh, R. K., & Mishra, D. K. (2012). Thermo-catalytic degradation of thermocol waste to value added liquid products. *Asian Journal of Chemistry*, *24*(12), 5539–5542.

Parikh, J., Channiwala, S. A., & Ghosal, G. K. (2004). *A correlation for calculating HHV from proximate analysis of solid fuels*. https://doi.org/10.1016/j.fuel.2004.10.010

Park, C., Jung, J., & Yun, G. J. (2019). Thermomechanical properties of mineralized nitrogen-doped carbon nanotube/polymer nanocomposites by molecular dynamics simulations. *Composites Part B: Engineering*, *161*, 639–650. https://doi.org/10.1016/J.COMPOSITESB.2019.01.002

Park, J. J., Park, K., Kim, J. S., Maken, S., Song, H., Shin, H., Park, J. W., & Choi, M. J. (2003). Characterization of Styrene Recovery from the Pyrolysis of Waste Expandable Polystyrene. *Energy and Fuels*, *17*(6), 1576–1582. https://doi.org/10.1021/EF030102L

Park, K. B., Jeong, Y. S., Guzelciftci, B., & Kim, J. S. (2019). Characteristics of a new type continuous two-stage pyrolysis of waste polyethylene. *Energy*, *166*, 343–351. https://doi.org/10.1016/J.ENERGY.2018.10.078

Patrick, J. F., Robb, M. J., Sottos, N. R., Moore, J. S., & White, S. R. (2016). Polymers with autonomous life-cycle control. *Nature 2016 540:7633*, *540*(7633), 363–370. https://doi.org/10.1038/nature21002

Peng, M., Tang, X., & Zhou, Y. (2016). Fast phase transfer of graphene oxide from water to triglycidyl para-aminophenol for epoxy composites with superior nanosheet dispersion. *Polymer*, *93*, 1–8. https://doi.org/10.1016/J.POLYMER.2016.03.016

Performance and combustion characteristics of biodiesel–diesel–methanol blend fuelled engine | Elsevier Enhanced Reader. (n.d.). Retrieved December 23, 2021, from https://reader.elsevier.com/reader/sd/pii/S0306261909004449?token=FFF1359A46280F4FDA56D884D6E3D8339960581ED41F4643DA0F4566FA79D817952FF0ACCC5B25512EF0D980B2188DFD&originRegion=eu-west-1&originCreation=20211223082228

Pielichowski, K., & Njuguna, J. (2005). *Thermal degradation of polymeric materials*. https://books.google.com/books?hl=en&lr=&id=bo8MVDXVy9kC&oi=fnd&pg=PR9&ots=mbGHzYZbG4&sig=6wB6NZXRixVycVeGHAob1iKd4rA

Pinto, F., Costa, P., Gulyurtlu, I., & Cabrita, I. (1999). Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield. *Journal of Analytical and Applied Pyrolysis*, *51*(1–2), 39–55. https://doi.org/10.1016/S0165-2370(99)00007-8

Porzio, G. F., Colla, V., Fornai, B., Vannucci, M., Larsson, M., & Stripple, H. (2016). Process integration analysis and some economic-environmental implications for an innovative environmentally friendly recovery and pre-treatment of steel scrap. *Applied Energy*, *161*, 656–672. https://doi.org/10.1016/J.APENERGY.2015.08.086

Punkkinen, H., Oasmaa, A., Laatikainen-Luntama, J., Nieminen, M., & Laine-Ylijoki, J. (n.d.). Thermal conversion of plastic containing waste: a review. *Arvifinalreport.Fi*. Retrieved July 25, 2022, from http://arvifinalreport.fi/files/Thermal%20conversion%20of%20plastic-containing%20waste%20A%20review.pdf

Rakopoulos, C. D., Antonopoulos, K. A., & Rakopoulos, D. C. (2007). Experimental heat release analysis and emissions of a HSDI diesel engine fueled with ethanol–diesel fuel blends. *Energy*, *32*(10), 1791–1808. https://doi.org/10.1016/J.ENERGY.2007.03.005

Rana, S., Döhler, D., Nia, A. S., Nasir, M., Beiner, M., & Binder, W. H. (2016). "Click"-Triggered Self-Healing Graphene Nanocomposites. *Macromolecular Rapid Communications*, *37*(21), 1715–1722. https://doi.org/10.1002/MARC.201600466

Renzini, M. S., Lerici, L. C., Sedran, U., & Pierella, L. B. (2011). Stability of ZSM-11 and BETA zeolites during the catalytic cracking of low-density polyethylene. *Journal of Analytical and Applied Pyrolysis*, *92*(2), 450–455. https://doi.org/10.1016/J.JAAP.2011.08.008

Robert F. Landel, L. E. N. (1994). *Mechanical Properties of Polymers and Composites, Second Edition*. Marcel Dekker, Inc. https://www.routledge.com/Mechanical-Properties-of-Polymers-and-Composites/Landel-Nielsen/p/book/9780824789640

Ruoppolo, G., Ammendola, P., Chirone, R., & Miccio, F. (2012). H2-rich syngas production by fluidized bed gasification of biomass and plastic fuel. *Waste Management*, *32*(4), 724–732. https://doi.org/10.1016/J.WASMAN.2011.12.004

