

**MICROWAVE CATALYTIC PYROLYSIS OF WASTE  
PLASTIC**

BY

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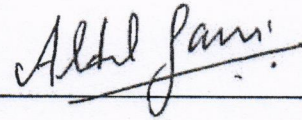
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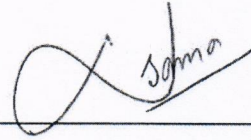
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I would like to dedicate my thesis work to my beloved mother.

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## ABSTRACT

Full Name : [K. M. Oajedul Islam]

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Converting waste plastic into value-added chemicals through pyrolysis is a modern approach. Pyrolysis involves the decomposition of plastic materials in an oxygen-free environment to produce value-added chemicals or fuel oil. The use of a catalyst during pyrolysis helps to selectively crack polymers, which increases product yield and quality. In this study, microwave-assisted catalytic pyrolysis of low-density polyethylene (LDPE) was investigated. The activity of gallium-doped catalysts on zeolite and the successive incorporation of nickel, cobalt, and copper with gallium-doped zeolite were studied to analyze the quality of the product. The quality of the liquid oil was investigated by SimDist, GC-MS, <sup>1</sup>HNMR, and FTIR. Pyrolysis-derived oil using copper-impregnated gallium-doped zeolite (GCuZ3) contained 90% of C<sub>9</sub>-C<sub>12</sub> aromatics, mostly benzene derivatives, proving it to be a potential feedstock to produce BTX (Benzene, Toluene, Xylene) as a building block in petrochemical industries. MicroGC analysis of the gas products provides the highest amount of hydrogen and syngas production by utilizing GCuZ3 as well. Catalyst activities were checked by the assessment of surface area (BET), crystallinity (XRD), thermal degradation behavior (TGA), morphology (SEM), and elemental composition (EDS). Fresh and spent catalyst characterization comparison proved the higher catalytic activity of GCuZ3.

## ملخص الرسالة

الاسم الكامل: ك م واجد الاسلام

عنوان الرسالة: تحفيز الدورة الدموية بالميكروويف لنفايات البلاستيك

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: ذو القعدة ١٤٤٤ هـ

يعد تحويل نفايات البلاستيك إلى مواد كيميائية ذات قيمة مضافة من خلال الانحلال الحراري نهجًا حديثًا. يتضمن الانحلال الحراري تحليل المواد البلاستيكية في بيئة خالية من الأكسجين لإنتاج مواد كيميائية ذات قيمة مضافة أو زيت الوقود. يساعد في هذه. استخدام المحفز أثناء الانحلال الحراري على تكسير البوليمرات بشكل انتقائي ، مما يزيد من إنتاجية المنتج وجودته تمت دراسة (LDPE) الدراسة ، تم فحص الانحلال الحراري التحفيزي بمساعدة الميكروويف للبولي إيثيلين منخفض الكثافة نشاط المحفزات المشبعة بالغاليوم على الزيوليت والدمج المتعاقب للنكل والكوبالت والنحاس مع زيوليت مخدر بالغاليوم لتحليل يحتوي الزيت المشتق من SimDist, GC-MS, <sup>1</sup>HNMR, FTIR. جودة المنتج. تم فحص جودة الزيت السائل بواسطة ، معظمها مشتقات C9-C12 على 90٪ من المواد العطرية (GCuZ3) الانحلال الحراري باستخدام زيوليت مشبع بالنحاس يوفر. (بنزين ، تولوين ، زيلين) كحجر بناء في الصناعات البتروكيمياوية BTX البنزين ، مما يثبت أنه مادة أولية محتملة لإنتاج أيضًا. تم فحص أنشطة GCuZ3 لمنتجات الغاز أكبر قدر من إنتاج الهيدروجين والغاز التخليقي باستخدام MicroGC تحليل (SEM) ، والتشكل (TGA) ، وسلوك التدهور الحراري (XRD) ، والتبلور (BET) المحفز من خلال تقييم مساحة السطح GCuZ3. أثبتت مقارنة خصائص الحفاز الطازجة والمستهلكة النشاط التحفيزي العالي لـ (EDS) ، والتكوين الأولي

# CHAPTER 1

## INTRODUCTION

### 1.1 Plastics consumption scenario

Plastic products have become very popular due to its light-weight, low cost and long-lasting characteristics [1]. It has been used widely since last decades to produce household items [2], medical accessories [3], electronic equipment [4,5], agricultural tools [6–8], packaging materials [9], automobile parts [10], furniture [11] and also a wide range products used in different fields. Therefore, the immense use of these plastic products has triggered a massive upsurge in plastic waste generation. It is highly assumed that the amount of discharged plastic waste would be around 12500 MT by 2050 according to the recent route of generation [12]. A huge amount of waste plastic is being generated daily throughout the world due to high consumption rate and poor management of the plastic products [13]. Undesirable species like soot, chloride, PAHs (polycyclic aromatic hydrocarbons) could be mixed in the environment due to improper management of the waste plastics [14].

Moreover, the microplastics and nano plastics particles have been found even in remote ecosystem zone which is a severe potential threat for the living creatures of the planet [15].

Again, during this COVID-19 outbreak, the utilization of single use plastic materials has been prompted [16,17]. In fact, 1.6 million tons of plastics waste have been generated in daily basis throughout the world during the COVID outbreak [18].

Therefore, proper waste management turned into a global issue rather than local due to its vast amount and heterogenous nature.

## 1.2 Available technology for the treatment of waste plastic

A large amount of waste plastic is simply discarded in the land without any treatment that causes a potential environmental threat without recovery of energy. Developed countries use the landfilling technique in an organized way whereas developing countries just throw the plastic in open dumps [19].

Recycling can be identified as another useful technique for the management of waste plastic. Used plastic products are collected from different sources and sorted according to various types and then re-introduced to the production chain to get the product. Same type of product is regenerated in a closed-loop and different type is regenerated in open-loop recycling [20].

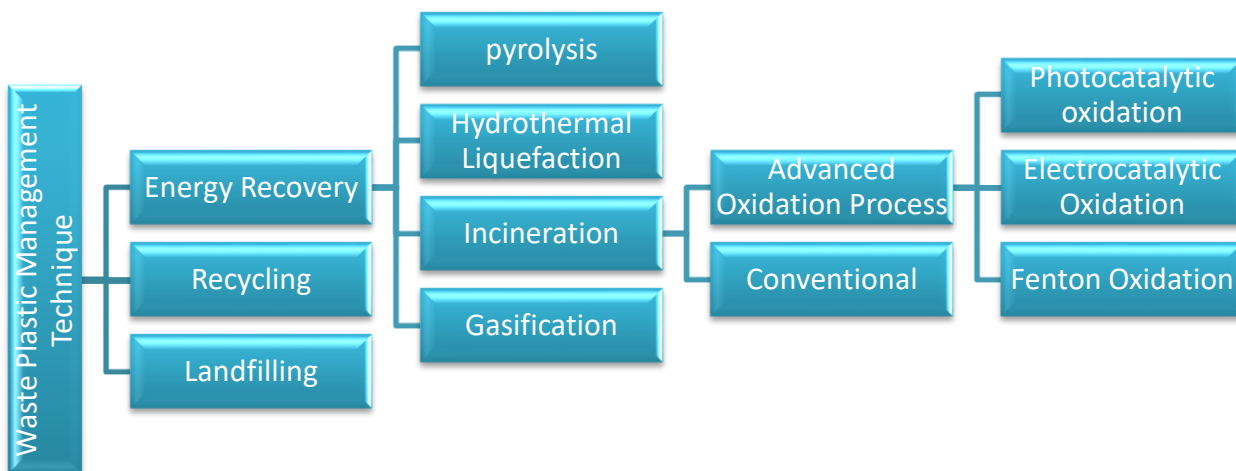


Figure 1 Waste plastic management technique flow chart

Another means of waste plastic treatment is through energy recovery which is proved as sustainable and commercially feasible [21–23]. Waste plastic could be converted to liquid fuel and act as a source of alternative energy in this way [24,25].

Energy recovery methods can be grouped into four categories (Figure 01). Incineration is one of the popular energy recovery method among them [26]. Usually, a large furnace is used to burn the waste materials to get rid of these. Due to the combustion of waste materials, a large quantity of greenhouse gases, soot, toxic emissions are formed [27]. Moreover, it is only the recovery of thermal energy, no chemical value could be obtained through conventional incineration. Again, the cleaning of flue gas after combustion is also challenging [28,29].

There are some advanced oxidation process like Photocatalytic [30–33], Electrocatalytic [34–37] and Fenton oxidation [38–40] process where controlled oxygen flow rate is maintained under some specific condition. Figure 01 demonstrates an available technology flow chart for the conversion of waste plastic.

There are some other advanced technologies to upcycle the plastic chemically like gasification and pyrolysis. It is a more energy intensive process but also returns value added products having with an economical benefit. In gasification, syngas is produced at high temperature in the presence of controlled amount of oxygen [41,42]. This syngas can be used as fuel or can be converted into liquid fuel. On the other hand, Pyrolysis also refers to thermal decomposition in the presence of inert [43–45]. It usually degrades the plastic polymer into its small constituents at high temperature. Pyrolysis technology can be categorized based on catalytic activity, heating method and residence time. The quality of liquid fuel derived from catalytic pyrolysis is good enough for application [46–49]. Conventional thermal pyrolysis requires high temperature where microwave

pyrolysis can be accomplished within medium range temperature [50]. Moreover, microwave pyrolysis heating requires less residence time. Based on residence time, pyrolysis is categorized as slow pyrolysis[51,52], fast pyrolysis [53–55] and flash pyrolysis [56,57]. Different pyrolysis technology is demonstrated in Figure 02.

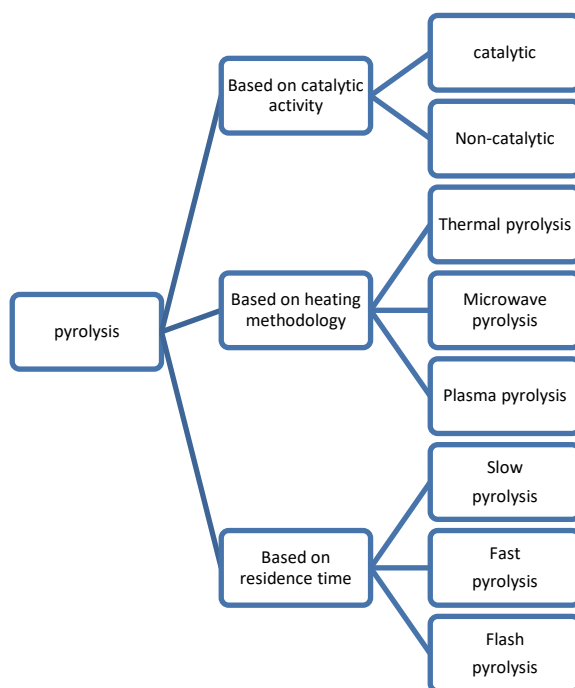


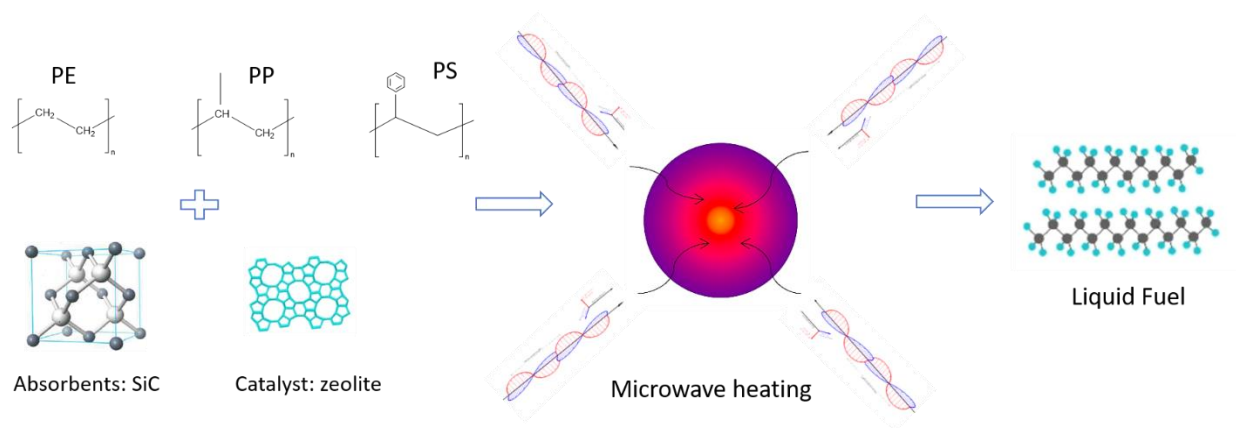
Figure 2 Different type of pyrolysis technology based on different criteria

### 1.3 Microwave catalytic pyrolysis for the treatment of waste plastic

Microwave-assisted pyrolysis (CMAP) could be the best alternative one. Microwave pyrolysis is a thermochemical conversion process where high temperature (400-800 C) is maintained to decompose the plastics or biomass to form valuable products like gas, oil and solid char using microwave irradiation. Rapid heating, short residence time, higher yield, and reduced power consumption make it attractive according to the recent findings. Moreover, relatively large sized

and moisture content materials can be dealt in microwave pyrolysis [58]. So, the cost of drying and grinding can be kept minimum by following this approach.

Microwaves are electromagnetic waves most used frequency of 2.45 GHz. A highly efficient microwave radiation generating tool, magnetron, is used to provide heat in the microwave reactor. In microwave field, dipolar molecules rotate aligned to the alternating electric field under the influence of electromagnetic radiation. Heat arises due to the resistance of the rotation on the molecular level. Therefore, the heat is generated from the molecular level not from the surface. Microwave heating requires microwave absorbents that have high dielectric properties and hence microwave absorbency. Mostly, carbon materials and metal oxides are used to do this [14,59–65].



**Figure 3 Catalytic microwave pyrolysis of PP/PS/PE**

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Types of plastic & reaction pathway for decomposition

Plastic products are manufactured mainly from polymer. There are different types of polymeric materials from where these are made. High Density Polyethylene (HDPE), Low Density Polyethylene (LDPE), Linear Low-Density Polyethylene (LLDPE), Polystyrene (PS), Polypropylene (PP), Polyethylene Terephthalate (PET), Polyvinyl chloride (PVC) are the main variations of plastic products. Although these have different chemical structures and properties, there are some common features like low moisture content but high volatile content, same trend of heating value and viscosity. Basically, all plastic waste can be categorized into seven groups. The uses of these plastic and important properties are noted briefly in the following **Table 01**. HDPE is harder than LDPE and has high chemical resistance [66–68]. It requires a high pyrolysis temperature. The most used plastic products are mainly from these polymers.

An important parameter, Hydrogen/carbon ratio reflects the potential to produce fuels or value-added products. The overall yield can be predicted by using this. It can be calculated by the following formula.

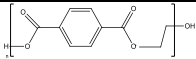
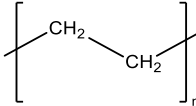
$$H/C_{eff} = \frac{H - 20 - 3N - 2S}{C} \quad (1)$$

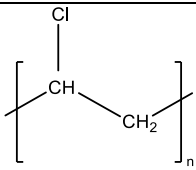
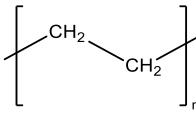
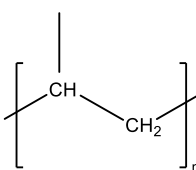
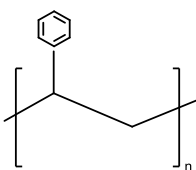
The decomposition pathway of different grades differs from one another. For example, the pyrolysis mechanism for PE is based on the random generation of free radicals along the polymer backbone, which is then followed by molecule scission and hydrogen chain transfer reactions.

On the other hand, PET thermal cracking is primarily cyclic because it is a polyester with  $\beta$ -hydrogen. Homolytic fission to produce the corresponding monomers is unlikely to occur during PET pyrolysis.

PVC pyrolysis is more complex than polyolefin pyrolysis because it involves three sequential steps: (1) cracking into intermediates and HCl; (2) decomposition of intermediates to polyene chains and other volatiles; and (3) decomposition of polyene into toluene (and other aromatics) and chars.

**Table 1 Different grades of plastic and its uses, properties**

| Recycle number | Abbreviation | Polymer                    | Structure                                                                           | Uses                                                                       | Properties                                                                   | Comments on pyrolysis            | Reference |
|----------------|--------------|----------------------------|-------------------------------------------------------------------------------------|----------------------------------------------------------------------------|------------------------------------------------------------------------------|----------------------------------|-----------|
| 1              | PET          | Polyethylene Terephthalate |  | Food containers, polyester, water bottle, domestic applications            | Microwave transparency, hard and tough                                       | Forms phthalic acid on pyrolysis | [69–73]   |
| 2              | HDPE         | High Density Polyethylene  |  | Toys, shampoo and conditioner bottle, ropes, agricultural and fishing nets | Harder, higher chemical resistance, higher temperature withstanding capacity | Mostly pyrolyzed                 | [74–76]   |

|   |      |                          |                                                                                    |                                                             |                                                   |                                                       |         |
|---|------|--------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------|---------------------------------------------------|-------------------------------------------------------|---------|
| 3 | PVC  | Polyvinyl Chloride       |   | Electric wires and cables, water piping, foodstuff wrapping | Higher stability, low gas permeability            | Contains chlorine, Forms HCl.                         | [74–82] |
| 4 | LDPE | Low Density Polyethylene |   | Bags, soft drinking bottles, films, cable insulation        | Melts at lower temperatures, flexible and softer. | Mostly pyrolyzed                                      | [83–85] |
| 5 | PP   | Polypropylene            |   | Bottle caps, drinking straws, food containers, luggage      | High melting point and chemical resistance        | Gasoline and diesel range products gain on pyrolysis. | [86,87] |
| 6 | PS   | Polystyrene              |  | Disposable coffee, plastic food boxes, refrigerator trays,  | Glassy surface, brittle, high clarity, hard       | Produce aromatic compounds on pyrolysis               | [88]    |

Even though PP is a branched polymer and PE is a linear polymer, the pyrolysis mechanism of PP is like that of PE, as both undergo random scissions to produce olefins. C-C bond cleavage requires less activation energy for PP than PE, with 176 kJ/mol and 225 kJ/mol, respectively. This is due to the presence of tertiary carbon atoms in the polymer backbone, which allows for more efficient cracking and the formation of more stable tertiary radical intermediates than secondary radical intermediates formed by PE.

PS degradation consists of four primary steps: initiation, transfer, decomposition, and termination, with both random chain and end-chain scission mechanisms involved.

## 2.2 Steps involved in catalytic microwave pyrolysis

Microwave assisted pyrolysis of waste plastic involves some basic steps which are illustrated in **Figure 04**. Firstly, the raw materials or feedstocks must be chosen in a proper way depending on their categories. The chosen feedstocks will be ready for microwave pyrolysis after sorting, washing, and cutting. Then, the raw material will be characterized by its composition and heating value. Microwave operation will be accomplished after it. Finally, the products will be collected and characterized to assess their quality. An explanation of each step is provided in the following subsections.