Sakata, Y., Azhar Uddin, M., Muto, A., Kanada, Y., Koizumi, K., & Murata, K. (1997). Catalytic degradation of polyethylene into fuel oil over mesoporous silica (KFS-16) catalyst. *Journal of Analytical and Applied Pyrolysis*, *43*(1), 15–25. https://doi.org/10.1016/S0165-2370(97)00052-1

Sakata, Y., Uddin, M. A., & Muto, A. (1999). Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts. *Journal of Analytical and Applied Pyrolysis*, *51*(1), 135–155. https://doi.org/10.1016/S0165-2370(99)00013-3

Sarker, M., Rashid, M. M., & Molla, M. (2012). Waste polypropylene plastic conversion into liquid hydrocarbon fuel for producing electricity and energies. *Http://Dx.Doi.Org/10.1080/09593330.2012.676075*, *33*(24), 2709–2721. https://doi.org/10.1080/09593330.2012.676075

Saving energy and reducing pollution by use of emulsified palm-biodiesel blends with bio-solution additive | Elsevier Enhanced Reader. (n.d.). Retrieved December 23, 2021, from https://reader.elsevier.com/reader/sd/pii/S036054421000023X?token=EC749D326B6D42B74AA83EBD35A602AE7D6E397953132A934E9A68A756364433853B7F56990E5C0A7C95E3C14DAF0F56&originRegion=eu-west-1&originCreation=20211223081241

Sayin, C., Ilhan, M., Canakci, M., & Gumus, M. (2009). Effect of injection timing on the exhaust emissions of a diesel engine using diesel–methanol blends. *Renewable Energy*, *34*(5), 1261–1269. https://doi.org/10.1016/J.RENENE.2008.10.010

Senthilkumar, P., & Sankaranarayanan, G. (2016). Effect of Jatropha methyl ester on waste plastic oil fueled DI diesel engine. *Journal of the Energy Institute*, *89*(4), 504–512. https://doi.org/10.1016/j.joei.2015.07.006

Serrano, D. P., Aguado, J., & Escola, J. M. (2000). Catalytic Cracking of a Polyolefin Mixture over Different Acid Solid Catalysts. *Industrial and Engineering Chemistry Research*, *39*(5), 1177–1184. https://doi.org/10.1021/IE9906363

Serrano, D. P., Aguado, J., & Escola, J. M. (2012). Developing advanced catalysts for the conversion of polyolefinic waste plastics into fuels and chemicals. *ACS Catalysis*, *2*(9), 1924–1941. https://doi.org/10.1021/CS3003403/ASSET/IMAGES/MEDIUM/CS-2012-003403_0022.GIF

Serrano, D. P., Aguado, J., Escola, J. M., & Rodríguez, J. M. (2005). Influence of nanocrystalline HZSM-5 external surface on the catalytic cracking of polyolefins. *Journal of Analytical and Applied Pyrolysis*, *74*(1–2), 353–360. https://doi.org/10.1016/J.JAAP.2004.11.037

Shah, S. H., Khan, Z. M., Raja, I. A., Mahmood, Q., Bhatti, Z. A., Khan, J., Farooq, A., Rashid, N., & Wu, D. (2010). Low temperature conversion of plastic waste into light hydrocarbons. *Journal of Hazardous Materials*, *179*(1–3), 15–20. https://doi.org/10.1016/J.JHAZMAT.2010.01.134

Sharma, A. K., Sharma, P. K., Chintala, V., Khatri, N., & Patel, A. (2020). Environment-Friendly Biodiesel/Diesel Blends for Improving the Exhaust Emission and Engine Performance to Reduce the Pollutants Emitted from Transportation Fleets. *International Journal of Environmental Research and Public Health*, *17*(11), 3896. https://doi.org/10.3390/ijerph17113896

Sharma, B. K., Moser, B. R., Vermillion, K. E., Doll, K. M., & Rajagopalan, N. (2014). *Production, characterization and fuel properties of alternative diesel fuel from pyrolysis of waste plastic grocery bags ☆*. https://doi.org/10.1016/j.fuproc.2014.01.019

Sharypov, V. I., Marin, N., Beregovtsova, N. G., Baryshnikov, S. V., Kuznetsov, B. N., Cebolla, V. L., & Weber, J. V. (2002). Co-pyrolysis of wood biomass and synthetic polymer mixtures. Part I: influence of experimental conditions on the evolution of solids, liquids and gases. *Journal of Analytical and Applied Pyrolysis*, *64*(1), 15–28. https://doi.org/10.1016/S0165-2370(01)00167-X

Singh, D., Sharma, D., Soni, S. L., Inda, C. S., Sharma, S., Sharma, P. K., & Jhalani, A. (2021). A comprehensive review of physicochemical properties, production process, performance and emissions characteristics of 2nd generation biodiesel feedstock: Jatropha curcas. *Fuel*, *285*, 119110. https://doi.org/https://doi.org/10.1016/j.fuel.2020.119110

Sjöberg, M., & Dec, J. E. (2011). Effects of EGR and its constituents on HCCI autoignition of ethanol. *Proceedings of the Combustion Institute*, *33*(2), 3031–3038. https://doi.org/10.1016/J.PROCI.2010.06.043

Sun, Y., Zhang, Z., Moon, K. S., & Wong, C. P. (2004). Glass transition and relaxation behavior of epoxy nanocomposites. *Journal of Polymer Science Part B: Polymer Physics*, *42*(21), 3849–3858. https://doi.org/10.1002/POLB.20251

Tan, H., Lee, C. T., Ong, P. Y., Wong, K. Y., Bong, C. P. C., Li, C., & Gao, Y. (2021). A Review On The Comparison Between Slow Pyrolysis And Fast Pyrolysis On The Quality Of Lignocellulosic And Lignin-Based Biochar. *IOP Conference Series: Materials Science and Engineering*, *1051*(1), 012075. https://doi.org/10.1088/1757-899x/1051/1/012075

Tesoro, G. (1988). Epoxy resins-chemistry and technology, 2nd Edition, Clayton A. May, Ed., Marcel Dekker, New York, 1988, 1,288 pp. Price: $195.00. *Journal of Polymer Science Part C: Polymer Letters*, *26*(12), 539–539. https://doi.org/10.1002/POL.1988.140261212

Thahir, R., Altway, A., Juliastuti, S. R., & Susianto. (2019). Production of liquid fuel from plastic waste using integrated pyrolysis method with refinery distillation bubble cap plate column. *Energy Reports*, *5*, 70–77. https://doi.org/10.1016/J.EGYR.2018.11.004

Thahir, R., Altway, A., & Rachmania Juliastuti, S. (2019). Production of liquid fuel from plastic waste using integrated pyrolysis method with refinery distillation bubble cap plate column. *Energy Reports*, *5*, 70–77. https://doi.org/10.1016/j.egyr.2018.11.004

Undri, A., Rosi, L., Frediani, M., & Frediani, P. (2014). Efficient disposal of waste polyolefins through microwave assisted pyrolysis. *Fuel*, *116*, 662–671. https://doi.org/10.1016/J.FUEL.2013.08.037

Valle, B., Gayubo, A. G., Aguayo, A. T., Olazar, M., & Bilbao, J. (2010). Selective Production of Aromatics by Crude Bio-oil Valorization with a Nickel-Modified HZSM-5 Zeolite Catalyst. *Energy and Fuels*, *24*(3), 2060–2070. https://doi.org/10.1021/EF901231J

Verma, A., Gaur, A., & Singh, V. K. (2017). Mechanical Properties and Microstructure of Starch and Sisal Fiber Biocomposite Modified with Epoxy Resin. *Materials Performance and Characterization*, *6*(1), 500–520. https://doi.org/10.1520/MPC20170069

Verma, A., Negi, P., & Singh, V. K. (2018). Experimental investigation of chicken feather fiber and crumb rubber reformed epoxy resin hybrid composite: mechanical and microstructural characterization. *Journal of the Mechanical Behavior of Materials*, *27*(3–4). https://doi.org/10.1515/JMBM-2018-0014

Verma, A., Negi, P., & Singh, V. K. (2019). Experimental Analysis on Carbon Residuum Transformed Epoxy Resin: Chicken Feather Fiber Hybrid Composite. *Polymer Composites*, *40*(7), 2690–2699. https://doi.org/10.1002/PC.25067

Walendziewski, J. (2005). Continuous flow cracking of waste plastics. *Fuel Processing Technology*, *86*(12–13), 1265–1278. https://doi.org/10.1016/J.FUPROC.2004.12.004

Werther, J., & Ogada, T. (n.d.). *Sewage sludge combustion*.

White, S. R., Moore, J. S., Sottos, N. R., Krull, B. P., Santa Cruz, W. A., & Gergely, R. C. R. (2014). Restoration of large damage volumes in polymers. *Science*, *344*(6184), 620–623. https://doi.org/10.1126/SCIENCE.1251135

White, S. R., Sottos, N. R., Geubelle, P. H., Moore, J. S., Kessler, M. R., Sriram, S. R., Brown, E. N., & Viswanathan, S. (2001). Autonomic healing of polymer composites. *Nature*, *409*(6822), 794–797. https://doi.org/10.1038/35057232

Williams, P. T., & Williams, E. A. (1998). Interaction of Plastics in Mixed-Plastics Pyrolysis. *Energy and Fuels*, *13*(1), 188–196. https://doi.org/10.1021/EF980163X

Xu, J., Liu, J., Ling, P., Zhang, X., Xu, K., He, L., Wang, Y., Su, S., Hu, S., & Xiang, J. (2020). Raman spectroscopy of biochar from the pyrolysis of three typical Chinese biomasses: A novel method for rapidly evaluating the biochar property. *Energy*, *202*, 117644. https://doi.org/10.1016/J.ENERGY.2020.117644

Yang, W. J., Tao, X., Zhao, T., Weng, L., Kang, E.-T., & Wang, L. (2015). Antifouling and antibacterial hydrogel coatings with self-healing properties based on a dynamic disulfide exchange reaction. *Polymer Chemistry*, *6*(39), 7027–7035. https://doi.org/10.1039/C5PY00936G

Yang, X., Liang, C., Ma, T., Guo, Y., Kong, J., Gu, J., Chen, M., & Zhu, J. (2018). A review on thermally conductive polymeric composites: classification, measurement, model and equations, mechanism and fabrication methods. *Advanced Composites and Hybrid Materials 2018 1:2*, *1*(2), 207–230. https://doi.org/10.1007/S42114-018-0031-8

Yang, Y., Brammer, J. G., Ouadi, M., Samanya, J., Hornung, A., Xu, H. M., & Li, Y. (2012). *Characterisation of waste derived intermediate pyrolysis oils for use as diesel engine fuels*. https://doi.org/10.1016/j.fuel.2012.07.014