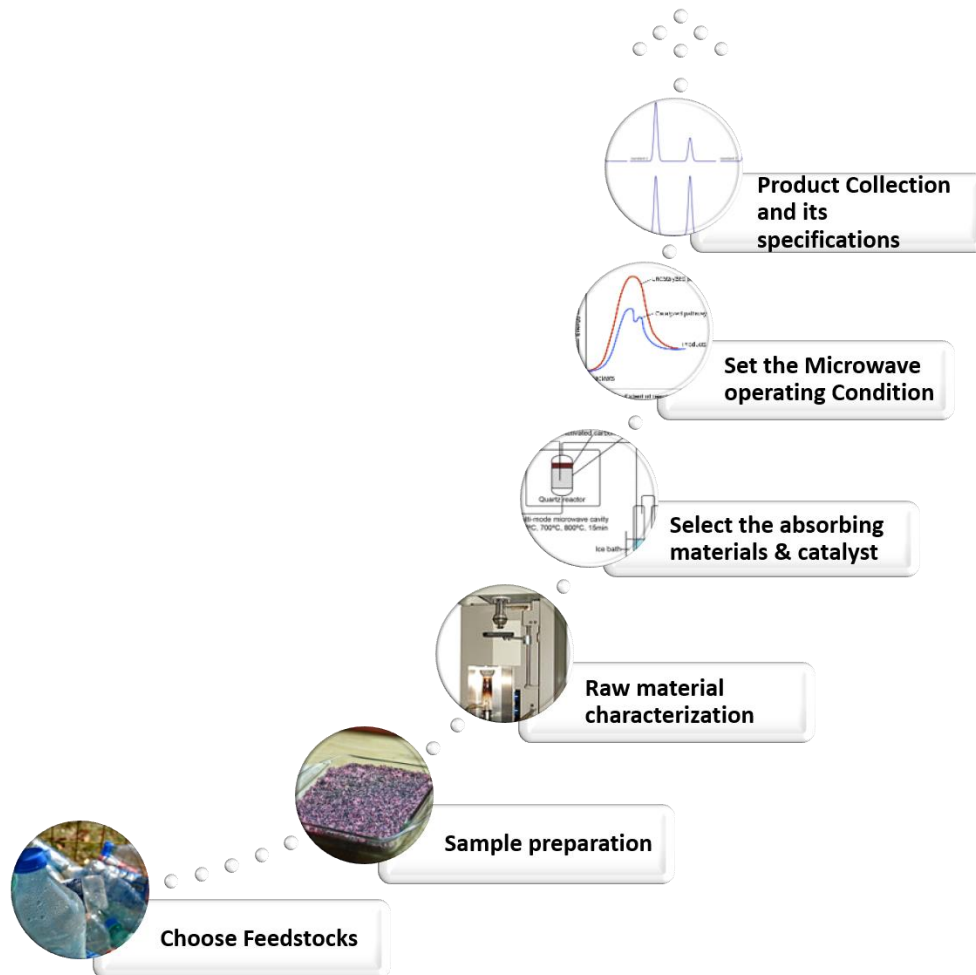
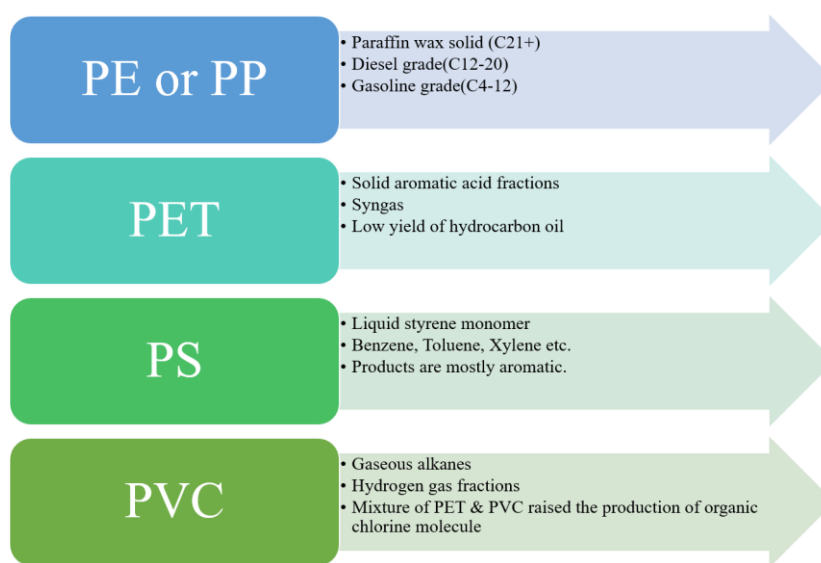


Figure 4 Steps illustration for the microwave pyrolysis

### 2.2.1 Selection of feedstocks

The difference in the properties of different plastic grades gives a wide variation in the quality of the produced fuel. For example, PVC contains chlorides where PS has aromatic benzene cycle in its chain. Moreover, the mixing of different grades of plastic gives a different yield scenario. Mixing could be either among plastic or with other particles like biomass, coal, waste tire. Possible yield quality is demonstrated in the following **Figure 05** for the pyrolysis of different grades of the plastics.

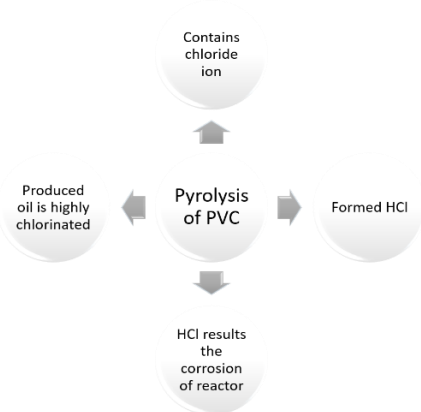


**Figure 5 Predicted Pyrolysis product from different grade of plastic**

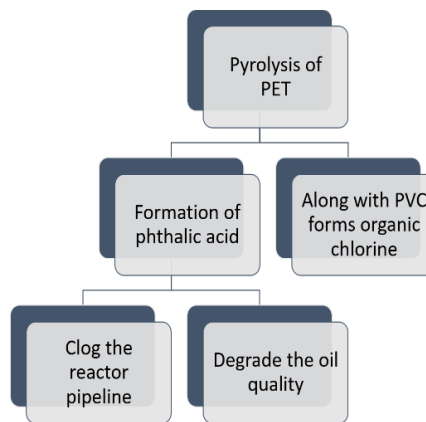
First, Polyethylene (PE) produces wax and high viscous liquid during pyrolysis. At higher temperature and longer residence time, wax converts to liquid and gases by going through secondary reactions. Aromatic compounds and saturated alkenes are preferable products while the pyrolysis of PE [70,89–91].

Secondly, the major product from PET is benzoic acid, terephthalic acid which could be converted to aromatic hydrocarbons over catalysts with the ability to be strongly deoxygenated. Specially, the metal oxides catalyst like CaO, ZnO, MgO, TiO<sub>2</sub>, ZrO<sub>2</sub> were successfully utilized to produce the aromatic rich liquid oil from the pyrolysis of PET while suppressing the formation of terephthalic acid [72,73]. In **Figure 07** shortcomings of the formation of terephthalic acid are shown.

Thirdly, the pyrolysis of PVC is not very frequent due to its low liquid yield. Furthermore, the chlorine molecule forms HCl which results a severe corrosion to the device [78,79,97,80–82,92–96]. An illustration is shown in **Figure 06** representing the difficulties of the pyrolysis of PVC.



**Figure 6** Difficulties during the pyrolysis of PVC



**Figure 7** Difficulties during the pyrolysis of PET

Fourthly, the Polypropylene (PP) produces a large amount of gases product under pyrolysis due to its more branched structure than PE. The quality of liquid product is a complex cocktail of different grades of hydrocarbon. But, the cracking tendency of PP is higher than PE and PS [98,99].

Fifthly, the degradation of Polystyrene (PS) results in a maximum yield to liquid (80%). Even, the portion of monomer in the products is significant. The presence of benzene cycle in PS influences the production of more aromatic and also hinders the formation of aliphatic hydrocarbon [100,101].

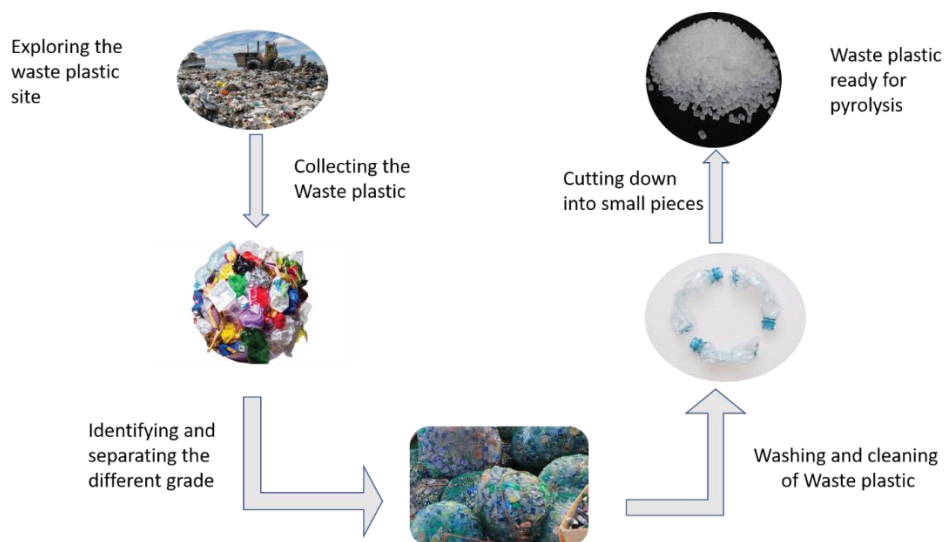
Finally, the pyrolysis of mixed plastic results in around 50% of oil product. The quality of the product depends on the selection of feedstocks [98,99,102]. For example, the co-pyrolysis of PVC, PP/PE have a tendency to form more solid char due to dehydrochlorination [99] .

In the field of microwave pyrolysis, most researchers select PS, PE (LLDPE, LDPE, HDPE), PP for pyrolysis [70,75,76,89–91,102,103]. The pyrolysis of PET and PVC was mostly avoided for the limitations that are already discussed above.

### 2.2.2 Sample preparation

The chosen plastic feedstock should be prepared properly to make it ready for pyrolysis. Waste plastic should be contaminant free to make the operation economically feasible. Usually, waste plastic dump sites contain a variety of waste materials having different sizes and shapes along with pollutants. Therefore, the plastic feedstocks must be sorted properly according to different grades and types after collecting from the sites. Sometimes, it contains toxic elements and contaminants which may corrode the reactor. So, the hazardous entities must be characterized properly and eliminated before microwave pyrolysis [104–106].

Moreover, the sizes of the plastic should be small and feasible to run the operation. Cutting, grinding, smashing etc. are the common techniques that is usually followed before the operation [13,107]. A flow path is given in **Figure 08** which illustrates the steps which are followed to get the plastic waste ready for pyrolysis.



**Figure 8** Waste plastic sample preparation for microwave pyrolysis

### 2.2.3 Raw material Characterization

The waste plastic materials should be characterized properly before microwave pyrolysis. Basically, there are three main characterization tools that give an overall picture regarding the feedstocks. The first characterization tool that is used to get the ultimate analysis of any sample is elemental analyzer. It gives a weight percentage of plastic materials in terms of carbon, hydrogen, nitrogen, oxygen, sulfur and chlorine. Because these basic molecules encompass the entire spectrum of waste plastic components.

**Table 2 Characterization techniques to characterize the raw materials**

| Measuring parameter                            | Characterization Tool               | Model Equipment                                                       | Working Principle                                                                                                                          | References |
|------------------------------------------------|-------------------------------------|-----------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|------------|
| Ultimate Analysis<br>(C, H, O, N, S etc.)      | Elemental analyzer                  | Elementar Vario<br>EL III/Vario<br>MACRO/ CE440<br>elemental analyzer | The sample is heated very quickly at a high temperature to combust and allow to pass through analyzer where element percentage is detected | [108,109]  |
| Calorific value                                | Bomb calorimeter                    | Bomb<br>Calorimeter ( <b>Model-IKA C2000</b> )                        | The sample is ignited inside a sealed metal cylinder in presence of oxygen and then the calorimeter measures the heating value.            | [110,111]  |
| Thermal Stability<br><br>Proximate<br>Analysis | Thermogravimetric<br>analyzer (TGA) | Seiko Exstar<br>TGDTA 6300/<br>PerkinElmer STA<br>600                 | The sample is decomposed in inert environment and the change of weight is recorded as function of Temperature/time.                        | [112–115]  |

|                     |                  |            |                                                    |       |
|---------------------|------------------|------------|----------------------------------------------------|-------|
| Dielectric constant | Network Analyzer | ENA 85033C | Works based on measuring the                       | [116] |
|                     |                  |            | phase and amplitude of reflected and incident wave |       |

In addition, the Thermogravimetric analyzer (TGA) is used to find the proximate analysis and thermal stability. Proximate analysis gives the weight percentage of fixed carbon, volatile matter, moisture and ash. From the fixed carbon and ash content, the solid product of pyrolysis can be anticipated. The volatile component provides the idea of the yield percentage of liquid and gases. Furthermore, the heating value of the plastic materials can be assessed by using bomb calorimeter. To calculate the energy recovery, the heating value must be calculated. A brief introduction of different characterization tools is tabulated in Table 02.

#### 2.2.4 Set the microwave operating condition

There are several parameters that are optimized to run the microwave reactor. One of the most important parameters is temperature. To decompose the plastic waste, temperature is usually fixed in the range of 450-550 °C. As plastic releases a range of hydrocarbons on heating, there is no fixed point to vaporize all constituents. As shown in **Table 03**, it is a range of temperature for decomposition that varies from grade to grade.

**Table 3 Thermal degradation range for different grade of plastic**

| Components | Temperature range for decomposition (° C) | References |
|------------|-------------------------------------------|------------|
| LLDPE      | 371- 467                                  | [117,118]  |
| LDPE       | 420 - 499                                 | [119–124]  |
| HDPE       | 398 - 456                                 | [125–132]  |
| PP         | 407- 483                                  | [133]      |
| PS         | 378 - 439                                 | [134]      |
| PET        | 350 - 438                                 | [135]      |

Another parameter is microwave power. High power facilitates the microwave reactor with quick heating while low power provides slow heating. It is usually set in the range of 300-2000 W and also altered to see the effect on product distribution.

Residence time is another key parameter in microwave operation. High temperature and power require less residence. On the other hand, high residence time is mandatory in case of low microwave power and temperature. Usually, it varies from 10- 30 min for each batch. For continuous system, space velocity is used to predict the residence time.

To maintain the inert environment in the reactor, mostly nitrogen is used. Besides maintaining inert conditions, it works as carrier gas. 40 ml/min - 200 ml/min is the usual range that is maintained in the reactor.

The effect of different parameters on yield is discussed comprehensively in section 05.

### 2.2.5 Select the absorbing materials

Microwave heating requires absorbents to absorb the microwave radiation. The extent to which absorbents heat up depends on its dielectric constant and dielectric loss factor. The proportion of reflected and absorbed electromagnetic energy can be anticipated from dielectric constant. The ratio of dielectric constant and dielectric loss results in the dielectric loss tangent, also known as dissipation factor. It indicates the ability to convert electric energy to thermal energy of those absorbents. Usually, a high value of dielectric loss factor and moderate value of dielectric constant results high dissipation factor, which indicates a good quality of absorbents [136,137].



Figure 9 Different types of Silicon Carbide

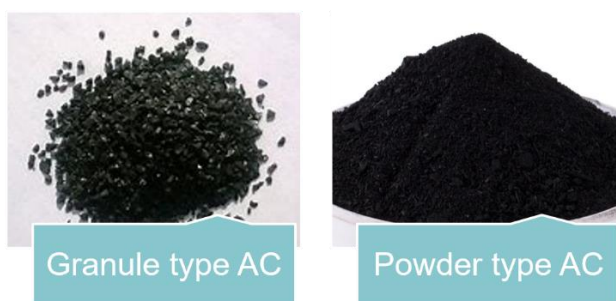


Figure 10 Different type of Activated Carbon

Usually, the carbon materials and oxide of inorganic compounds show satisfactory dielectric properties. Some silicon carbide and activated carbon absorbents are demonstrated in Figure 09 which are widely used as absorbents. Recently, ball type and foam type silicon carbide are used for the flexibility for the recovery of the absorbents. Activated carbon could be derived from different biomass. Coconut sheath activated carbon absorbents are popular one due to its high microwave absorbing capacity.

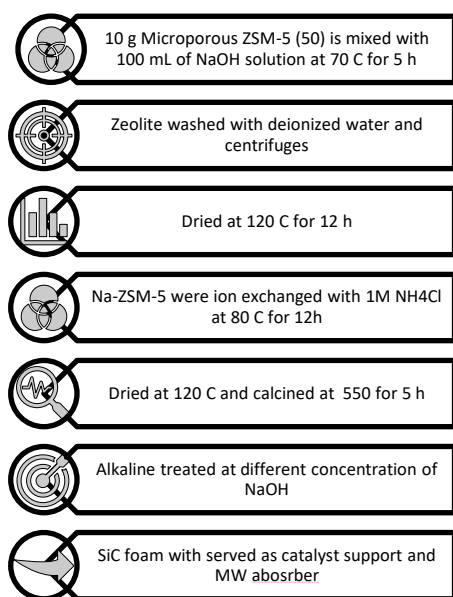
Usually, after each cycle of operation, the absorbents are sieved to separate solid pyrolyzed product. Then, acetone/heptane solvent is used to wash out the residual waxy part of the plastic sample using filtering flask having bolt neck tubulation equipped with vacuum pump. Finally, the absorbents are dried in dryer to make it ready for the next run.

### **2.2.6 Selection of the catalyst and its preparation**

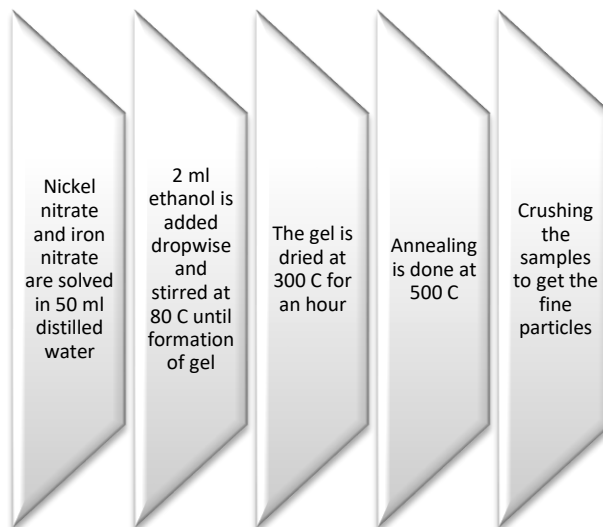
Selection of catalyst is very important for the decomposition of waste plastic in microwave pyrolysis. Most researchers showed the uses of zeolite-based catalyst and its advantages in pyrolysis. Mostly, HZSM-5 with different Si/Al ratio are used [138–140]. Recently, uses of SiC foam at zeolite core-shell structured catalyst has been explored as it has the advantages of easy regeneration [141] .