Yassin, K., & Hojjati, M. (2017). Processing of thermoplastic matrix composites through automated fiber placement and tape laying methods: A review. *Https://Doi.Org/10.1177/0892705717738305*, *31*(12), 1676–1725. https://doi.org/10.1177/0892705717738305

Zako, M., & Takano, N. (2016). Intelligent Material Systems Using Epoxy Particles to Repair Microcracks and Delamination Damage in GFRP: *Http://Dx.Doi.Org/10.1106/YEIH-QUDH-FC7W-4QFM*, *10*(10), 836–841. https://doi.org/10.1106/YEIH-QUDH-FC7W-4QFM

Zhang, S., Liu, T., Hao, C., Wang, L., Han, J., Liu, H., & Zhang, J. (2018). Preparation of a lignin-based vitrimer material and its potential use for recoverable adhesives. *Green Chemistry*, *20*(13), 2995–3000. https://doi.org/10.1039/C8GC01299G

Zhang, Y., Ghaly, A., and, B. L.-A. J. of B., & 2012, undefined. (n.d.). Physical properties of corn residues. *Cabdirect.Org*. Retrieved July 25, 2022, from https://www.cabdirect.org/cabdirect/abstract/20123299174

Zhang, Y., Nahil, M. A., Wu, C., & Williams, P. T. (2017). Pyrolysis–catalysis of waste plastic using a nickel–stainless-steel mesh catalyst for high-value carbon products. *Http://Dx.Doi.Org/10.1080/09593330.2017.1281351*, *38*(22), 2889–2897. https://doi.org/10.1080/09593330.2017.1281351

Zhang, Y., Wu, C., Nahil, M. A., & Williams, P. (2015). Pyrolysis-catalytic reforming/gasification of waste tires for production of carbon nanotubes and hydrogen. *Energy and Fuels*, *29*(5), 3328–3334. https://doi.org/10.1021/ACS.ENERGYFUELS.5B00408/ASSET/IMAGES/MEDIUM/EF-2015-00408Z_0009.GIF

Zhao, W., Hasegawa, S., Fujita, J., Yoshii, F., Sasaki, T., Makuuchi, K., Sun, J., & Nishimoto, S. I. (1996). Effects of zeolites on the pyrolysis of polypropylene. *Polymer Degradation and Stability*, *53*(1), 129–135. https://doi.org/10.1016/0141-3910(96)00080-8

LIST OF PATENT GRANTED AND JOURNAL PUBLICATIONS

A) Patent granted

1. Patent granted on 17.09.2020 title: "A catalyst for pyrolysis of mixed plastic waste and a method of pyrolysis thereof, Indian Patent. Patent no: 346952

B) Articles publication

1. Review paper entitled "Review of catalyst materials in achieving the liquid hydrocarbon fuels from Municipal mixed plastic waste (MMPW)" has been published in Materials Today Communications by Elsevier (SCI indexed) IF=3.662, Volume 24, Sep 2020. https://doi.org/10.1016/j.mtcomm.2020.100982

2. Research paper entitled "Production and characterization of hydrocarbon fuels from Municipal Mixed Plastic Waste obtained through Pilot Scale Pyrolysis Reactor" has been published in Materials Today Proceeding by Elsevier (Scopus indexed) https://doi.org/10.1016/j.matpr.2023.02.277.

3. Research paper entitled "Self-healing and thermomechanical performance of activated carbon pyrochar from municipal mixed plastic waste pyrolysis process added self-healing epoxy vitrimer bio composites" has been published in Nature environment and pollution technology (Scopus indexed) 10.46488/NEPT.2023.v22i01.038.

4. Research paper entitled "Experimental investigation on pyrolysis of domestic plastic wastes for fuel grade hydrocarbons" has been published in Processes by MDPI, *11*(1), 71, Dec 2022. (IF:3.352) https://doi.org/10.3390/pr11010071

C) International conference presentation

1. A paper entitled "CFD simulations on effect of plate spacing for better performance of parallel plate column for Carbon dioxide absorption" has been presented in 1st International Conference on clean and renewable energy 2019 hosted by NIT Durgapur, India.

2. A paper entitled "A Novel Plasma based Gasification for Treatment of Municipal Solid Wastes and Textile Sludge Wastes", has been presented in 1st International Conference

Advance in Plasma Science and Technology 2020 hosted by Sri Shakthi Institute of Engineering and Technology, Tamilnadu, India.

3. A paper entitled “Comparative assessment on the production of transportation fuels from mixed plastic waste and virgin plastics”, has been presented in Advances & Innovations in Recycling engineering (AIR) - 2021 hosted by UPES, Dehradun, Uttarakhand, India.

APPENDIX

Krishna Moorthy Rajendran

EDUCATION

Examination	Institute	University	Year	CPI / %
Doctorate	University of Petroleum and Energy Studies, Dehradun	University of Petroleum and Energy Studies, Dehradun	2019-Present	Thesis submitted
Post-Graduation (Energy Engineering)	PSG College of Technology, Coimbatore	Anna university, Chennai	2016	7.08
Graduation (Mechanical Engineering)	Shivani institute of Technology, Trichy	Anna university, Chennai	2013	7.68
HSC/+2	Thiakesar Alai Hr. Sec. school, Manapparai	State Board, Tamil Nadu	2009	69.75
SSLC	Thiakesar Alai Hr. Sec. school, Manapparai	State Board, Tamil Nadu	2007	75.6

UPES
UNIVERSITY OF TOMORROW

PLAGIARISM CERTIFICATE

1. We **Dr. Deepak kumar (Supervisor) and Dr. Bhawna Yadav Lamba (Co Supervisor)** certify that the Thesis titled **"Development of a novel technology for production and utilization of hydrocarbon fuels from mixed plastic waste"** submitted by Scholar **Mr. Krishna Moorthy. R** having **SAP ID 500073637** has been run through a Plagiarism Check Software and the Plagiarism Percentage is reported to be 10 %.

2. Plagiarism Report generated by the Plagiarism Software is attached .

Signature of the Supervisor

Signature of the Co-Supervisor

Signature of the Scholar

PLAGIARISM CERTIFICATE

1. We **Dr. Deepak kumar (Supervisor) and Dr. Bhawna Yadav Lamba (Co Supervisor)** certify that the Thesis titled **"Development of a novel technology for production and utilization of hydrocarbon fuels from mixed plastic waste"** submitted by Scholar **Mr. Krishna Moorthy. R** having **SAP ID 500073637** has been run through a Plagiarism Check Software and the Plagiarism Percentage is reported to be 10 %.

2. Plagiarism Report generated by the Plagiarism Software is attached .

Signature of the Supervisor **Signature of the Co-Supervisor**

Signature of the Scholar

T 8

ORIGINALITY REPORT

10%	4%	9%	1%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Praveen Kumar Ghodke. "High-quality hydrocarbon fuel production from municipal mixed plastic waste using a locally available low-cost catalyst", Fuel Communications, 2021 Publication	1%
2	Dezhen Chen, Lijie Yin, Huan Wang, Pinjing He. "Pyrolysis technologies for municipal solid waste: A review", Waste Management, 2014 Publication	<1%
3	Balaji Krishnakumar, R.V.Siva Prasanna Sanka, Wolfgang H. Binder, Chanwook Park et al. "Catalyst free self-healable vitrimer/graphene oxide nanocomposites", Composites Part B: Engineering, 2020 Publication	<1%
4	Funda Ateş, Norbert Miskolczi, Nikolett Borsodi. "Comparision of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part I: Product yields, gas and pyrolysis oil properties", Bioresource Technology, 2013 Publication	<1%

5	www.science.gov Internet Source	<1%
6	Anuar Sharuddin, Shafferina Dayana, Faisal Abnisa, Wan Mohd Ashri Wan Daud, and Mohamed Kheireddine Aroua. "A review on pyrolysis of plastic wastes", Energy Conversion and Management, 2016. Publication	<1%
7	umexpert.um.edu.my Internet Source	<1%
8	"Advances in IC Engines and Combustion Technology", Springer Science and Business Media LLC, 2021 Publication	<1%
9	Kaixin Li, Junxi Lei, Guoan Yuan, Piyarat Weerachanchai, Jing-Yuan Wang, Jun Zhao, Yanhui Yang. "Fe-, Ti-, Zr- and Al-pillared clays for efficient catalytic pyrolysis of mixed plastics", Chemical Engineering Journal, 2017 Publication	<1%
10	D. P. Serrano, J. Aguado, J. M. Escola. "Developing Advanced Catalysts for the Conversion of Polyolefinic Waste Plastics into Fuels and Chemicals", ACS Catalysis, 2012 Publication	<1%
11	Dong Hui Qi, Hao Chen, Chia Fon Lee, Li Min Geng, Yao Zhang Bian. "Experimental Studies	<1%

	of a Naturally Aspirated, DI Diesel Engine Fuelled with Ethanol–Biodiesel–Water Microemulsions", Energy & Fuels, 2010 Publication	
12	www.rsc.org Internet Source	<1 %
13	www.researchgate.net Internet Source	<1 %
14	K. Viswanath Allamraju. "Mechanical behaviour of nano jute filler glass fiber self healing and epoxy resin composite", Materials Today: Proceedings, 2018 Publication	<1 %
15	Bhawna Yadav Lamba, Sapna Jain, Amit Kumar Sharma, Sanjeev Kumar. "PPE kit to bio-oil: an experimental investigation", Biofuels, 2022 Publication	<1 %
16	Rahul Mishra, Aman Kumar, Ekta Singh, Sunil Kumar. "Recent Research Advancements in Catalytic Pyrolysis of Plastic Waste", ACS Sustainable Chemistry & Engineering, 2023 Publication	<1 %
17	openarchive.usn.no Internet Source	<1 %
18	Swapnil Bhurat, Shyam Pandey, Venkateshwarlu Chintala, Manas Jaiswal,	<1 %

Aditya Kumar. "Investigation of partially pre-mixed charge compression ignition engine characteristics implemented with toroidal combustion chamber and exhaust gas recirculation", Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 2021
Publication

---

19 Venkateswarlu Chintala, Praveen Godkhe, Shirish Phadtare, Medha Tadpatrikar, J.K. Pandey, Suresh Kumar. "A comparative assessment of single cylinder diesel engine characteristics with plasto-oils derived from municipal mixed plastic waste", Energy Conversion and Management, 2018 <1%
Publication