Iron-based catalyst [142,143] , Ni-based catalyst [143,144], MgO [145], Sodium borohydrate [146] was also used in microwave pyrolysis. The uses of KOH catalyst which is easy to get and cheap is also notable in this case.

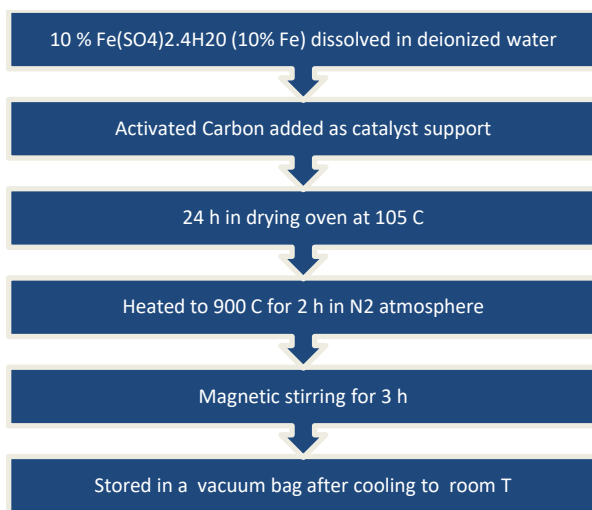
Preparation of some catalyst is explored step by step in Figure 11.



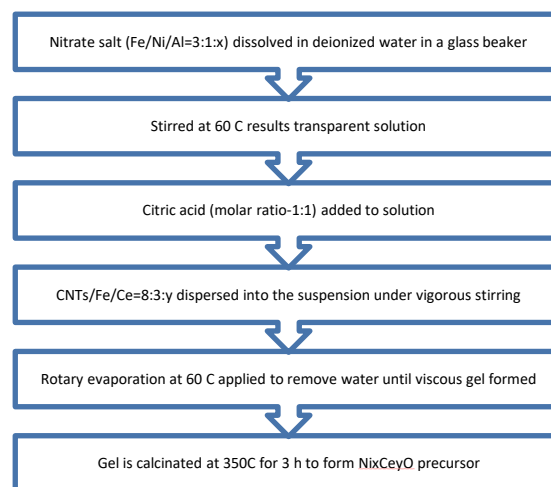
A



B



C



D

**Figure 11 Preparation of catalyst of in microwave operation**

**A.** SiC foam @ zeolite core-shell structured catalyst [147]; **B.** NiFe<sub>2</sub>O<sub>4</sub> catalyst [148]; **C.** 10 % Fe/AC catalyst [149] **D.** Heterogeneous bimetallic iron/nickel/cerium catalyst [143]

## 2.2.7 Product Analytical Method

Chemical composition of the product is mainly obtained by GC-MS equipped with capillary column where FTIR is used to identify the functional group.  $^1\text{H}$ NMR predicts the proton fractions in functional group more accurately.

**Table 4 Features of some methods used to characterize the product**

| Measuring parameter            | Characterization Tool                                                | Features                                                                                      | References    |
|--------------------------------|----------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|---------------|
| Chemical composition of liquid | GC-MS                                                                | Provides detailed                                                                             | [150]         |
|                                | gas chromatography mass spectrometer<br>(Ex. GC MS ultra QP2010)     | chemical composition;<br>long-chain hydrocarbon<br>shows different solubility<br>in solvents. |               |
| Functional group               | FTIR                                                                 | Only identifies functional                                                                    | [151]         |
|                                | Fourier Transform Infrared Spectrum                                  | group, doesn't give<br>chemical composition                                                   |               |
| NMR-spectroscopy               | NMR                                                                  | Provides chemical groups<br>for some selected groups<br>very accurately                       | [151–153]     |
| characterize the gas product   | GC-TCD/FID; MicroGC                                                  | MicroGC provides both                                                                         | [104,154–156] |
|                                | Gas chromatograph thermal conductivity and flame ionization detector | qualitative and<br>quantitative analysis of<br>the gas product.                               |               |

## 2.3 Experimental Procedure for microwave pyrolysis

### 2.3.1 Batch, In-Situ

In the in-situ catalyst bed, plastic sample, absorbents, and catalyst put together in the reactor vessel. Line heaters are used to keep the temperature high of the pyrolysis vapor with proper temperature controller system. Then, the product is passed through condensation section where continuously cool water is supplied to maintain the low temperature. One of the researchers explored low temperature silica oil ( $-5^{\circ}\text{C}$ ) for cooling purpose [116]. Liquid oil is collected in the round bottom flask for further process and characterization. Gas products could be analyzed by MicroGC. Most researchers use IR-based temperature measurement device to measure the pyrolysis temperature. A special contact-type of thermometer (K-thermocouple) fabricated by Suriapparao et al. (2015) found also beneficial for microwave operation [157]. A sample schematic is demonstrated in Figure 12 for illustration.

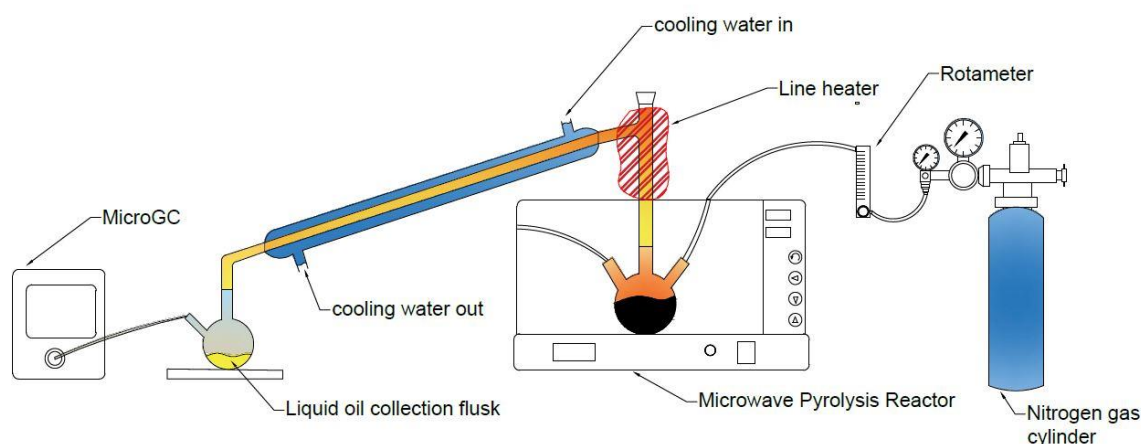


Figure 12 MAP batch pyrolysis; in-situ catalyst bed

### 2.3.2 Batch, Ex-situ

In ex-situ catalyst bed, the catalyst bed is designed in such a way so that only pyrolysis vapor could pass through the bed rather than mixing along with absorbents and plastic sample. Catalysts are regenerated easily in this operation. Ex-situ catalyst bed gained well acceptance due to its use of flexibility for the pyrolysis of plastic as well as biomass[158–160]. Quartz wool and glass made porous disc are used to hold the catalyst in the glass tube to pass the pyrolysis vapor (Figure 13). This catalyst bed is externally heated to activate the catalyst by heating the coil with proper temperature controller. The variation of this catalysis temperature affects the product yield.

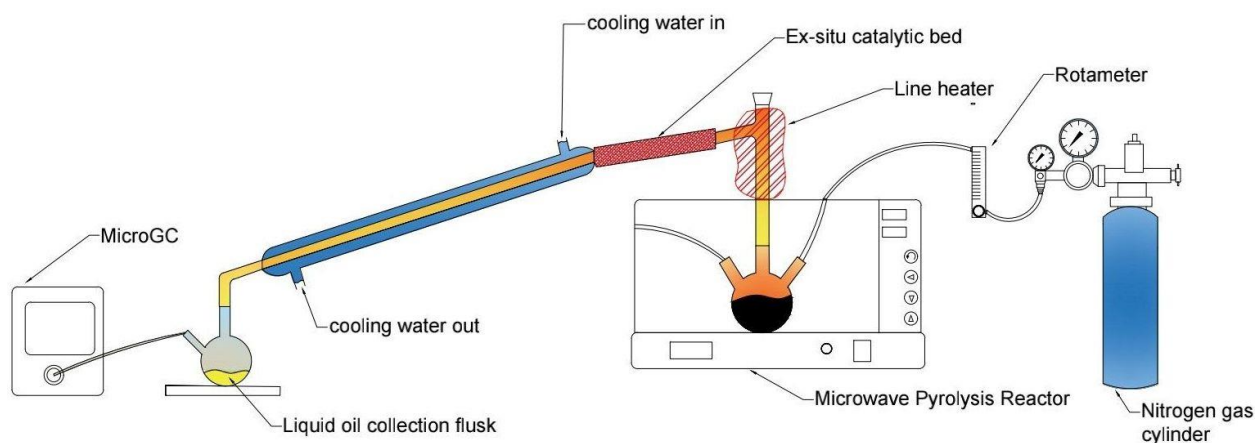


Figure 13 MAP batch pyrolysis; ex-situ catalyst bed

### 2.3.3 Continuous, Ex-situ

In continuous microwave reactor, the feedstock is put on hopper to feed it in the reactor [161]. Some researchers showed the screw feeder to feed the waste plastic (Figure 14). Ex-situ catalyst beds are mostly used in continuous pyrolysis reactor. Air tightness and proper sealing of each joining is very important for the operation. Zhou et al. (2021) showed 10 kg/h of waste plastic could be processed in continuous microwave ex-situ operation [162].

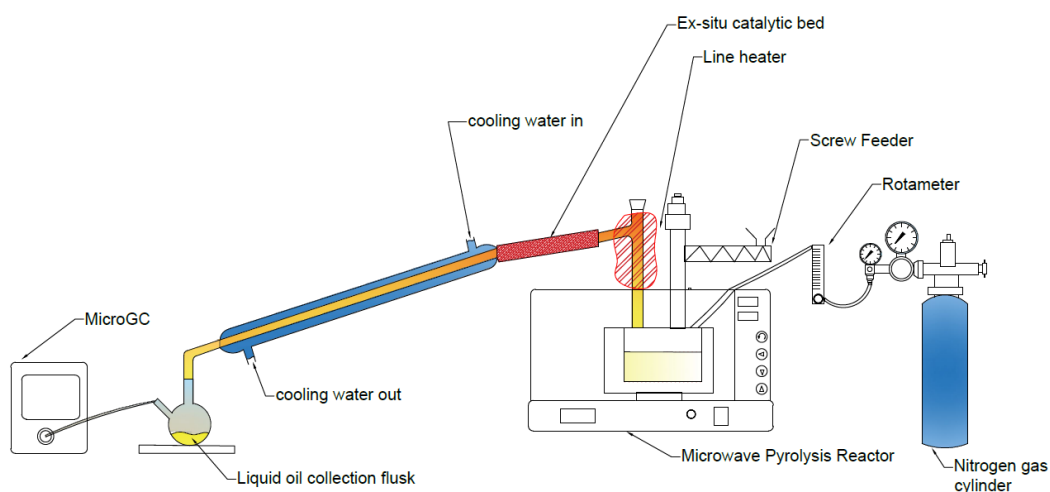


Figure 14 MAP continuous pyrolysis, ex-situ pyrolysis

## 2.4 Analysis of the effects: Microwave Assisted Pyrolysis of Plastic

There are some important parameters, these can be listed as temperature, residence time, type of catalyst, reactor type which influence the production of overall yield of liquid oil, char, and gaseous products [163–168]. To get the desired product, these parameters must be controlled optimally. Comprehensive discussions are provided in the following subsections to get a clear image of the effects of these parameters on the overall yield.

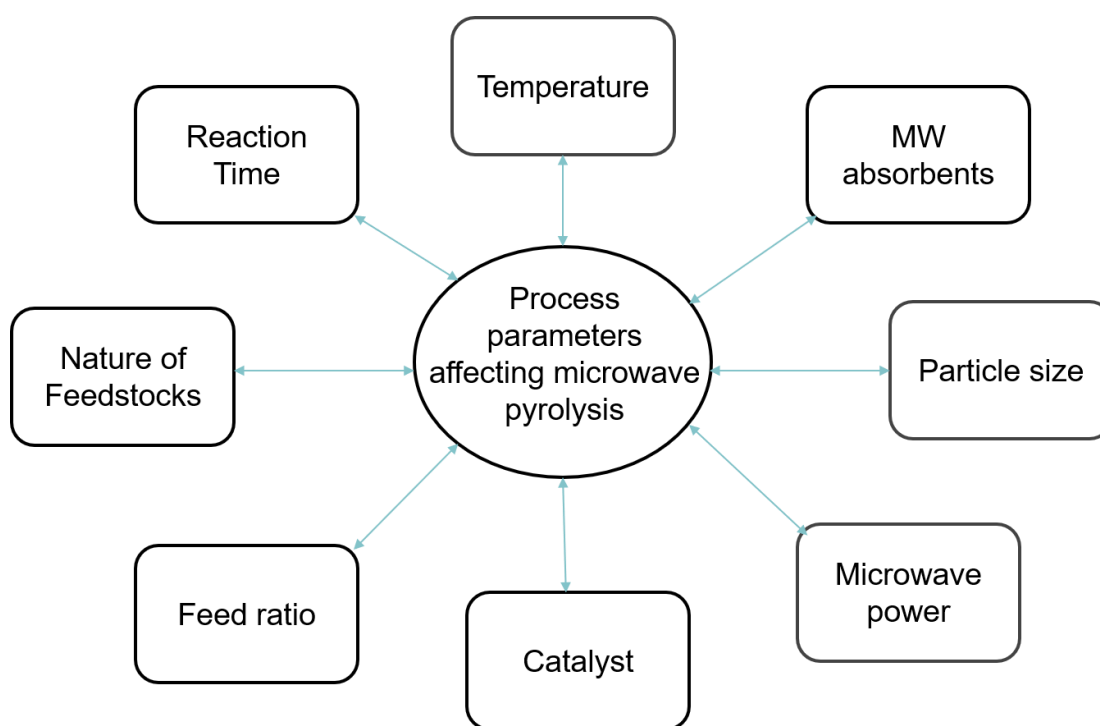


Figure 15 Important parameters effecting the microwave pyrolysis

## 2.4.1 Effect of catalyst

### 2.4.1.1 Zeolite-based catalyst

Ding et al. (2019) analyzed the effect of catalyst and feedstock ratio on the production of gasoline range fuel from the pyrolysis of the LDPE. HY-zeolite catalyst was used in ex-situ method whereas NiO co-catalyst used in in-situ method along with the feedstock in the quartz reactor. Highest oil yield (60%) was obtained at HY: LDPE=1:15(ratio of the catalyst and feed) which contained a high amount of monocyclic aromatic hydrocarbon which has higher octane number that indicates a good quality of gasoline range product. In fact, the octane number in a gasoline product maintain the following sequence MAHs (Monocyclic Aromatic HC) > PAHs (Polycyclic Aromatic HC) > iso-aliphatics > cyclo- aliphatics > n-aliphatics. Here, the aliphatics compound are mainly alkenes and alkanes. Having this sequence in the consideration, the quality of the fuel has been analyzed.

The quality of the product rose significantly when a ratio of NiO:HY=1:10 was used along with zeolite. So, the best combination of the catalyst was HY:LDPE=1:10 along with co catalyst NiO:HY=1:10 gave the best quality of fuel in pyrolysis of LDPE [139]. Detail of the results has been tabulated in Table 05 [139].

Zhou et al. (2021) introduced a continuous, novel, down-draft microwave assisted pyrolysis system, which is very feasible for large scale, continuous production of fuel from waste plastics. HDPE plastic particle with a small dimension and ZSM-5 catalyst has been used to operate the system. An important observation from his experiment was the achievement of the required time for the de-activation of the catalyst bed. It was shown that within the time range of 30-60 min, the composition of the product was degraded which can be compared to thermal pyrolysis without

catalyst. That means catalyst deactivation occurred at this stage [162]. Details of the results has been tabulated in Table 05.

Fan et al. (2021) integrated ex-situ catalytic pyrolysis along with continuous-stirred microwave mechanism. The pyrolysis of LLDPE was studied with HZSM-5 catalyst. It was demonstrated that by increasing the catalyst loading in respect of reactant, the percentage of gas yield was also increased as more active site of the catalyst was utilized [169].

In another paper, Fan, Liu et al. (2021) did an excellent study. The authors compared the continuous and batch microwave pyrolysis system for catalytic and non-catalytic conditions. It has been shown that catalytic pyrolysis had a selective and lower carbon contents yield both for batch and continuous system. In the other hand, non-catalytic catalysis gave a wide range of product distribution [140]. In a batch system, the residence time is higher compared to continuous system. As a result of it, the fractions of the products faced secondary cracking and hence the formation of the non-condensable fractions increased.

#### **2.4.1.2 Iron-based catalyst**

Shen et al. (2022) demonstrated the production of hydrogen and carbon nanotubes (CNTs) from the pyrolysis of HDPE using iron-based catalyst. Fe-based catalyst promoted the formation of surface hot spots by means of increasing the dielectric loss and, hence, the gaseous product(mainly hydrogen) and carbon nanotubes production were established by the pyrolysis of HDPE [142]

Another paper also demonstrated the recent study of the formation of hydrogen and carbon nanotubes from HDPE. Here the proposed reaction is as follows.



In this paper, Ramzan et al. (2022) described the use of the following catalysts, iron oxide, aluminum oxide, nickel oxide prepared by sol-gel method. Only one single step of microwave pyrolysis was developed to get the multiwalled CNTs [148].

Wang et al. (2021) demonstrated an efficient hydrogen production methodology by microwave technology from waste plastic. A high quality and higher percentage of hydrogen were achieved over Fe/Ni supported by CeO<sub>2</sub> with CNTs substrates. The excellence and robustness of the catalyst were proved by getting a H<sub>2</sub> selectivity after five regeneration cycles [143].