---

20 Devy K. Ratnasari, Mohamad A. Nahil, Paul T. Williams. "Catalytic pyrolysis of waste plastics using staged catalysis for production of gasoline range hydrocarbon oils", Journal of Analytical and Applied Pyrolysis, 2017 <1%
Publication

---

21 Guadagno, L.. "Mechanical and barrier properties of epoxy resin filled with multi-walled carbon nanotubes", Carbon, 200908 <1%
Publication

---

22 www.tandfonline.com <1%
Internet Source

23	N. Miskolczi, L. Bartha, G. Deák, B. Jóver. "Thermal degradation of municipal plastic waste for production of fuel-like hydrocarbons", Polymer Degradation and Stability, 2004 Publication	<1 %
24	Vallinayagam, R., S. Vedharaj, W.M. Yang, P.S. Lee, K.J.E. Chua, and S.K. Chou. "Combustion performance and emission characteristics study of pine oil in a diesel engine", Energy, 2013. Publication	<1 %
25	Submitted to University of Western Ontario Student Paper	<1 %
26	hdl.handle.net Internet Source	<1 %
27	F. Faisal, M.G. Rasul, M.I. Jahirul, D. Schaller. "Pyrolytic conversion of waste plastics to energy products: A review on yields, properties, and production costs", Science of The Total Environment, 2022 Publication	<1 %
28	www.mdpi.com Internet Source	<1 %
29	dokumen.pub Internet Source	<1 %

30	Zhiyan Ma, Yan Wang, Jing Zhu, Junrong Yu, Zuming Hu. "Bio-based epoxy vitrimers: Reprocessibility, controllable shape memory, and degradability", Journal of Polymer Science Part A: Polymer Chemistry, 2017 Publication	<1 %
31	De Stefanis, Adriana, Patrizia Cafarelli, Fortunata Gallese, Elisabetta Borsella, Agostino Nana, and Giorgio Perez. "Catalytic pyrolysis of polyethylene: A comparison between pillared and restructured clays", Journal of Analytical and Applied Pyrolysis, 2013. Publication	<1 %
32	Soundararajan Gopinath, P. K. Devan, K. Pitchandi. "Production of pyrolytic oil from ULDP plastics using silica-alumina catalyst and used as fuel for DI diesel engine", RSC Advances, 2020 Publication	<1 %
33	Yujie Peng, Yunpu Wang, Linyao Ke, Leilei Dai, Qiuhao Wu, Kirk Cobb, Yuan Zeng, Rongge Zou, Yuhuan Liu, Roger Ruan. "A review on catalytic pyrolysis of plastic wastes to high-value products", Energy Conversion and Management, 2022 Publication	<1 %
	ethesis.nitrkl.ac.in	

34	Internet Source	<1 %
35	Shilpa Mahamulkar, Kehua Yin, Pradeep K. Agrawal, Robert J. Davis, Christopher W. Jones, Andrzej Malek, Hirokazu Shibata. "Formation and Oxidation/Gasification of Carbonaceous Deposits: A Review", Industrial & Engineering Chemistry Research, 2016 Publication	<1 %
36	addi.ehu.es Internet Source	<1 %
37	Submitted to University of Leeds Student Paper	<1 %
38	mafiadoc.com Internet Source	<1 %
39	Marvin Kusenberg, Andreas Eschenbacher, Marko R. Djokic, Azd Zayoud, Kim Ragaert, Steven De Meester, Kevin M. Van Geem. "Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate?", Waste Management, 2022 Publication	<1 %
40	Merve Soganciogl u, Esra Yel, Gulnare Ahmetli. "Behaviour of waste polypropylene pyrolysis char-based epoxy composite materials",	<1 %

Environmental Science and Pollution Research, 2019
Publication

41	www.ijert.org Internet Source	<1%
42	Maite Artetxe, Gartzen Lopez, Maider Amutio, Gorka Elordi, Javier Bilbao, Martin Olazar. "Cracking of High Density Polyethylene Pyrolysis Waxes on HZSM-5 Catalysts of Different Acidity", Industrial & Engineering Chemistry Research, 2013 Publication	<1%
43	Hao Zhang, Liang Guo, Yuying Yan, Wanchen Sun, Jun Li, Qiao Wang, Yi Sun. "Experimental investigation on the combustion and emissions characteristics of an N-butanol/CTL dual fuel engine", Fuel, 2020 Publication	<1%
44	Qian Zhou, Yu-Zhong Wang, Chao Tang, Yu-Hua Zhang. "Modifications of ZSM-5 zeolites and their applications in catalytic degradation of LDPE", Polymer Degradation and Stability, 2003 Publication	<1%
45	www.marketsandmarkets.com Internet Source	<1%

46	A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados. "Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor", Chemical Engineering Journal, 2011 Publication	<1 %
47	Kiran Raj Bukkarapu, D. Siva Gangadhar, Y. Jyothi, Prasad Kanasani. "Management, conversion, and utilization of waste plastic as a source of sustainable energy to run automotive: a review", Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 2018 Publication	<1 %
48	Mani, M.. "Characterisation and effect of using waste plastic oil and diesel fuel blends in compression ignition engine", Energy, 201101 Publication	<1 %
49	link.springer.com Internet Source	<1 %
50	www.jree.ir Internet Source	<1 %
51	Suek Joo Choi, Young-Kwon Park, Kwang-Eun Jeong, Tae-Wan Kim, Ho-Jeong Chae, Sung Hoon Park, Jong-Ki Jeon, Seung-Soo Kim. "Catalytic degradation of polyethylene over	<1 %

SBA-16", Korean Journal of Chemical Engineering, 2010
Publication

52	Eleni Antonakou, Angelos Lappas, Merete H. Nilsen, Aud Bouzga, Michael Stöcker. "Evaluation of various types of Al-MCM-41 materials as catalysts in biomass pyrolysis for the production of bio-fuels and chemicals", Fuel, 2006 Publication	<1 %
53	libratez.cu.edu.tr Internet Source	<1 %
54	A. Lopez-Urionabarrenechea, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados. "Upgrading of chlorinated oils coming from pyrolysis of plastic waste", Fuel Processing Technology, 2015 Publication	<1 %
55	Ren-Xuan Yang, Kalsoom Jan, Ching-Tien Chen, Wan-Ting Chen, Kevin C.-W. Wu. "Thermochemical conversion of plastic waste into fuels, chemicals, and value‐added materials: A critical review and outlooks", ChemSusChem, 2022 Publication	<1 %
56	Yuan Xue, Patrick Johnston, Xianglan Bai. "Effect of catalyst contact mode and gas atmosphere during catalytic pyrolysis of	<1 %

waste plastics", Energy Conversion and Management, 2017
Publication

57	www.ncbi.nlm.nih.gov Internet Source	<1%
58	www.scielo.br Internet Source	<1%
59	Ahmetli, Gulnare, Suheyla Kocaman, Ilkay Ozaytekin, and Pınar Bozkurt. "Epoxy composites based on inexpensive char filler obtained from plastic waste and natural resources", Polymer Composites, 2013. Publication	<1%
60	Syamsiro, Mochamad, Wu Hu, Shuta Komoto, Shuo Cheng, Putri Noviasri, Pandji Prawisudha, and Kunio Yoshikawa. "Co-Production of Liquid and Gaseous Fuels from Polyethylene and Polystyrene in a Continuous Sequential Pyrolysis and Catalytic Reforming System", Energy and Environment Research, 2013. Publication	<1%
61	www.ijetas.com Internet Source	<1%
62	A. Pakiya Pradeep, S. Gowthaman. "Combustion and emission characteristics of diesel engine fuelled with waste plastic oil – a	<1%

review", International Journal of Ambient Energy, 2019
Publication

63	Dimitris S., Lefteris Andriotis, Ioannis A., Dimitra A., Nikolaos P., Panoraia Siafaka, Ioannis Tsagkalias, Georgia Tsintzou. "Chapter 1 Recent Advances in the Chemical Recycling of Polymers (PP, PS, LDPE, HDPE, PVC, PC, Nylon, PMMA)", IntechOpen, 2012 Publication	<1 %
64	Minugu Om Prakash, Raghavendra Gujjala, Manoj Panchal, Shakuntala Ojha. "Mechanical characterization of arhar biomass based porous nano activated carbon polymer composites", Polymer Composites, 2020 Publication	<1 %
65	Renzini, M.S.. "Stability of ZSM-11 and BETA zeolites during the catalytic cracking of low-density polyethylene", Journal of Analytical and Applied Pyrolysis, 201111 Publication	<1 %
66	nanoscalereslett.springeropen.com Internet Source	<1 %
67	thermalscience.vinca.rs Internet Source	<1 %
68	Submitted to The Hong Kong Polytechnic University Student Paper	<1 %

69	Submitted to Central Queensland University Student Paper	<1 %
70	patents.google.com Internet Source	<1 %
71	repository.sustech.edu Internet Source	<1 %
72	www.ijasre.net Internet Source	<1 %
73	S. Jaikumar, S. K. Bhatti, V. Srinivas, R. Satyameher, D. Chandravathi. "Investigations on performance and emission parameters of direct injection diesel engine running with Mesua ferrea oil methyl ester blends", SN Applied Sciences, 2019 Publication	<1 %
74	Zhijie Zhu, Xingyu Liang, Yuesen Wang, Bo Liu. "A Simulation Research on Emission Control Technology of Low-Speed Two-Stroke Diesel Engine Based on EGR and Miller Cycle", SAE International, 2019 Publication	<1 %
75	folia.unifr.ch Internet Source	<1 %
76	ijsrst.com Internet Source	<1 %

77	Aleksandar D. Bugarski, Jon A. Hummer, Shawn Vanderslice. "Effects of hydrotreated vegetable oil on emissions of aerosols and gases from light-duty and medium-duty older technology engines", Journal of Occupational and Environmental Hygiene, 2016 Publication	<1 %
78	Y.-H. Lin, H.-Y. Yen. "Fluidised bed pyrolysis of polypropylene over cracking catalysts for producing hydrocarbons", Polymer Degradation and Stability, 2005 Publication	<1 %
79	repository.tudelft.nl Internet Source	<1 %
80	upcommons.upc.edu Internet Source	<1 %
81	www.thaiscience.info Internet Source	<1 %
82	yubase.com Internet Source	<1 %
83	Xuesong Zhang, Ruolan Xu, Quan Liu, Ge Kong, Hanwu Lei, Roger Ruan, Lujia Han. "Enhancing the activity of Zn, Fe, and Ni-embedded microporous biocarbon: towards efficiently catalytic fast co-pyrolysis/gasification of lignocellulosic and	<1 %