Table 5 Effect of catalyst on production yield for the MAP of waste plastic

| References                   | Feedstocks                     | Condition                                                                                                                                                               | Catalyst                                                                                                                                     | catalyst ratio                                                     | Products                                       | Comments on relative content                                                                                                                                                    |
|------------------------------|--------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Ding et al.<br>2019<br>[139] | LDPE<br>powdered<br>500 micron | 15 g LDPE<br>500 g SiC<br>connecting tubes were<br>at 250 C by using<br>heating tape<br><br>Tpyr=500 C<br>Tcat=450 C                                                    | HY zeolite<br>ex-situ                                                                                                                        | HY: LDPE=1:20                                                      | Oil 57%<br>Gas 42.5%                           | MAHs~20%; n-alkenes~25%;<br>medium quality gasoline. The proportion of the<br>aromatics and straight-chain alkene is almost the<br>same.                                        |
|                              |                                |                                                                                                                                                                         |                                                                                                                                              | HY: LDPE=1:15                                                      | Oil 60%<br>Gas 39%                             | MAHs~20%; iso-alkenes~25%; n-alkenes ~18%<br>Good quality of gasoline range product.                                                                                            |
|                              |                                |                                                                                                                                                                         |                                                                                                                                              | <b>HY: LDPE=1:10</b>                                               | Oil 56%<br>Gas 42%                             | MAHs~30%; iso-alkenes~20%; iso-alkanes~18%<br>Very Good quality of gasoline product. High aromatic<br>and branched (iso) HC. High Octane Number.                                |
|                              |                                |                                                                                                                                                                         | NiO<br>( @HY: LDPE<br>=1:10)<br>added as in- situ<br>catalyst                                                                                | HY: LDPE=0<br>(without catalyst)                                   | Oil 52%<br>Gas 48%                             | MAHs ~ 12%, n-alkenes >42% etc.<br>Poor quality of gasoline. High n-alkene, low ON.                                                                                             |
|                              |                                |                                                                                                                                                                         |                                                                                                                                              | NiO: HY=1:15                                                       | Oil 51%<br>Gas 48%                             | MAHs~35%; iso-alkenes~20%;<br>MAHs & iso-alkenes have high percentage, high ON.                                                                                                 |
|                              |                                |                                                                                                                                                                         |                                                                                                                                              | <b>NiO: HY=1:10</b>                                                | Oil 50%<br>Gas 48.5%                           | MAHs~45%; iso-alkenes 10%; cyclo-alkanes10%;<br>High MAHs indicates excellent quality of gasoline                                                                               |
| Nan Zhou,<br>2021<br>[141]   | HDPE<br>2 mm*3 mm<br>*1 mm.    | continuous down-drift<br>microwave<br>assisted pyrolysis<br>(CMAV)<br>Feed in rate 2kg/h<br>P=9kW (output)<br>SiC=absorbent (6kg<br>of 12 mm)<br>Tpyr=620<br>Tcat=400 C | ZSM-5 pellets<br>(dimension $\Phi 2 \times 2-10$ mm,<br>Si/Al molar ratio =<br>19)<br>ex-situ<br>200 g pellets packed<br>in the catalyst bed | plastic=2000g/h*0.5h=1000<br>g)<br>plastic: ZSM-5<br>=1000:500=2:1 | liquid 48.9%<br>gas 49%<br>wax 1.2%            | catalytic pyrolysis 0-30 min<br>aromatic 45%; n-alkene 12.8%;<br>It indicates a good quality of fuel having an<br>excellent catalyst activity                                   |
|                              |                                |                                                                                                                                                                         |                                                                                                                                              | plastic=2000g/h*1h=2000 g<br>plastic: ZSM-5<br>=2000:500=5:1       | liquid 42.2%<br>gas 35.5%<br>wax 17%           | catalytic pyrolysis 30-60 min<br>aromatic 23.3%; n-alkene 42.1%;<br>This indicates the rapid loss of catalytic activity. This<br>composition is analogous to thermal pyrolysis. |
| Leilei Dai,<br>2022<br>[170] | HDPE<br>2-4 mm                 | Tpyr. =500;<br>Tcat. =460;<br>Feed rate= 42 g/h<br>N2=80 ml/min<br>space velocity 7 h-1<br>1 kg SiC balls                                                               | ZSM-5 powder<br>loading on SiC foam<br>disc of 6 g<br>Stream time= 30<br>min                                                                 | SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =280              | 92%<br>aromatics<br>3% alkenes                 | aromatics include benzene, toluene, xylene, benzene,<br>1-ethyl-2-methyl-                                                                                                       |
|                              |                                |                                                                                                                                                                         |                                                                                                                                              | SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =800              | 28%<br>aromatics<br>55% alkenes<br>10% alkanes | the aromatic selectivity is much lower with the C5-<br>C12 olefins as the main products                                                                                         |

|                                                                                    |              |                                                                                                                      |                                                                                                                                                                                                |                                                          |                                                   |                                                                                                                                                                                                                                                           |
|------------------------------------------------------------------------------------|--------------|----------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------|---------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Shen et al. 2022<br>[142]                                                          | HDPE<br>30 g | P <sub>max</sub> =900 W,<br>F=2.45GHz<br>N <sub>2</sub> = 2 mL/s<br>T <sub>pyr</sub> =500C                           | Fe based catalyst.<br>catalyst support:<br>AC, SiC, SiO <sub>2</sub><br>1 g catalyst<br>Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O Fe<br>precursor.<br>Fe loading 3.7 wt%<br>In situ | Fe & AC<br>(High MW absorbing<br>capacity)               | 17% liquid<br>77% gas<br>(83.46% H <sub>2</sub> ) | promoted gaseous products. dielectric loss is high,<br>strongest ability to MW energy.<br>Average CNTs diameter is 141 nm. Due to<br>microscopic hot spot, high dielectric loss enables high<br>heating rate and hence higher production rate of<br>CNTs. |
|                                                                                    |              |                                                                                                                      |                                                                                                                                                                                                | Fe at SiC<br>(Medium MW absorbing<br>capacity)           | 20% liquid<br>73% gas<br>(87.20% H <sub>2</sub> ) | Highest formation of hydrogen gas. In evolved gas<br>composition, C <sub>9</sub> -C <sub>12</sub> is comparatively high. Average<br>CNTs diameter is 26 nm. Medium growth rate of<br>CNTs.                                                                |
|                                                                                    |              |                                                                                                                      |                                                                                                                                                                                                | Fe at SiO <sub>2</sub><br>(Low MW absorbing<br>capacity) | 55% liquid<br>40% gas<br>(73.12% H <sub>2</sub> ) | promoted liquid products. Very low dielectric loss.<br>CNTs were not observed because of the absence of<br>surface hot spots.                                                                                                                             |
|                                                                                    |              |                                                                                                                      |                                                                                                                                                                                                | FeAlO <sub>x</sub> catalysts<br>(Fe loading 22%)         | liquid 6%<br>gas 92%<br>(H <sub>2</sub> 96.82%)   | In gas composition, mostly higher HC. C <sub>17</sub> ~C <sub>22</sub> .<br>It shows the highest proportion of gas products.<br>Highest catalytic activity. CNTs diameter 53 nm                                                                           |
|                                                                                    |              |                                                                                                                      |                                                                                                                                                                                                | FeAlO <sub>x</sub> catalysts<br>(Fe loading 07%)         | liquid 13%<br>gas 85%<br>(H <sub>2</sub> 91.17%)  | In gas composition, C <sub>9</sub> -C <sub>16</sub> is higher.<br>CNTs diameter 76 nm. In the production of CNTs, the<br>morphology and diameter are almost similar.                                                                                      |
| Ramzan et al.<br>2022<br>[148]                                                     | HDPE<br>2 mm | P <sub>max</sub> =1000 W,<br>F=2.45GHz<br>T <sub>pyr</sub> =400 C<br>time=2-10 min                                   | Oxides of Iron,<br>Nickel, Aluminum<br>was prepared using<br>sol gel method<br>In-situ<br>catalyst: feedstock<br>=40:60                                                                        | NiF <sub>2</sub> O <sub>4</sub> : PP                     | H <sub>2</sub> 46<br>mmol/g PP<br>CNTs 45%        | five test cycles of this experiment were operated.<br>Maximum H <sub>2</sub> production and CNTs formation<br>achieved at second cycle. Values are marked at<br>previous column.                                                                          |
|                                                                                    |              |                                                                                                                      |                                                                                                                                                                                                | NiF <sub>2</sub> O <sub>4</sub> :PS                      | H <sub>2</sub> 22<br>mmol/g PS<br>CNTs 60%        | the maximum amount of CNTs was<br>achieved from PS pyrolysis.                                                                                                                                                                                             |
|                                                                                    |              |                                                                                                                      |                                                                                                                                                                                                | NiF <sub>2</sub> O <sub>4</sub> : HDPE                   | H <sub>2</sub> 53<br>mmol/g PS<br>CNTs 52%        | the maximum amount of hydrogen production was<br>achieved from HDPE pyrolysis.                                                                                                                                                                            |
| Fan et al. 2021<br>(Journal of<br>analytical and<br>applied<br>Pyrolysis)<br>[169] | LLDPE        | CSMP<br>Absorber: ball type<br>SiC<br>(D=6 mm)<br>F=6-30 g/min<br>T <sub>pyr</sub> =550 C<br>T <sub>cat</sub> =500 C | ex-situ,<br>conts feeding,<br>HZSM-5<br>Si/Al=80; surface<br>area=425 m <sup>2</sup> /g                                                                                                        | catalyst loading 5%<br>based on reactant                 | condensate<br>41.5%<br>gas 56%                    | In both cases, the yield of char is very low that<br>indicates the complete conversion of LLDPE at 550 C<br>high condensate and low gas percentage                                                                                                        |
|                                                                                    |              |                                                                                                                      |                                                                                                                                                                                                | catalyst loading 20%<br>based on reactant                | condensate<br>25.4%<br>gas 70.3%                  | By increasing high catalyst loading, the yield of gas<br>was increased by a significant amount.                                                                                                                                                           |

|                                                  |                                              |                                                                                                                                                       |                                                                                                                                      |                                                                 |                                         |                                                                                                                                                                                                                 |
|--------------------------------------------------|----------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Wang et al.<br>2022<br>[143]                     | HDPE piece<br>(0.3 g)                        | P=100 W<br>F=2.45 GHz<br>N <sub>2</sub> =150 mL/min<br>(for 10 min before the<br>experiment)<br>substrate: CNTs<br>T <sub>pyr</sub> =800 C            | In-situ<br>Fe/Ni-CeO <sub>2</sub> @CNTs<br>catalyst =0.5g<br>sol-gel method                                                          | Ni <sub>1.15</sub> Ce <sub>0.5</sub><br>feed: cat=3:5           | Gas 25%<br>liquid 10%<br>solid 67%      | Fe/Ni alloy nanoparticles has higher H <sub>2</sub> selectivity.<br>H <sub>2</sub> 91.5% (volume percentage)<br>H <sub>2</sub> 50.2 (mmol/g plastic)                                                            |
| Fan et al. 2021<br>journal of<br>energy<br>[140] | LLDPE                                        | batch                                                                                                                                                 | 1kg SiC<br>(Microwave<br>absorbents)<br>F=2450 Hz<br>P=100 W                                                                         |                                                                 | condensate<br>34%<br>gas 62%<br>char 4% | low condensate yields as volatiles decomposed the<br>smaller molecules. High selectivity in low carbon<br>number C7-C11 that means carbon chain over-<br>cracking reactions occurred.                           |
|                                                  |                                              |                                                                                                                                                       | non cat.                                                                                                                             | N/A                                                             | condensate<br>45%<br>gas 50%<br>char 5% | cracking occurs at a wide range of temperature, long<br>residence time result in secondary cracking and hence<br>the formation of large non-condensable fractions.<br>Wide range of carbon number distribution. |
|                                                  |                                              | CSMP<br>Initially, 30 g<br>weighted LLDPE<br>added.<br>Feed rate=6 g/min<br>absorbents=SiC ball<br>T <sub>pyr</sub> =550 C<br>T <sub>cat</sub> =500 C | ex-situ<br>HZSM-5                                                                                                                    | Catalyst: plastic=0.15                                          | condensate<br>30%<br>gas 67%<br>char 3% | CSMP system has low coal compared to the batch<br>system. High selectivity in high carbon number like<br>C14-C20. narrow distribution of carbon number.                                                         |
|                                                  |                                              |                                                                                                                                                       | non cat.                                                                                                                             | N/A                                                             | condensate<br>85%<br>gas 10%<br>char 5% | high condensate production due to relatively high<br>constant temperature.                                                                                                                                      |
| Zhaohui Chen<br>2022<br>[147]                    | LDPE<br>(< 400 μm)<br>plastic<br>powder=10 g | SiC foam=20 mm*<br>100<br>F=2.45 GHz<br>P=500-600 W<br>T=450 C<br>N <sub>2</sub> =500 ml/min<br>(purging for 10 min)                                  | SiC foam@zeolite<br>core-shell<br>structured catalyst<br>zeolite=1.5 g; coated<br>in SiC foam<br>mm<br>zeolite/plastic<br>ratio=0.15 | ZSM-5<br>(SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =23) | liquid 22%<br>gas 77.1%<br>char 0.9%    | Liquid products were gasoline range hydrocarbons<br>(C <sub>5</sub> -C <sub>12</sub> ) without wax production.<br>Aromatics contents in liquid is very high(97.2%)                                              |
|                                                  |                                              |                                                                                                                                                       |                                                                                                                                      | ZSM-5<br>(SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =80) | liquid 17.8%<br>gas 81.7%<br>char 0.5%  | C <sub>1</sub> ,C <sub>2</sub> decreased. C <sub>4</sub> ,C <sub>4</sub> =,C <sub>5</sub> ,C <sub>5</sub> = increased.<br>The concentration of H <sub>2</sub> decreased<br>Aromatics contents in liquid is 91%  |

### **2.4.2 Effect of pyrolysis temperature**

Pyrolysis temperature holds an important key for the desired product distribution. To get the liquid product, temperature should be optimized. Low temperature causes high residue formation which indicates incomplete decomposition. The pyrolysis or degradation rate of any plastic particle is slow at low temperatures in the microwave reactor. Again, at high temperatures, secondary cracking of the oil is enhanced. Therefore, the production of the gases increases at high temperatures.

Ding et al. presented the effect of temperature on the pyrolysis of LDPE. It was shown that at 450 C, the oil yield was minimum and the maximum oil yield was tabulated at 500 C which is the optimum temperature [139].

### **2.4.3 Effect of Different type of absorbents**

As hydrocarbons are not responsive to microwave radiation, microwave absorbers must be used for the cracking of the plastic materials. Usually, microwave absorbers absorb the microwave the radiation and transfer the heat by conduction and radiation.

Jing et al. focused on reusing the Spherical Activated Carbon (SAC) absorbents for the microwave pyrolysis of PP. The influence of this catalyst on heating rate was also analyzed. The formation of light oil was accelerated by choosing the appropriate heating rate along with co-cracking of PP and wax which was from the previous operation. In terms of heat transfer from the absorbents to the feedstock, SAC has unique excellence. The effect of different proportion of SAC was analyzed on the yield of product [171].

Rex et al. demonstrated the microwave pyrolysis of PS and PP mixtures using various activated carbon derived from rice husk (RH), corn husk (CH) and coconut sheath (CS). The carbon generated from these biomasses were also utilized in the operation of pyrolysis. It was shown that the highest yield of the liquid product was achieved by the utilization of coconut sheath activated carbon. The quality of the liquid oil was also compared by putting gasoline as a reference fuel and the result was quite satisfactory. The effect of different types of carbon & activated carbon derived from biomass was analyzed in this literature. Furthermore, the effect of polymer to absorbents ratio both for individual plastic and mixed plastic, the effect of power was critically examined in this paper. The composition of gas fraction was high while using activated carbon as it had higher potential to decompose the plastic materials. The ignition quality of the fuel using coconut sheath activated carbon was neat to gasoline. [172].

**Table 6 Using different materials as MW absorbents**

| Reference                    | Feed                                                      | Operating Condition                                                                                     | Absorber                                | ratio of absorber        | product                                    |
|------------------------------|-----------------------------------------------------------|---------------------------------------------------------------------------------------------------------|-----------------------------------------|--------------------------|--------------------------------------------|
| Jing et al,<br>2019<br>[171] | PP<br>2-4 mm<br>grains                                    | Pmax=1300 W<br>500 mL flask<br>P=40% of Pmax<br>N <sub>2</sub> purge rate 200<br>ml/min<br>time= 40 min | Spherical<br>Activated Carbon<br>(SAC)  | SAC: PP=140 g: 70 g AR1  | liquid 62%<br>gas 36%                      |
|                              |                                                           |                                                                                                         |                                         | SAC: PP=140 g: 100 g CR1 | liquid 35%<br>gas 65%                      |
| Rex et al.,<br>2020<br>[172] | PSW (0.5<br>cm)<br>10 g<br>and<br>PPW (0.3<br>cm)<br>10 g | Microwave Batch<br>P =900 W<br>250 ml flask<br>Carbon 2g<br>Feed: Absorbent=10:1<br>time= 10 min        | Rice Husk<br>Carbon (RHC)               | RHC: PSW=1:10            | liquid 66.70%<br>gas 14.90%<br>Char 18.40% |
|                              |                                                           |                                                                                                         | Corn Husk<br>Carbon (CHC)               | CHC: PSW=1:10            | liquid 83.30%<br>gas 15.80%<br>Char 0.90%  |
|                              |                                                           |                                                                                                         | Coconut Sheath<br>Carbon (CSC)          | CSC: PSW=1:10            | liquid 86.10%<br>gas 10.50%<br>Char 3.40%  |
|                              |                                                           |                                                                                                         | Rice Husk<br>Activated Carbon<br>(RHAC) | RHAC:(PSW+PPW) =2:10     | liquid 58.90%<br>gas 38.48%<br>Char 2.62%  |
|                              |                                                           |                                                                                                         | Corn Husk<br>Activated Carbon<br>(CHAC) | CHAC:(PSW+PPW) =2:10     | liquid 63.95%<br>gas 34.01%<br>Char 2.04%  |

|                                              |                                                                   |                                                                                               |                                              |                       |                                           |
|----------------------------------------------|-------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|----------------------------------------------|-----------------------|-------------------------------------------|
|                                              |                                                                   |                                                                                               | Coconut Sheath<br>Activated Carbon<br>(CSAC) | CSAC:(PSW+PPW) =2:10  | liquid 72.36%<br>gas 25.31%<br>Char 2.33% |
| Suriappapra<br>o<br>& Vanu,<br>2015<br>[157] | PP (5-10<br>mm)<br>5 g<br><br>LDPE &<br>LLDPE<br>(5-10 mm)<br>5 g | Microwave Batch<br>P =450 W<br>N <sub>2</sub> =1 L/min before<br>the experiment for<br>10 min | Graphite                                     | graphite: PP= 1:100   | liquid 48.16%<br>gas 50.66%               |
|                                              |                                                                   |                                                                                               |                                              | graphite: PP= 1:25    | liquid 16.19%<br>gas 82.61%               |
|                                              |                                                                   |                                                                                               |                                              | graphite: LDPE=1:100  | liquid 46.50%<br>gas 60.20%               |
|                                              |                                                                   |                                                                                               |                                              | graphite: LLDPE=1:100 | liquid 39.12%<br>gas 52.70%               |
|                                              |                                                                   |                                                                                               | Activated carbon                             | AC: PP=1:100          | liquid 29.80%<br>gas 69.80%               |
|                                              |                                                                   |                                                                                               | Silicon Carbide                              | SiC: PP=1:100         | liquid 31.89%<br>gas 66.52%               |
|                                              |                                                                   |                                                                                               | Aluminum                                     | Al: PP=1:100          | liquid 45.40%<br>gas 53.42%               |
|                                              |                                                                   |                                                                                               | Fly Ash                                      | Fly Ash: PP=1:100     | liquid 21.07%<br>gas 78.23%               |
|                                              |                                                                   |                                                                                               | Lignin                                       | Lignin: PP=1:100      | liquid 41.86%<br>gas 56.98%               |

Another excellent paper which was written by Suriapparao & Vinu, different type of susceptors behavior was analyzed in terms of product yield. They used PP, LDPE and LLDPE type plastic waste and also analyzed the effect of microwave power and susceptor to produce temperature & heating rate, profile. The yield for gas, liquid and residue was tabulated (Table 06) for six different susceptors, graphite, Activated Carbon (AC), Silicon Carbide (SiC), Aluminum powder (Al), Fly Ash (FA) and Lignin. From the analysis, it could be said that graphite showed highest yield of the liquid oil for the pyrolysis of PP. Regarding the quality of obtained gas, highest amount of C5 HC was obtained by the pyrolysis of LLDPE and graphite [157].