plastic wastes", Energy Conversion and Management: X, 2022
Publication

84	chemistry.tutorvista.com Internet Source	<1%
85	citeseerx.ist.psu.edu Internet Source	<1%
86	tel.archives-ouvertes.fr Internet Source	<1%
87	"Emerging Trends in Science, Engineering and Technology", Springer Science and Business Media LLC, 2012 Publication	<1%
88	Ani, F.N.I.R.Z.F.N.. "Pyrolytic oil from fluidised bed pyrolysis of oil palm shell and itscharacterisation", Renewable Energy, 19990501 Publication	<1%
89	Ayhan Demirbaş. "Recovery of Chemicals and Gasoline-Range Fuels from Plastic Wastes via Pyrolysis", Energy Sources, 2005 Publication	<1%
90	Devaraj, J., Y. Robinson, and P. Ganapathi. "Experimental investigation of performance, emission and combustion characteristics of waste plastic pyrolysis oil blended with diethyl	<1%

ether used as fuel for diesel engine", Energy, 2015.
Publication

91	Gerhart Eigenberger. "Fixed-Bed Reactors", Wiley, 2000 Publication	<1 %
92	M. Olazar, G. Lopez, M. Amutio, G. Elordi, R. Aguado, J. Bilbao. "Influence of FCC catalyst steaming on HDPE pyrolysis product distribution", Journal of Analytical and Applied Pyrolysis, 2009 Publication	<1 %
93	Valeria Trombettoni, Daniela Lanari, Pepijn Prinsen, Rafael Luque, Assunta Marrocchi, Luigi Vaccaro. "Recent advances in sulfonated resin catalysts for efficient biodiesel and bio-derived additives production", Progress in Energy and Combustion Science, 2018 Publication	<1 %
94	Vincent Schenk, Karine Labastie, Mathias Destarac, Philippe Olivier, Marc Guerre. "Vitrimer composites: current state and future challenges", Materials Advances, 2022 Publication	<1 %
95	coek.info Internet Source	<1 %
96	epdf.tips Internet Source	<1 %

97	idr.nitk.ac.in Internet Source	<1 %
98	rucore.libraries.rutgers.edu Internet Source	<1 %
99	wedocs.unep.org Internet Source	<1 %
100	wikileaks.org Internet Source	<1 %
101	worldwidescience.org Internet Source	<1 %
102	www.genengnews.com Internet Source	<1 %
103	www.ijesrt.com Internet Source	<1 %
104	www.studymode.com Internet Source	<1 %
105	Celik, Mehmet, H.Serdar Yucesu, and Metin Guru. "Investigation of the effects of organic based manganese addition to biodiesel on combustion and exhaust emissions", Fuel Processing Technology, 2016. Publication	<1 %
106	Chen, Yu, Yulong Wu, Derun Hua, Chun Li, Michael P. Harold, Jianlong Wang, and Mingde Yang. "Thermochemical conversion of low-	<1 %

lipid microalgae for the production of liquid fuels: challenges and opportunities", RSC Advances, 2015.
Publication

---

107 Jun Cong Ge, Guiring Wu, Byeong O. Yoo, Nag Jung Choi. "Effect of injection timing on combustion, emission and particle morphology of an old diesel engine fueled with ternary blends at low idling operations", Energy, 2022 <1 %
Publication

---

108 Maite Artetxe, Gartzen Lopez, Gorka Elordi, Maider Amutio, Javier Bilbao, Martin Olazar. "Production of Light Olefins from Polyethylene in a Two-Step Process: Pyrolysis in a Conical Spouted Bed and Downstream High-Temperature Thermal Cracking", Industrial & Engineering Chemistry Research, 2012 <1 %
Publication

---

109 Panakaduwa Gamage Imesha Uthpalani, Jagath Kumara Premachandra, Deeyagahage Sujeewa Mallika De Silva, Vithanage Primali Anuruddhika Weerasinghe et al. "Pyrolysis as a value added method for plastic waste management: A review on converting LDPE and HDPE waste into fuel", Research Square Platform LLC, 2022 <1 %
Publication

110	Rafael Kandiyoti, Alan Herod, Keith Bartle, Trevor Morgan. "High-pressure reactor design", Elsevier BV, 2017 Publication	<1 %
111	Anil Vyas, Suresh Kumar Singh, Komal Sharma, Sukhwant Singh. "Catalytic Cracking of Waste Polypropylene in a Nitrogen Fluidized Bed Reactor", Journal of Geoscience and Environment Protection, 2016 Publication	<1 %
112	Breda Kegl, Marko Kegl, Stanislav Pehan. "Green Diesel Engines", Springer Science and Business Media LLC, 2013 Publication	<1 %
113	M. Gowtham, R. Prakash. "Effects of n-butanol/calophyllum inophyllum biodiesel blend injection on the combustion characteristics of reactivity controlled compression ignition engine", International Journal of Oil, Gas and Coal Technology, 2021 Publication	<1 %
114	Suh, D.J.. "Synthesis of high-surface-area ruthenium oxide aerogels by non-alkoxide sol-gel route", Journal of Power Sources, 20030515 Publication	<1 %
115	eprints.whiterose.ac.uk Internet Source	<1 %

Exclude quotes	Off	Exclude matches	Off
Exclude bibliography	On		