## 2.4.4 Effect of particle sizes

In the study of microwave pyrolysis, Liu et al. (2022) demonstrated the effect of sheet size on polyethylene terephthalate (PET) bottles along with absorber load and the pyrolysis temperature. It was shown that increasing the particle size or sheet size of the plastic bottle increases the solid and gas product percentage in the products. At the specified conditions, the PET's molecular structure resulted in no pyrolysis oil. It was shown that with the increase in the sheet size, the heating rate and energy efficiency (both recovered energy and overall energy) increased [173]. Details of the results are illustrated in the Table 07.

**Table 7 Effect of plastic sizes on product distribution**

| References               | Feed       | Operating condition                                                              | size (mm <sup>2</sup> ) | Heating rate(C/min) | Products distribution               |
|--------------------------|------------|----------------------------------------------------------------------------------|-------------------------|---------------------|-------------------------------------|
| Liu et al. 2022<br>[173] | PET bottle | PET plastics 30 g<br>SiC load 40 g<br>pyrolysis T= 500 C<br>Power tuned at 500 W | 2.5 × 2.5               | 19.99               | solid 10%<br>Gas 15%<br>Residue 75% |
|                          |            |                                                                                  | 5.0 × 5.0               | 24.81               | solid 12%<br>Gas 22%<br>Residue 68% |
|                          |            |                                                                                  | 7.5 × 7.5               | 28.85               | solid 20%<br>Gas 30%<br>Residue 50% |
|                          |            |                                                                                  | 10 × 10                 | 33.32               | solid 25%<br>Gas 35%<br>Residue 40% |

### 2.4.5 Effect of Microwave Power

Microwave power consumption is directly associated with the yield. It is proportional. But this increase has a limit. It was found that further increase of power output led to the formation of non-condensable gas because of lifting of the system temperature [174–179].

Again, the power rating strongly depends on the nature of the feedstock. 300 W is the threshold value for the pyrolysis of biomass [180–185] while plastics require around 500 W to be pyrolyzed.

Moreover, every process has a minimum temperature requirement to start the pyrolysis. So, there is a strong relationship between the output power and optimum temperature. It also depends on the catalyst and feedstock ratio and size of the reactor [177,186–189].

For industrial cases, the power range varies from 1-3 kW while it is maximum 800 W for lab scale [174–176].

Suriapparao et al. (2021) demonstrated the effect of power in the pyrolysis of waste polypropylene. The experiment was done at three different power 600, 450 & 300 W to check the product distribution. The highest oil yield was recorded at 450 W and highest gas yield was recorded at 300 W. Regarding the char yield, it was almost same around 4% for three power ratings. In all cases, 50 g graphite susceptor was used to absorb the microwave energy and to transfer it to the WPP [190]. Important findings are tabulated in Table 07.

In another paper, Arshad et al. (2020) showed the effect of power for the microwave assisted pyrolysis of PP, PS, LDPE individually and as a mixtures of a different ratio [191].

Hong et al. described the effect of power on the heating performances of LDPE plastic particles. The results suggested that the temperatures of the plastics particles reached to the maximum for highest microwave power [164].

**Table 8 Effects of powers for different grade of plastic on product yield**

| References                          | Feed                   | Oearating condition                                                                                                                                                | Power(W) | Processing time (min) | Product distribution                 | Comments                                                                                                                                                                    |
|-------------------------------------|------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|-----------------------|--------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Suriapparao et al.<br>2020<br>[190] | Waste<br>Polypropylene | Feed 50 g(melted)<br>Graphite susceptor 50g<br>T=600 C<br>F=2.45 GHz                                                                                               | 600      | 8                     | Oil 58.7%<br>Gas 37.3%<br>Char 4.0 % | heating rate 38.5 C/min                                                                                                                                                     |
|                                     |                        |                                                                                                                                                                    | 450      | 12                    | Oil 63.4%<br>Gas 32.4%<br>Char 4.2%  | heating rate 24.9 C/min                                                                                                                                                     |
|                                     |                        |                                                                                                                                                                    | 300      | 22                    | Oil 44.2%<br>Gas 51.9%<br>Char 3.9   | heating rate 16.3 C/min                                                                                                                                                     |
| Arshad et. al<br>2020<br>[191]      | PS                     | Two magnetrons,<br>each 1.5 kW.<br>Galvanized iron (GI)<br>was used as a reaction<br>chamber.<br>Bottom part of the GI<br>pipe was surrounded by a<br>an iron coil | 2100     | 19                    | oil 88.7%<br>gas 6.70%               | conversion 95.40%. PS has highest oil yield due to<br>its low cracking temperature. It has polycyclic structure<br>rather than crossed chain HC which is easy to breakdown. |
|                                     | PP                     |                                                                                                                                                                    | 2500     | 23                    | oil 54.65%<br>gas 40.45%             | conversion 95.10%                                                                                                                                                           |
|                                     | LDPE                   |                                                                                                                                                                    | 2500     | 26                    | oil 30.15%<br>gas 24.15%             | conversion 54.30%                                                                                                                                                           |
|                                     | PS-PP                  |                                                                                                                                                                    | 2300     |                       | oil 77.50%<br>gas 18.75%             | conversion 96.25%                                                                                                                                                           |
|                                     | PS-LDPE                |                                                                                                                                                                    | 2500     |                       | oil 71.30%<br>gas 17.10%             | conversion 88.40%                                                                                                                                                           |
|                                     | PP-LDPE                |                                                                                                                                                                    | 2500     |                       | oil 44.45%<br>gas 30.54%             | conversion 74.99%                                                                                                                                                           |
|                                     | PS-PP-LDPE             |                                                                                                                                                                    | 2300     |                       | oil 67.30%<br>gas 28.43%             | conversion 95.73%                                                                                                                                                           |

## **2.5 Analysis of the effect: Microwave Assisted Co-Pyrolysis of Plastic & Biomass**

When the combined outcome is higher than the individual summation of two substance, it is known as synergistic effect [116,192–196]. An important issue is that only pyro-oil from waste plastic has high viscosity and contains waxy paraffinic components. To get an improved oil yield and properties, the conventional microwave pyrolysis of plastic is replaced with the co-pyrolysis of waste plastics and biomass [197–199]. Many of the researchers reported the synergistic effect of co-pyrolysis of waste plastic and biomass [150,200–202].

Potnuri et al. (2022) described the microwave assisted co-pyrolysis of PS and Torrefied Saw Dust (TSD) in the presence of graphite susceptor and KOH catalyst. The author and his team showed the effect of torrefied temperature of saw dust and feeding ratio on the product yield, energy scenario and synergistic effect. It was described that the higher torrefied temperature along with higher catalyst ratio gave the higher yield. The polynomial regression-based machine learning approach was also implemented to evaluate the effect of the process parameters with a good regression value [203].

Zhang et al. (2022) showed the co-pyrolysis of LDPE and Spent bleaching clay (SBC) derived from refined rice oil in the presence of HZMS-5 ex-situ catalyst bed. The author and his team explored the synergistic effect in terms of the increment of the mono aromatic hydrocarbon in the liquid product and hence increased the quality of the liquid oil. It was also demonstrated the production hydrogen fraction in the gas due to the synergistic effect. The effect of different feedstock ratio, catalytic bed temperature, mass of the catalyst, pyrolysis temperature was also well analyzed on the production and the quality of the fuel [204] .

Chen et al. (2022) explored the microwave catalytic pyrolysis of *Chlorella vulgaris* and HDPE. The activated carbon supported Cerium, Ferrous and Nickel based catalyst were explored with different ratios. Both Ce/AC and Fe/AC showed good catalytic activity in the production of bio-oil [205].

Suraipparao et al. (2022) demonstrated the MACCP in the presence of KOH catalyst and graphite absorber of PS and WTP (Waste Tea Powder) and showed the maximum conversion achieved at PS:WTP=5:1 [206].

The same author introduced the MACCP of wheat straw (WS), Rice Straw (RS) along with PP and PS using ZSM-5 catalyst. The author and his team used two successive microwave reactors where one was used to feed the plastic and biomass sample and another one was used to hold the catalyst [207].

Neha et al. (2022) focused on the upgradation process of pyrolysis oil using hydrodeoxygenation (HDO) produced from the microwave catalytic co-pyrolysis of food waste and LDPE. The quality of bio-oil was also benchmarked against standard bio-fuel (ASTM D7544) in this study [208]. In the previous paper of same author showed, the optimized condition for the production of bio-oil achieved by utilization of synergic effect [209].

Sridevi et al. (2022) also did a similar study with PS and Rice Husk (RH). Like one of the previous study, graphite susceptor and KOH catalyst was explored here [210].

Zhao et al. (2022) explored different microwave absorbents for the co-pyrolysis of PET and sawdust biomass. It was showed that dielectric loss of carbon powder is higher so it can convert microwave to thermal energy more efficiently. Moreover,  $\text{Fe}_3\text{O}_4$  acts as an acid catalyst which accelerates the decarboxylation and esterification reaction. Finally, CaO acts as a basic catalyst

which enhances thermal cracking, catalytic cracking and converts acid to ketones and HCs. In individual pyrolysis of PET pyro-oil contained the following composition: 58.7 wt% benzoic acid and its derivatives, 14.5 wt% benzene and its derivatives, 17.48 wt% ring like compounds. Regarding the quality of liquid phase as a synergistic effect in co-pyrolysis, 7.9 wt% terephthalic acid, 12 wt% phenol, 5.8 % furfural, 6 % PAH were found. Then the obtained liquid dissolved and diluted to dichloromethane to process further. In this paper, the quality of liquid oil was discussed comprehensively [116].

Utilizing the medical waste plastic during COVID-19 outbreak along biomass also attracted the attention of the researchers [18,211]. Co-pyrolysis are also being vastly implemented to pyrolyze the microalgae [212–219], waste cooking oil [220], agro-residuals biowaste[221], food waste[222–230] along with waste plastics.

**Table 9 Different type of feedstocks, operating condition, yield is listed for MACP**

| Reference                     | Feedstock                                         |                                                                                       | Ratio of plastic: Biomass | Reactor parameters                                                                                                 | Operating Condition                                        |                                                     | Yield (wt%)           |                       |                        | Synergistic effect/Comments                                                                    |
|-------------------------------|---------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------|--------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|-----------------------------------------------------|-----------------------|-----------------------|------------------------|------------------------------------------------------------------------------------------------|
|                               | plastic                                           | Biomass                                                                               |                           |                                                                                                                    | absorbent                                                  | catalyst                                            | gas                   | liquid                | char                   |                                                                                                |
| Potnuri et al. 2022 [203]     | PS (Polystyrene) spherical granules <1 mm<br>10 g | TSD (Torrefied Saw Dust) sieved powder <1 mm<br>Torrefied at 125, 150 & 175 C<br>10 g | 1:01                      | Type= MACCP, batch, in-situ<br>P=300 W<br>Time =10 min                                                             | Graphite powder 150 µm<br>20 g                             | KOH powder (5-15 g)<br>100 µm                       | 11.4                  | 59.6                  | 29                     | highest positive synergy in the liquid yield (-10.6 wt%) at 5 g KOH & T <sub>torr</sub> =125 C |
| Zhang et al. 2022 [204]       | LDPE                                              | Spent Bleaching Clay (SBC) clay left over from the refined rice oil.                  | 18.5:50                   | MACCP, batch, ex-situ<br>P=800 W<br>Time =30 min<br>inert: N <sub>2</sub> at 40 ml/min<br>T <sub>pyr</sub> = 550 C | SiC, 31.5 g. Also, SBC (biomass feed) acts as MW absorbent | HZSM-5 (Si/Al=50)<br>7 g<br>T <sub>cat</sub> =400 C | 50                    | 50                    | 0                      | 8% MAHs in oil<br>30% H <sub>2</sub> in gas                                                    |
| Chen et al. 2022 [205]        | HDPE 15 g                                         | Chlorella Vulgaris 15 g                                                               | 1:1                       | MACCP, batch, in-situ<br>N <sub>2</sub> =700 ml/min                                                                | Activated Carbon                                           | 40% Ce/AC<br>40% Fe/AC<br>10% Ni/AC                 | 70.1<br>25.6<br>19.25 | 22.5<br>57.39<br>68.5 | 7.39<br>17.01<br>12.25 | mostly C7-C12 highest Aromatic HC<br>mostly C13-C23                                            |
| Suriapparao et al. 2022 [206] | PS (Polystyrene) 25 g                             | Waste Tea Powder (WTP) 5 g                                                            | 5:1                       | MACCP, batch, in-situ<br>T <sub>pyr</sub> =700 C                                                                   | 10 g Graphite                                              | 5 g KOH                                             | 0.5                   | 79.6                  | 2.3                    | highest 97.7% conversion achieved                                                              |
| Suriapparao et al. 2022 [231] | PS 10 g                                           | Wheat straw (WS) 10 g                                                                 | 1:1                       | MACCP, batch, ex-situ<br>T <sub>pyr</sub> =600 C,                                                                  | 5 g graphite susceptor                                     | 2 g commercial grade ZSM-5                          | 34.1                  | 58.4                  | 7.5                    | conversion 92.5%                                                                               |

|                                 |            |                            |                          |                                                                                                                                                                                                                                             |                                                                     |                                                                    |                                                                                                                             |      |      |                                                                    |
|---------------------------------|------------|----------------------------|--------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------|--------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|------|------|--------------------------------------------------------------------|
|                                 | PP<br>10 g | Rice Straw<br>(RS)<br>10 g | 1:1                      | P=450 W<br>T <sub>cat</sub> = 600 C;<br>catalyst<br>holds in a<br>second MW.<br>MACP,<br>batch, in-situ<br>P=1000 W;<br>T <sub>pyr</sub> = 550<br>C;<br>N <sub>2</sub> =0.25<br>L/min<br>MACCP;<br>P=450 W;<br>T <sub>pyr</sub> =600 C<br>; | Granular<br>activated<br>Carbon<br>(GAC)                            | Ni-Mo supported<br>on Zirconia for<br>hydrodeoxygenatio<br>n (HDO) | 42.6                                                                                                                        | 46.1 | 11.3 | conversion<br>88.7%                                                |
| Neha et al.<br>2022<br>[208]    | LDPE       | Food Waste<br>(FW)         | 13:87<br>(Total 50<br>g) |                                                                                                                                                                                                                                             |                                                                     |                                                                    | 16                                                                                                                          | 42   | 42   | synergy<br>achieved by the<br>production of<br>HC and H<br>radical |
| Sridevi et al.<br>2022<br>[210] | PS<br>15 g | Rice Husk<br>(RH)<br>5 g   | 3:1                      |                                                                                                                                                                                                                                             | graphite<br>powder<br>10 g                                          | KOH powder<br>~100 µm<br>5 g                                       | 53.2                                                                                                                        | 36.6 | 6.5  | conversion<br>93.5%                                                |
| Zhao et al.<br>2021<br>[116]    | PET<br>8 g | Sawdust<br>8 g             | 1:1                      |                                                                                                                                                                                                                                             | Carbon<br>powder (0.8<br>g)/<br>Fe <sub>3</sub> O <sub>4</sub> /CaO | N/A                                                                | Liquid product<br>analysis: 35%<br>Benzoic acid and its<br>derivatives<br>12% phenols; 5.8%<br>furfural; 20% esters<br>etc. |      |      | Synergy:<br>promotes<br>aromatic<br>acid and phenols<br>conversion |

## 2.6 Literature gap on Microwave catalytic pyrolysis

In recent years, extensive research has been done for the microwave assisted pyrolysis of waste plastics. Still, investigations are going on to upgrade the process efficiency, products yield, quality of the fuel etc. To develop the pyrolysis technology in industrial and commercial stage as well as successful implementation in lab-scale and pilot scale, following challenges are addressed.

1. Firstly, the type of fuel (gasoline range/ naphtha range/ jet fuel / aviation fuel / heavy oil/ syngas/ hydrogen etc.) from microwave pyrolysis is determined from the demand of customer. Most of the cases, the quality of the fuel achieved from pyrolysis differs from the quality of above-mentioned fuel due to the fluctuations of the process parameters. In this case, further upgradation is required to meet the demand. For example, if gasoline range product is demanded from the pyrolysis to use as a fuel in a car, it must hold almost same quality as gasoline. Otherwise, it will corrode the engine. Therefore, there is a huge scope to have more study to get the product as demanded.
2. In most of the recent reviews, mostly pellet or resin/fluff of PP, PS, LLDPE, LDPE, HDPE were studied which contains almost zero impurities. Moreover, real-world plastic waste mixtures contain dyes, pigments, metal impurities, glasses, dirt etc. First of all, these impurities must be removed in case of large-scale implementation of this technology where real-world plastic will be chosen. The second concern is to separate the different grades of plastic, especially the removal of PVC is a must as hydrochloric acid forms on its pyrolysis. Even, the study of PVC and PET is comparatively less due to the formation of hydrochloric acid and phthalic acid respectively on pyrolysis. Therefore, real-world plastics could be addressed more extensively in the future study.

3. Measuring the temperature inside the microwave reactor is another challenge. One of the researchers fabricated a special contact type thermometer (K-type thermocouple; having the wiring of chromel, alumel, alumina and glass tube covering) which allowed to measure the temperature inside the microwave reactor in OFF mode. In this case, it had the limitation to measure the temperature at ON mode. Moreover, only a short distance thermocouple can be used inside the reactor as long-distance wire interacts the electromagnetic field. Using IR-based thermometer has also taken the attraction of researchers. But only the surface temperature can be estimated using IR-based temperature. The inner temperature varies in different zones inside the reactor, it cannot be predicted using this. Though some microwave temperature software (Quick Wave 3D) is available, there is enough scope to develop novel methods to measure the temperature inside the microwave pyrolysis reactor.
4. The formation of hotspot due to electromagnetic field is another problem that makes the temperature measuring task more difficult. During the propagating of microwave, antinode zones are heated where node zones remain unheated. So, a proper stirring system that provides the rotation of sample along with internal circulation is very important. However, some authors discussed this issue, there is still chance to develop more robust system considering this.
5. As microwave reactors require absorbents to absorb the microwave radiation, the cyclic use of microwave absorbents is very important in terms of developing an economically

viable process. After the completion of each cycle, absorbents end with some char and wax part of the sample. Separating this part from absorbents is a laborious job. Sieving, washing with solvent, drying; following all steps involve hard work. Even after the recovery of the absorbents, impurities exist that create a problem for the next cycle. This part of the operation is mostly unstated in the literature. Finding a more efficient way to accomplish this step and also finding more efficient absorbents need attention of the researchers.

6. Regarding the catalyst, there are two ways to use it, in-situ and ex-situ. All the materials (plastic sample, absorbents, catalyst) are put together inside the reactor in in-situ catalysis. Once, the catalyst is used in this manner, it cannot be used for the next (non-regenerable). In ex-situ bed, catalyst bed is heated externally where quartz wool holds it in a quartz glass tube and pyrolysis vapor allows to pass through it. Catalyst can be used several times in this way, but each time it requires regeneration. Researchers focus on zeolite-based catalyst mostly. There is an opportunity to explore more.
7. The batch-mode operation was mostly utilized for the study of microwave pyrolysis where the amount of plastic is very less like 5~25 g. The study of continuous microwave pyrolysis process is not as much like batch. One of the continuous studies, 10 kg/h waste plastic was pyrolyzed. The continuous study should be wider and more feasible considering catalyst regeneration system for the commercial implementation.
8. There is a gap in the literature regarding the use of metal-doped zeolites for the pyrolysis of plastic materials under microwave irradiance. Metal impregnated zeolite possesses both acid sites and metal sites where alumina-silicate supports provide acid sites and supported

metals like Ni, Cu, Co, or their mixtures provide metal sites. Moreover, the addition of second metal brings variations on the basic property of zeolite-based catalyst.

## **2.7 Research Objectives**

- ✓ Develop Microwave pyrolysis facilities for the decomposition of plastics.
- ✓ To experimentally produce liquid and gaseous fuels from waste plastics
- ✓ Assessing pyrolysis oil quality by SimDist, GC-MS, FTIR,  $^1\text{H}$  NMR.
- ✓ Analysis the syn gases using MicroGC.
- ✓ Develop catalysts and understanding catalytic activity by XRD, SEM-EDS, BET, DSC-TGA.
- ✓ Overall, developing sustainable methods for waste management.

## CHAPTER 3

# RESULTS AND DISCUSSION

### 3.1 Characteristics of LDPE feedstocks

Thermogravimetric analysis (TGA) was employed to investigate the thermal degradation characteristics of the feedstocks, which allowed for the determination of the optimal pyrolysis temperature. This method measures the change in weight as a function of temperature. By examining the TGA curve, the sample's weight loss could be determined with respect to the increase in temperature. Figure 16 illustrates the TGA curve of LDPE. The mass loss in the first region (98.57-348.01 °C) was not significant as it is only for water and physical absorbents removal. The second region shows the highest weight loss at 348.01-501.33 °C temperature zone. All the LDPE vaporized before 500 °C. Therefore, there is no weight loss after 500 °C. It also certifies that there is no ash content in this sample. Consequently, the selected pyrolysis temperature for pyrolysis reaction LDPE was 500°C.

The derivative weight (%/min) profile provides a clearer demonstration of the weight loss behavior. A large peak between 348.01-501.33 °C temperature zone indicates significant mass loss of LDPE. Maximum peak position at 470 °C supports the maximum weight loss at this temperature. Then, it reduces gradually. It becomes straight after 500 °C signifying there is no weight loss anymore.

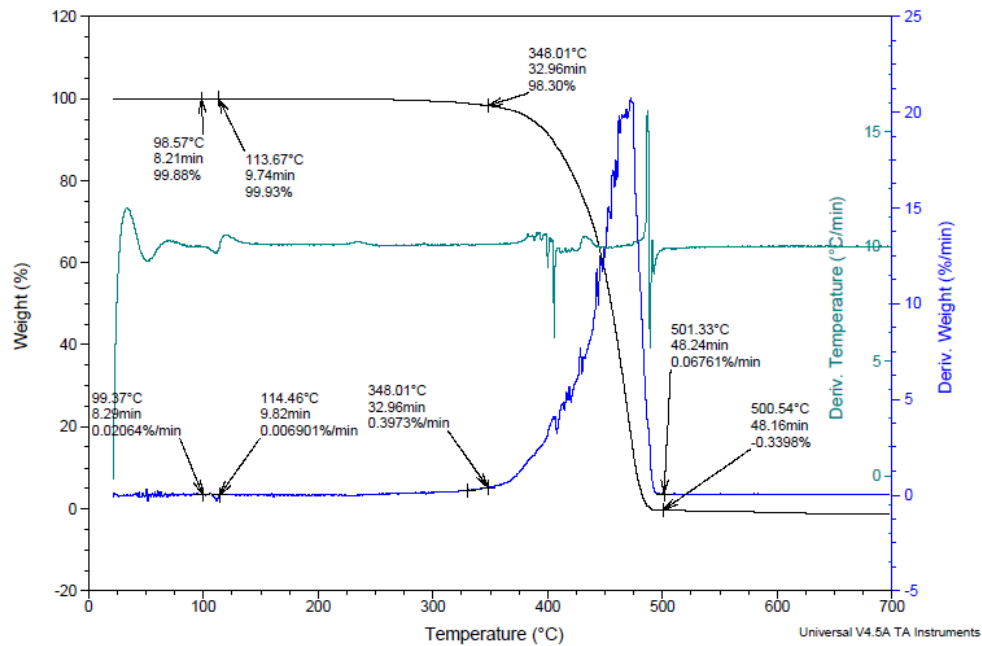


Figure 16. Thermogravimetry curves of LDPE

The derivative temperature ( $^{\circ}\text{C}/\text{min}$ ) profile is almost straight throughout the operation. It is observed that the temperature change sharply decreases right before the second region and then immediately increases after the second region. In between these the temperature doesn't change in unit time. This sudden change of the temperature is due to phase transition and thermal decomposition of the LDPE.

### 3.2 Comparative yield analysis

Figure 17 shows the yields of pyrolysis oil and gas obtained using different catalysts (Z3, GZ3, GNiZ3, GCoZ3, and GCuZ3). As the yield of coke was very negligible, it was not shown as a product yield. Coke was mixed along with spent catalyst. The characteristics of this coke along with spent catalyst will be discussed in catalyst characterization section.

Looking at the data, it can be observed that the yield of pyrolysis oil varies between 15.33% and 26.05%, while the yield of gas varies between 73.95% and 84.67%.

Among the catalysts tested, GZ3 appears to give the highest yield of pyrolysis oil (26.05%), while Z3 gives the lowest yield (15.33%). On the other hand, Z3 gives the highest yield of gas (84.67%), while GZ3 gives the lowest yield (73.95%).

It's worth noting that the yields of pyrolysis oil and gas obtained with the other catalysts (GNiZ3, GCoZ3, and GCuZ3) fall in between the values obtained with Z3 and GZ3. The yield using GCuZ3 gives almost the same yield as GZ3. So, GCuZ3 could also be considered as a good option along with GZ3.

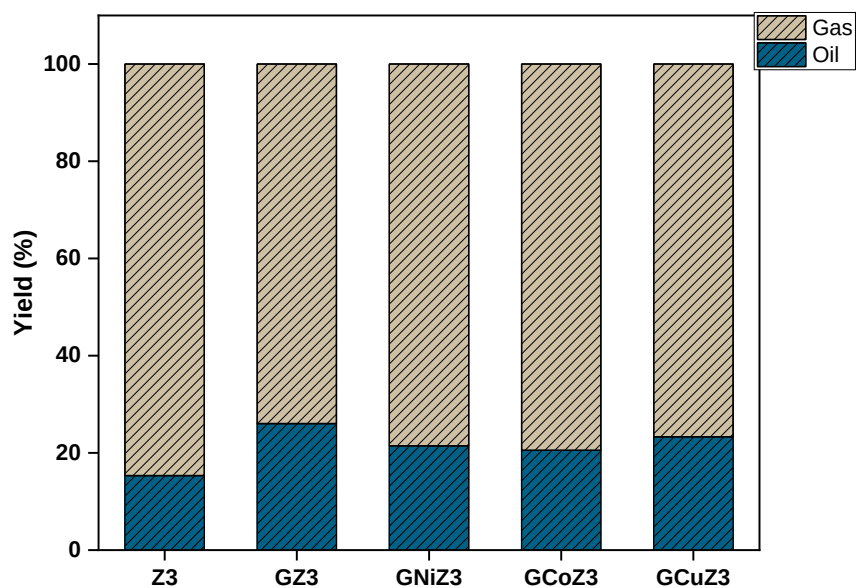


Figure 17. Yield percentage for different catalysts.

However, the addition of Gallium shows improvement in liquid yield. The influence of adding a second metal will be more understandable from the GC-MS and gas analysis data.

### 3.3 Characterization of pyro-oil samples

#### 3.3.1 Simulated Distillation (SimDist) analysis

Simulated distillation GC analysis is employed to analyze the boiling-point distribution of various petroleum fractions, including heavy oil, diesel oil, and gasoline. A nonpolar column-equipped gas chromatograph is utilized to separate the components according to their boiling points, resulting in a retention time - boiling point curve. By dividing the chromatogram's total area into equivalent time intervals, the proportion of elution volume in each interval can be calculated. This data is used to determine the elution volume (%) in each boiling point range, allowing for the creation of a distillation characteristics curve that illustrates the relationship between the elution volume (%) and boiling point.

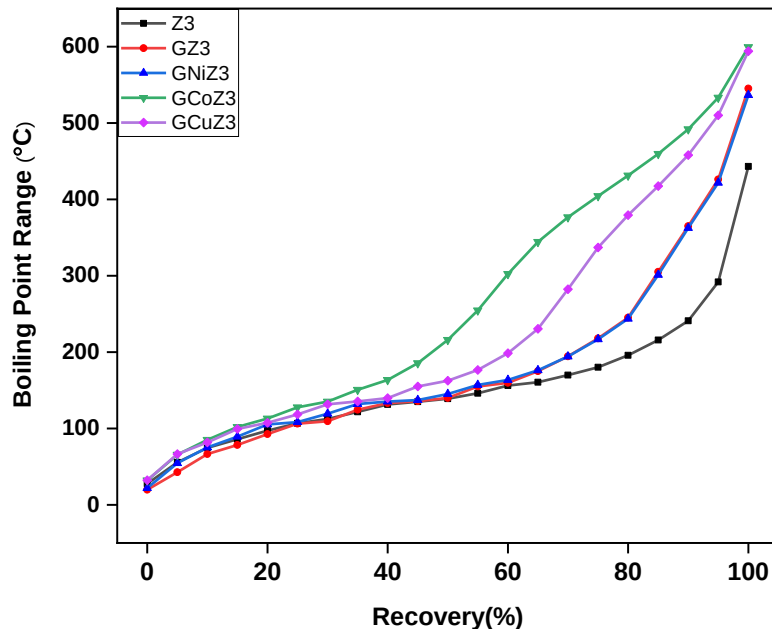


Figure 18. Boiling Point range vs. recovery (%) percentages of pyrolysis oil (SimDist)

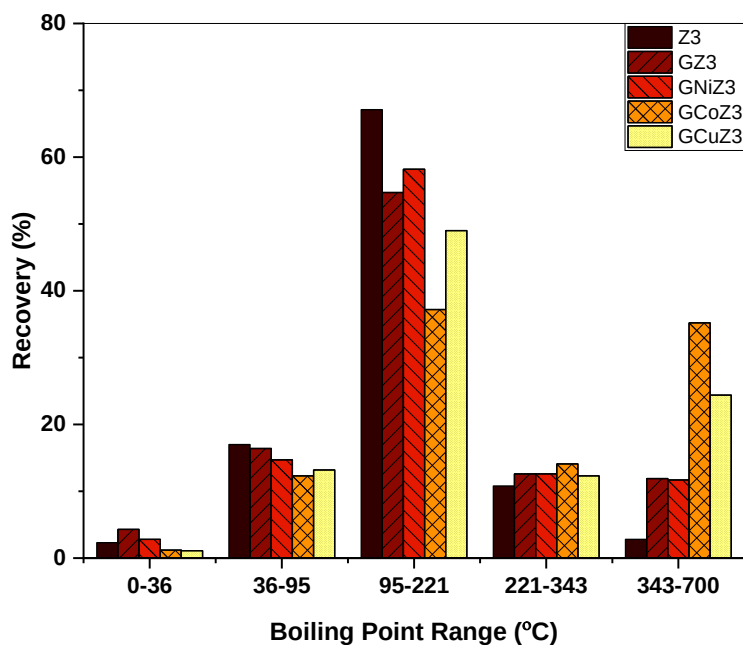


Figure 19. Recovery (%) vs. Boiling Point range (SimDist)

Figures 18 & 19 represent boiling point range data for pyrolysis oil and its recovery percentage for different catalysts. The typical boiling point range of gasoline is between 30-200°C, while for diesel, it is between 200-350°C.

Among the catalysts used, the highest gasoline range product was observed with Z3 catalyst at around 86%. GZ3 and GNiZ3 catalysts showed almost the same boiling point range product distribution, with the gasoline range fraction at around 75% and the diesel range fraction at around 12%. The addition of cobalt in the GZ3 catalyst resulted in a reduction of the gasoline range fraction to 50%, while the diesel range fraction increased to 14%, which was the maximum of all. However, the heavier fraction recovery was also very high, making this catalyst unsuitable for this purpose. The addition of Copper in the GZ3 catalyst resulted with the gasoline range product at around 63% and the diesel range product at around 12%.

In conclusion, it can be said that the addition of Gallium slightly enhances the formation of heavier hydrocarbons. Ni addition doesn't bring any extra change, whereas Cobalt and Copper further enhance the formation of heavy hydrocarbons.

### **3.3.2 GC-MS analysis**

GC-MS is a powerful analytical technique used to identify and quantify the chemical composition of complex mixtures like pyrolysis oil. The method involves separating the mixture using gas chromatography and then analyzing the individual components using mass spectrometry to determine their molecular weight and structural information. GC-MS spectrum of pyrolysis oil shows that aromatics are the main products. The formation of C<sub>9</sub> aromatic was the minimum for GZ3 which was 11%. GCuZ3 resulted with maximum C<sub>9</sub> aromatics conversion which was almost 55% of the total product yield. From Figure 20, it is quite understandable GNiZ3 and GCoZ3 showed 19% and 35% C<sub>9</sub> aromatic conversion respectively. C<sub>9</sub> aromatics are mainly benzene derivatives. C<sub>9</sub>-C<sub>12</sub> aromatics content was maximum 90% for GCuZ3, minimum 61% for GCoZ3. Catalysts Z3 & GZ3 showed almost same percentage of this C<sub>9</sub>-C<sub>12</sub> aromatic, and it was around 69%.

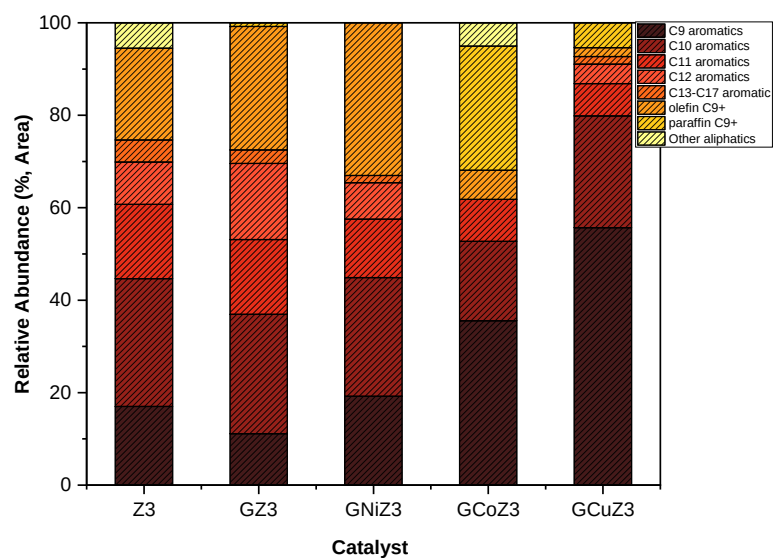


Figure 20. GC-MS analysis of the pyrolysis oil

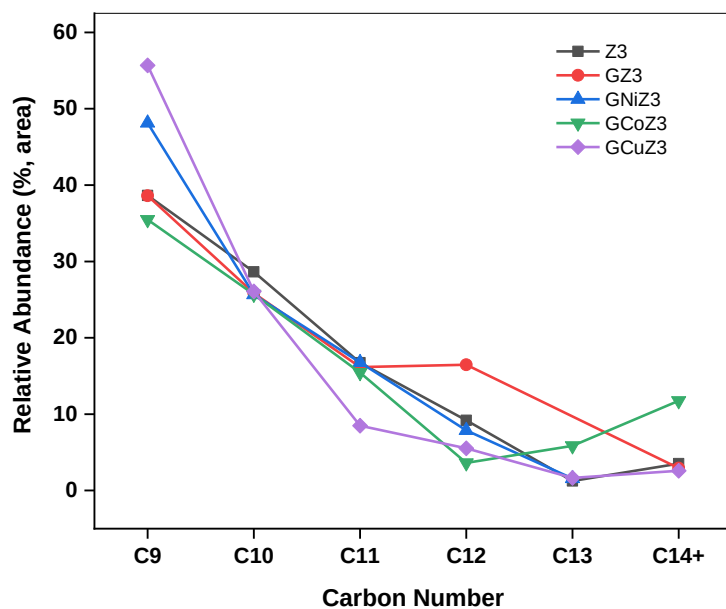


Figure 21. Carbon number distribution of the pyrolysis oil

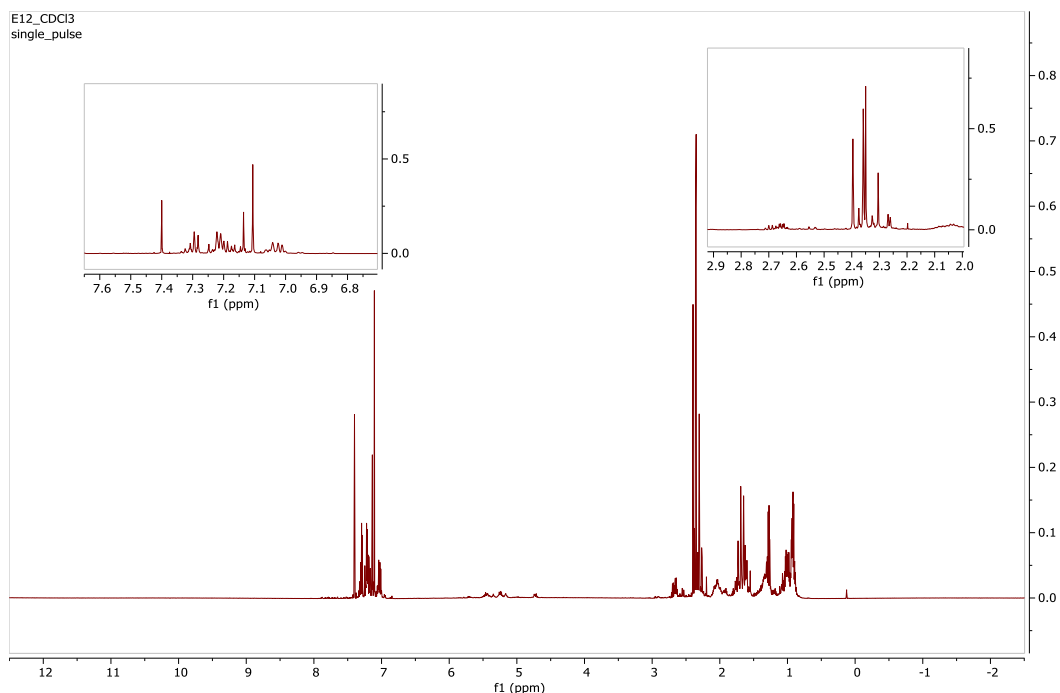
Pyrolysis oil contains around 90% of C9-C12 aromatics while using GCuZ3 which could potentially be used as a feedstock for producing various chemicals, including benzene, toluene, xylene, and other heavier aromatic compounds. These compounds are important building blocks for the production of plastics, synthetic fibers, and other materials.

One way to convert the C9-C12 aromatics in pyrolysis oil into higher-value chemicals is by catalytic reforming or hydrocracking. In catalytic reforming, the pyrolysis oil is heated and mixed with a catalyst, which breaks down the larger aromatic compounds into smaller ones. The smaller aromatics can then be separated and used as feedstock for producing chemicals. Hydrocracking, on the other hand, involves the use of hydrogen and a catalyst to break down the larger aromatic compounds into smaller ones.

Figure 21 demonstrates the carbon number distribution for the pyrolysis derived oil. GCuZ3 catalyst shows highest C9 product and lowest higher carbon production. The formation of Mesitylene comparative higher in this case which is a precursor to diverse fine chemicals.

### **3.3.3 <sup>1</sup>H-NMR analysis**

The <sup>1</sup>H-NMR spectra provide information about the chemical composition of a sample, with the x-axis representing the chemical shift and the y-axis representing the signal intensity (Figure 22 & 23). Chemical shift refers to the resonant frequency of a nucleus in a magnetic field, typically within the range of 0-12 ppm for <sup>1</sup>H-NMR spectra. In complex mixtures like pyrolysis oil and gasoline, there may be overlap in the peaks, so a specified range is used to determine the occurrence of functional groups[153,232,233]. Table 10 represents the chemical shifts in ppm for different functional groups.



**Figure 22  $^1\text{H}$ NMR peak for Z3 catalytic pyrolysis derived oil**

Figures 22 & 23 describe the  $^1\text{H}$ NMR spectra for Z3 & GZ3 catalytic pyrolysis derived oil, respectively. Following Table 10, spectral line proves the presence of aromatic H, paraffinic  $\text{CH}_3$  group in alpha position to aromatic ring, paraffinic  $\text{CH}_2$  group in alpha position to aromatic ring, naphthenic CH in the pyrolysis oil. The integral value of the NMR data suggests the higher percentages of aromatic presence in the pyrolysis oil.

The presence of these aromatics was also found from GC-MS. Therefore,  $^1\text{H}$ -NMR data is aligned with GC-MS data.

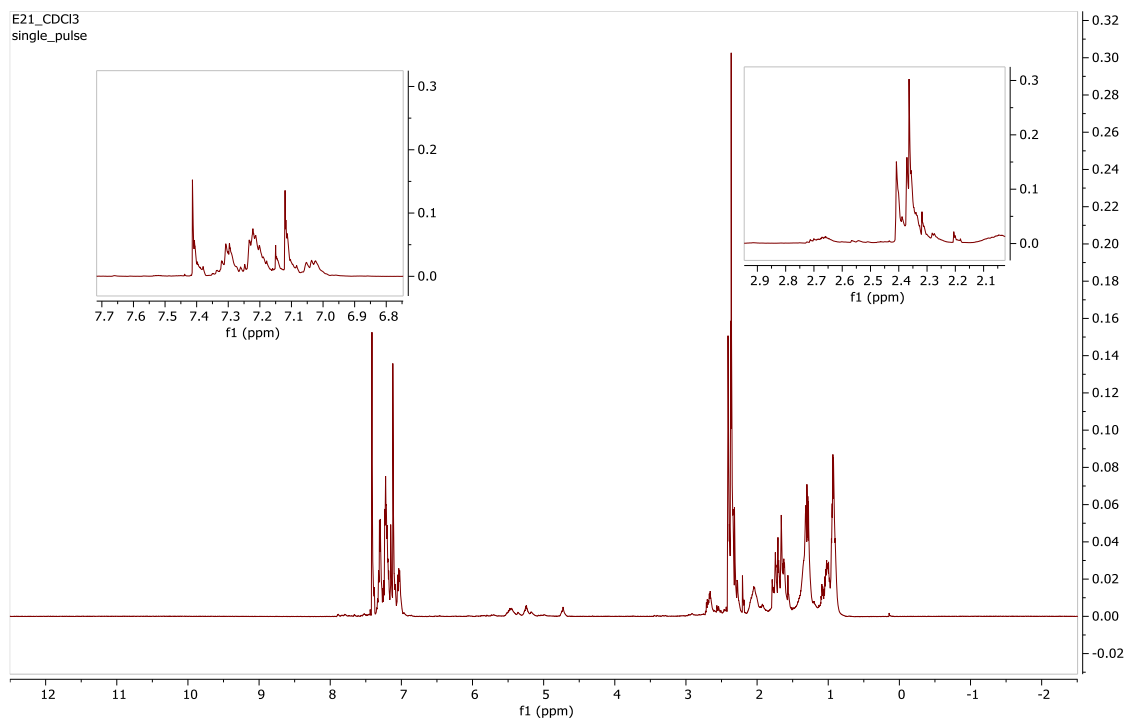


Figure 23  $^1\text{H}$ NMR peak for GZ3 catalytic pyrolysis derived oil

**Table 10 Characteristics  $^1\text{H}$ -NMR chemical shift to identify the functional groups.**

| Functional Group | H atom                                                                  | chemical shift region (ppm) |
|------------------|-------------------------------------------------------------------------|-----------------------------|
| paraffin         | paraffinic $\text{CH}_3$                                                | 0.5 – 1.09                  |
|                  | paraffinic $\text{CH}_2$                                                | 1.09 – 1.5                  |
|                  | Paraffinic CH/ naphthenic<br>CH                                         | 1.5-2                       |
| Olefin           | olefinic $\text{CH}_2$                                                  | 4.3 – 5.1                   |
|                  | olefinic CH                                                             | 5.1 – 6.2                   |
| Aromatic         | paraffinic $\text{CH}_3$ group<br>in alpha position to aromatic<br>ring | 2 – 2.4                     |
|                  | paraffinic $\text{CH}_2$ group<br>in alpha position to aromatic<br>ring | 2.4 – 4.3                   |
|                  | aromatic H                                                              | 6.2 – 7.4                   |
|                  |                                                                         |                             |
|                  |                                                                         |                             |

### 3.3.4 FTIR analysis

The Fourier Transform Infrared (FTIR) technique is utilized to collect the infrared spectrum of the pyrolysis oil either through transmission or absorption, enabling the identification of aliphatic and aromatic-compounds.

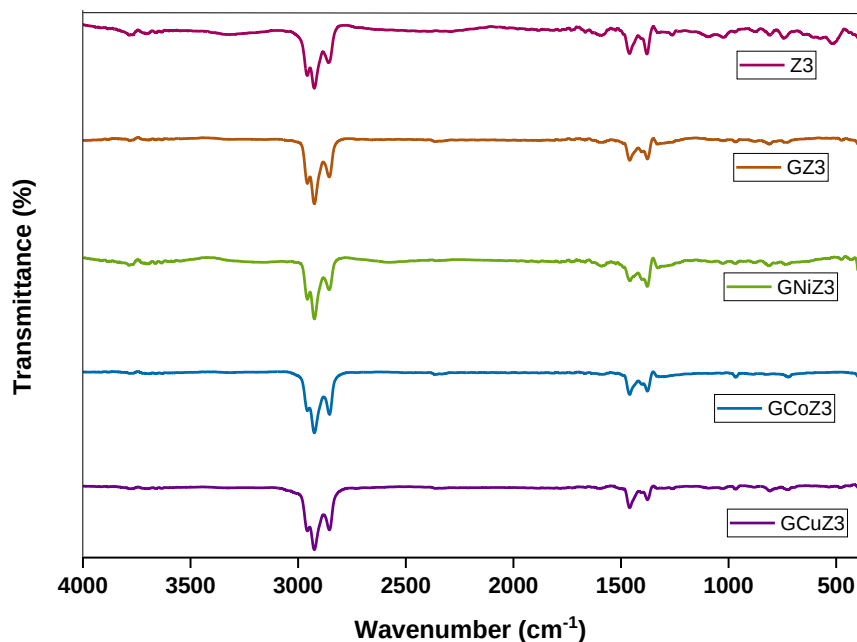


Figure 24. FTIR analysis of the pyrolysis oil sample.

Figure 24 illustrated that the peaks between  $3200\text{ cm}^{-1}$  to  $2300\text{ cm}^{-1}$  wavenumbers confirm the presence of hydrocarbon components in all pyro-oil samples. Bending vibrations of C-H bonds gives the peak in the region of  $1150\text{-}1500\text{ cm}^{-1}$  range that confirms the presence of aliphatic hydrocarbon. There is no peak for wavenumber  $3000\text{ cm}^{-1}$  that indicates the absence of absorption peak for C-H stretching vibration. According to the absorption characteristics of hydrocarbons these findings suggest that pyrolysis oil comprises of saturated carbon components. More specifically, wavenumbers  $2954\text{ cm}^{-1}$  and  $1377\text{ cm}^{-1}$  correspond to the antisymmetric stretching

and in-plane bending vibration of methyl groups ( $-\text{CH}_3$ ). As the pyrolysis oil is a cocktail of hydrocarbon, the presence of these groups is obvious.

### 3.4 Analysis of the gases

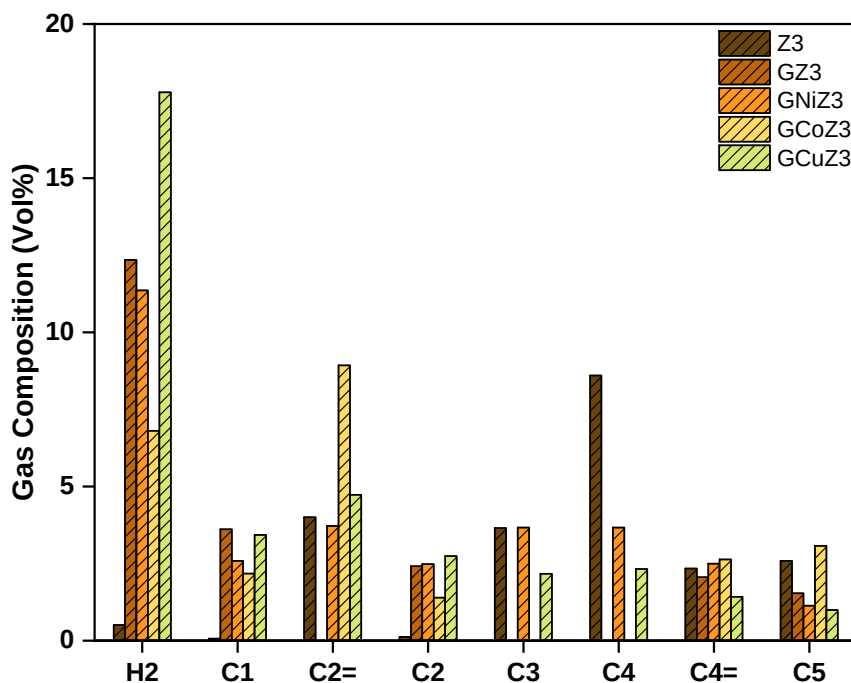


Figure 25 Analysis of the evolved gases during pyrolysis

The composition of non-condensable gases varied by the changes of catalysts, as shown in Figure 25. In all samples of gas products, the concentration of alkanes ( $\text{C}_1\text{-C}_5$ ) was found to be higher than that of olefins ( $\text{C}_2=$ ,  $\text{C}_4=$ ). However, the catalytic pyrolysis of LDPE was observed to predominantly yield light olefin products through an end-chain cracking mechanism. As a result, the formation of alkanes was primarily attributed to secondary reactions, specifically hydrogen transfer reactions of olefins. Therefore, it can be said that although the initial product distribution favored the production of olefins, subsequent reactions led to an increased concentration of alkanes

in the gas products. According to reports, the process of catalytic pyrolysis of LDPE resulted in the production of light olefin products as the primary outcome, achieved through end-chain cracking mechanism. On the other hand, the formation of alkanes mainly occurred through secondary reactions, specifically the hydrogen transfer reaction of olefins [234].

## 3.5 Characterization of the catalysts

### 3.5.1 Textual properties (N<sub>2</sub> sorption)

Among the bi-metallic series, samples containing either Ni, Co, or Cu along with Ga are characterized in detail and the results are given in Table 11 below and Figure 27. These results indicate that the microporosity is maintained even after loading ~7% of extra metal on the zeolite materials. Surface area and other parameters show an expected decrease upon metal addition.

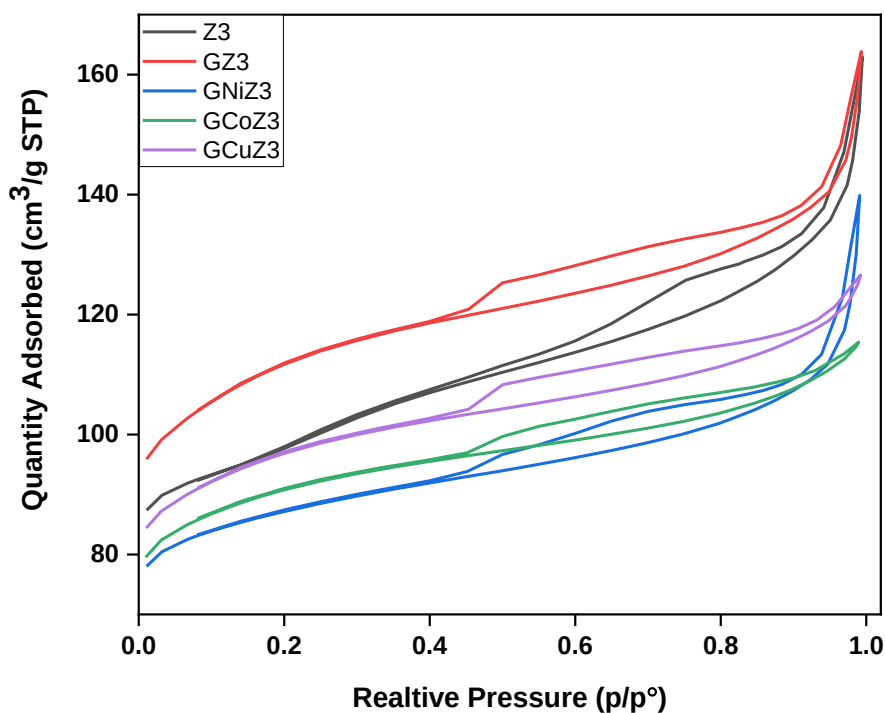


Figure 26 N<sub>2</sub> adsorption-desorption isotherms of fresh metal doped zeolites.

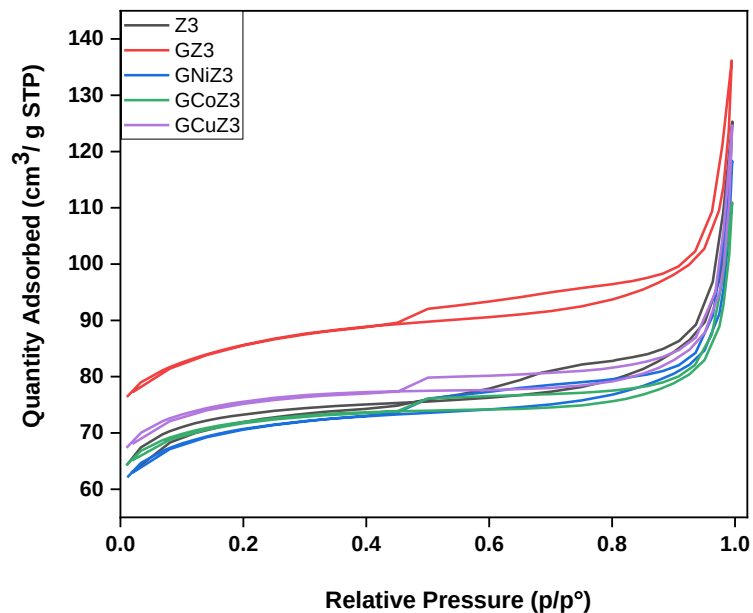


Figure 27 N<sub>2</sub> adsorption-desorption isotherms of spent metal doped zeolites.

Table 11 N<sub>2</sub> adsorption Results for Fresh and Spent catalysts.

| Parameters         | Z3    |        | GZ3    |         | GNiZ3 |         | GCoZ3  |         | GCuZ3  |         |
|--------------------|-------|--------|--------|---------|-------|---------|--------|---------|--------|---------|
|                    | Fresh | Spent  | Fresh  | Spent   | Fresh | Spent   | Fresh  | Spent   | Fresh  | Spent   |
| S <sub>BET</sub>   | 307.3 | 222.5  | 348.5  | 262.23  | 268.5 | 215.96  | 280.7  | 218.58  | 300.5  | 229.357 |
| S <sub>micro</sub> | 205.6 | 174.8  | 213.7  | 195.06  | 196.9 | 160.81  | 193.7  | 173.114 | 198.3  | 180.851 |
| S <sub>extr</sub>  | 101.2 | 47.7   | 134.8  | 67.17   | 71.6  | 55.15   | 86.9   | 45.463  | 102.2  | 48.5063 |
| S <sub>des</sub>   | 118.1 | 43.8   | 137.4  | 48.072  | 80.99 | 38.48   | 89.9   | 29.767  | 106.8  | 30.9604 |
| V <sub>micro</sub> | 0.107 | 0.0924 | 0.1137 | 0.10302 | 0.103 | 0.085   | 0.1023 | 0.09135 | 0.105  | 0.09559 |
| V <sub>des</sub>   | 0.154 | 0.103  | 0.1426 | 0.10056 | 0.118 | 0.09174 | 0.0786 | 0.07451 | 0.0938 | 0.09098 |

S<sub>BET</sub> = BET Surface Area, m<sup>2</sup>/g; S<sub>micro</sub> = t-plot Micro area, m<sup>2</sup>/g; S<sub>extr</sub> = t-plot External area, m<sup>2</sup>/g; S<sub>des</sub> = BJH Desorption area, m<sup>2</sup>/g; V<sub>micro</sub> = t-plot micro pore volume, cm<sup>3</sup>/g; V<sub>des</sub> = BJH Des. pore volume, cm<sup>3</sup>/g

N<sub>2</sub> adsorption and desorption profiles for fresh catalyst illustrates that GZ3 shows highest quantity of nitrogen adsorption and GNiZ3 shows the minimum. When relative pressure reaches to the unity, the quantity adsorbed shows sudden high value for Z3, GZ3, and GNiZ3. On the other hand, GCoZ3 and GCuZ3 almost shows similar pattern where quantity adsorbed doesn't increase sharply while increasing the relative pressure. During desorption, Z3 exhibits unique features (desorption doesn't decrease sharply while reducing relative pressure) where the other four catalysts show almost the same desorption behavior (Figure 27).

For spent catalyst, N<sub>2</sub> adsorption and desorption isotherms for GZ3 demonstrate the highest quantity nitrogen adsorption. The other four catalysts profiles have almost the same quantity adsorption and desorption trend (Figure 28).

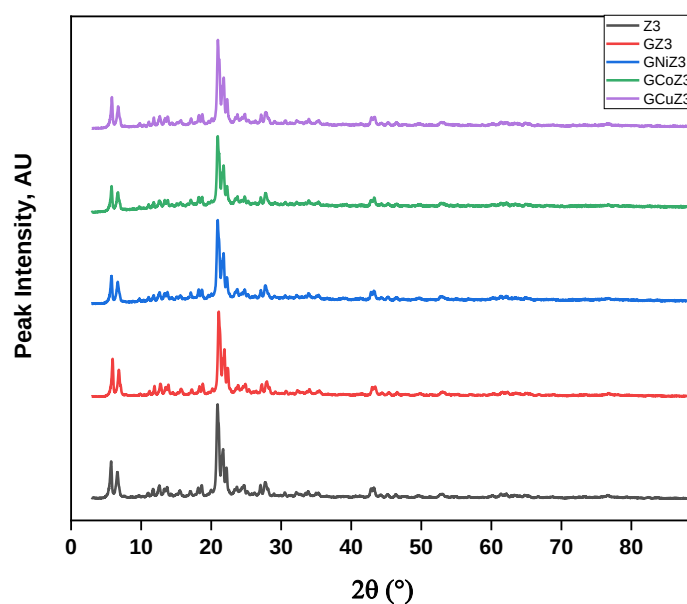
Analysis of the fresh catalyst provides that BET surface area, t-plot micro area, external area, BJH desorption area follow the following order GZ3>Z3>GCuZ3>GCoZ3>GNiZ3 (Table 02). Nickel doping reduced the surface area in higher order. This outcome also aligns to the understanding of Figure 28.

For spent catalyst, same parameters follow the following order, GZ3>GCuZ3>Z3>GCoZ3>GNiZ3.

The surface area/micro area/external area reduction after pyrolysis for bi-metallic catalysts has less than the parent zeolite. This idea also matches the findings of Figure 28

### 3.5.2 Crystal Phase (XRD)

**Figure 29** presents the diffraction patterns for bimetallic samples containing one metal out of Ni, Co, and Cu along with Ga. The I/I<sub>0</sub> values are given in Table-12. Gallium concentration is around 5% and the second metal is around 2% w/w. Considering that gallium is present at 5% some diffraction peaks of oxides of gallium are expected. However, none were detected. This might be due to the distribution of gallium in the large pores as fine particles, which may not be adequately crystalline to produce diffraction patterns.



**Figure 28.** XRD patterns of Fresh catalyst samples loaded with dual metals.

Intense diffraction peaks were identified at  $5.82^\circ$ ,  $6.82^\circ$ ,  $21.1^\circ$ ,  $21.95^\circ$ ,  $22.36^\circ$  positions. By observing the figure 29 & 30, it can be noted that the initial segment of the  $2\theta$  values corresponds to the JCPDS patterns for  $\text{SiO}_2$  (JCPDS card no 89–1668) and  $\text{Al}_2\text{O}_3$  (JCPDS card no 88–0107). Characteristic diffraction peaks of Ga, Ni, Co and Cu were not clearly identified, suggesting high dispersion of these metals on parent zeolite.

Table 12 Peak intensity ratio of the catalysts

| Sample | Peak 2 (2theta of 8.5) |       |
|--------|------------------------|-------|
|        | I/I <sub>0</sub>       | Size  |
| Z3     | 100.0                  | 227.1 |
| GZ3    | 72.0                   | 228.5 |
| GNiZ3  | 54.7                   | 192.1 |
| GCoZ3  | 62.3                   | 195.7 |
| GCuZ3  | 65.9                   | 190.4 |

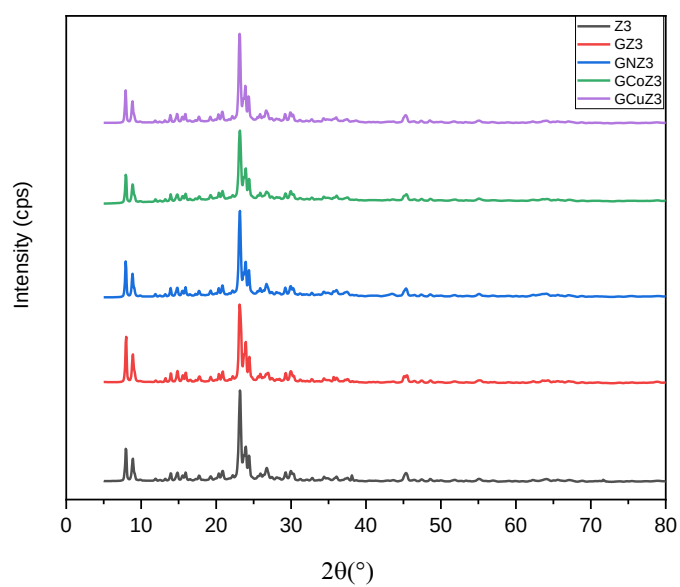


Figure 29. XRD of spent catalyst

### 3.5.3 DSC-TGA

**Figure 31** shows the weight loss percentage profiles where **Figure 32** describes the derivative weight loss of the spent catalysts. From these two figures three distinct stages of mass loss are identified. All the stages are illustrated in **Figure 32** (First stage  $T=25-230^{\circ}\text{C}$ ; second stage  $T=230-410^{\circ}\text{C}$ ; third stage  $T=410-670^{\circ}\text{C}$ ). The first peak resembles the moisture and physical absorbents release in  $25-230^{\circ}\text{C}$  temperature range. At the second stage, the weight loss was not very significant. The major weight loss was at the third stage and the corresponding coke was termed as “hard coke” where the soft coke could be found from the weight loss at moderate temperature [235]. Most of the carbon species in the coke were in graphitic, fibrous forms which caused the catalyst deactivation [236]. XRD and SEM observations also support this result.

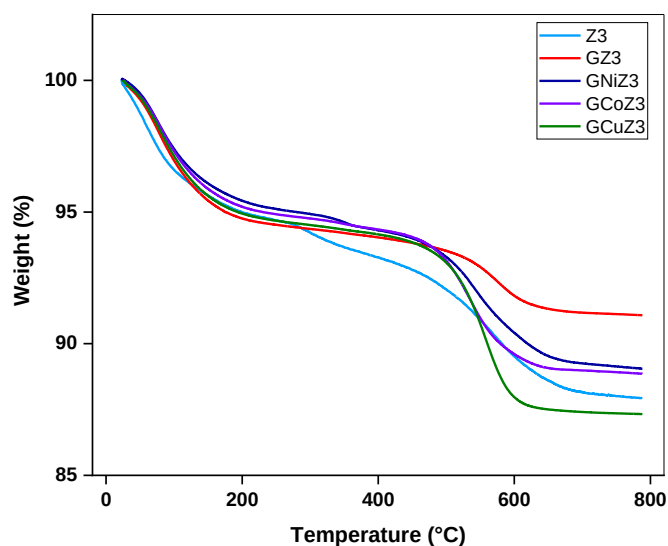


Figure 30. Weight loss in percentage (TGA) of spent catalysts

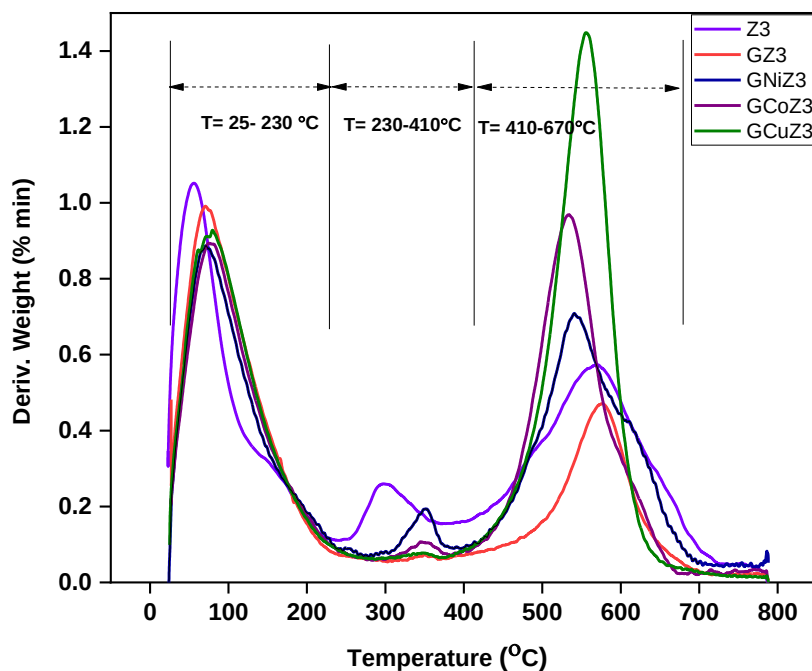
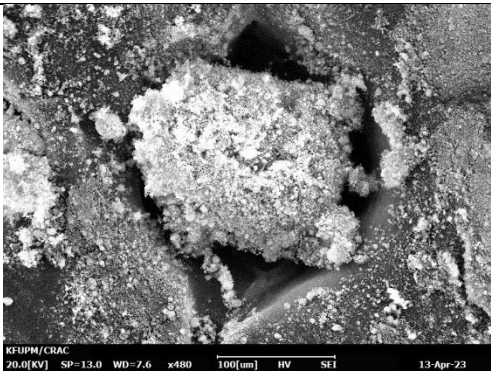
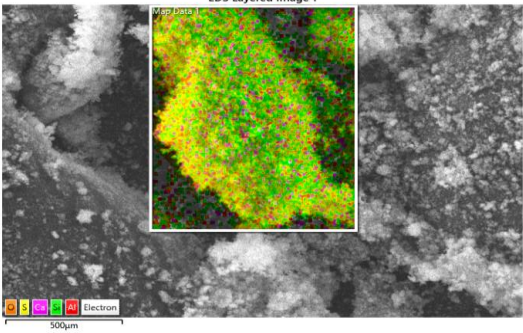
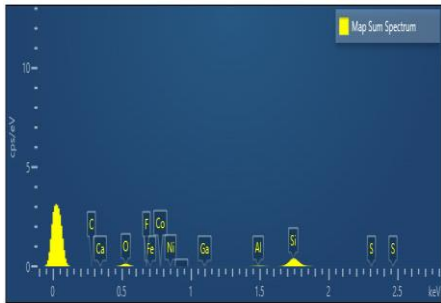
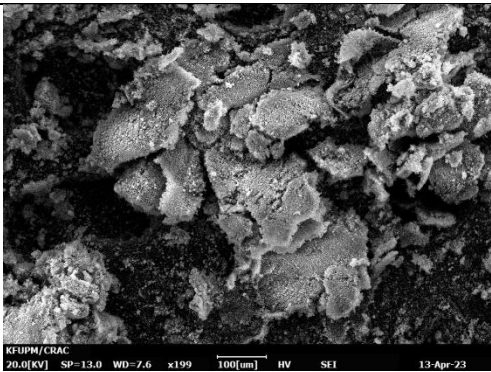
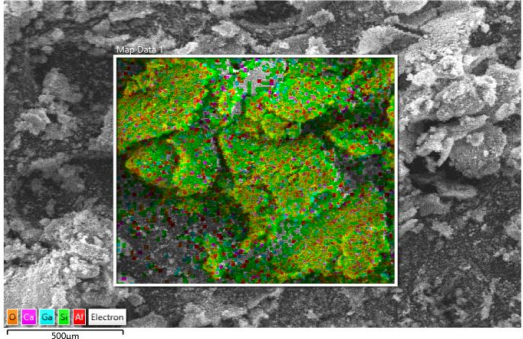
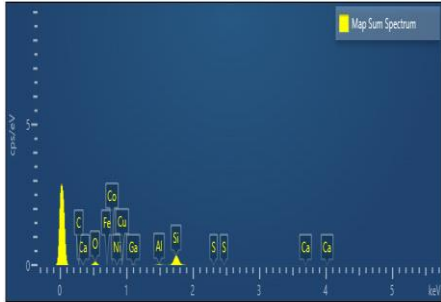


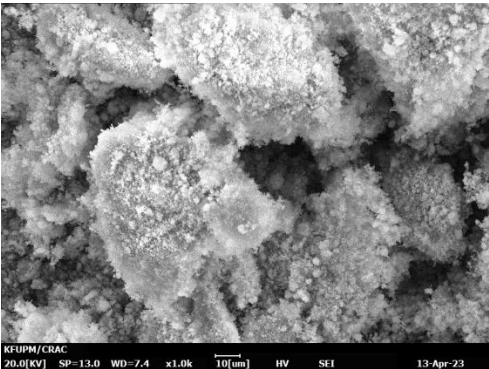
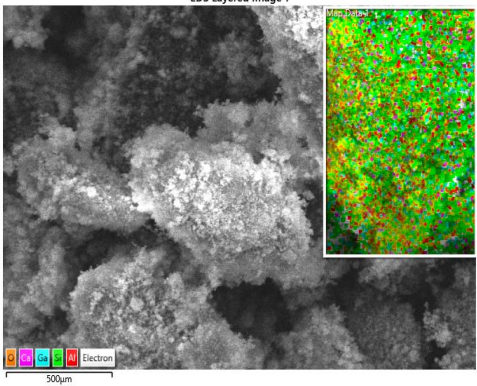
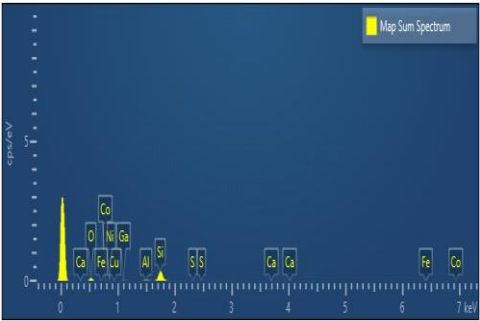
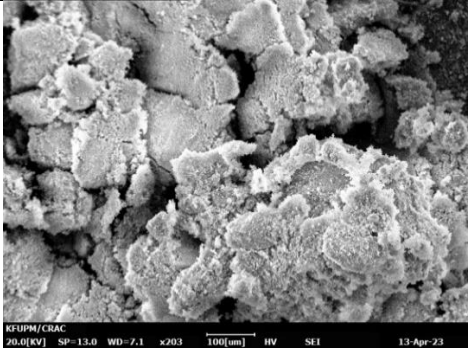
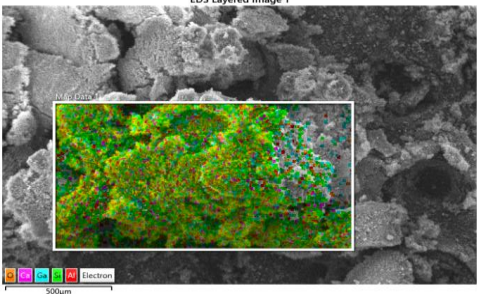
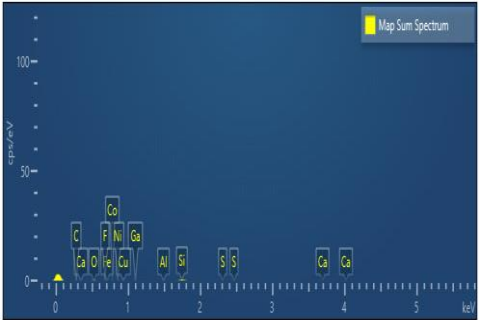
Figure 31. Derivative Weight Loss in percentage per minute (TGA) of spent catalysts

**Figure 32** reveals that the catalysts contain almost the same amount of soft coke. Regarding the hard coke, GCuZ3 catalyst contains the maximum, GZ3 contains the minimum. Other three catalyst follow the following sequence  $Z3 > GCoZ3 > GNiZ3$ . It was mentioned before that aromatic hydrocarbon content in pyrolysis oil was highest and hydrogen release was maximum for GCuZ3. Therefore, spent GCuZ3 left with maximum hard coke.

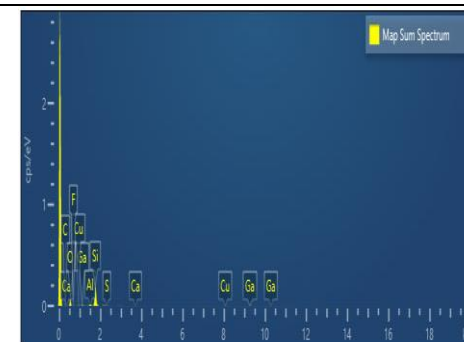
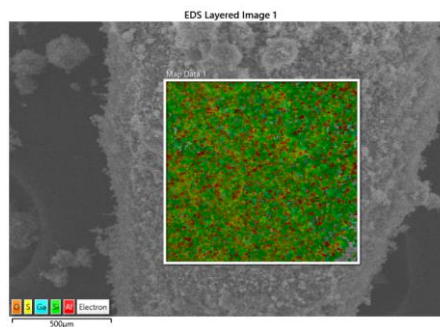
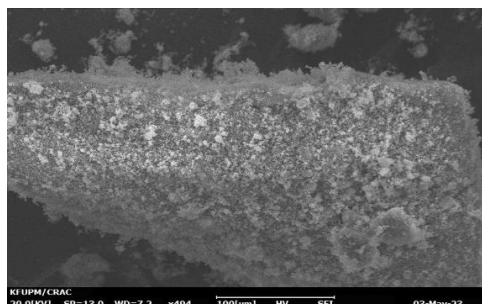
### 3.5.4 Morphology (SEM-EDS)

**Table 13 Fresh catalyst SEM and EDS**

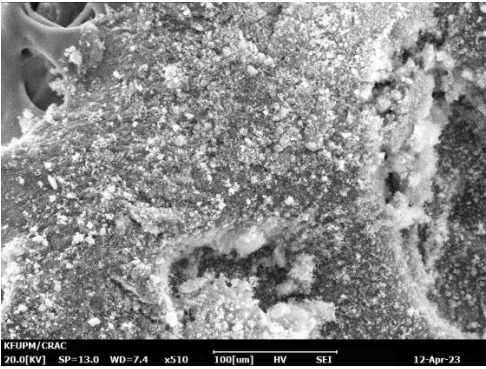
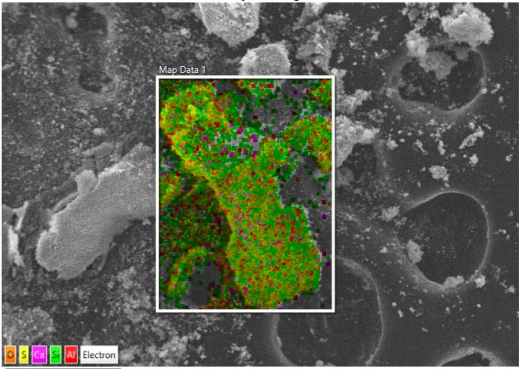
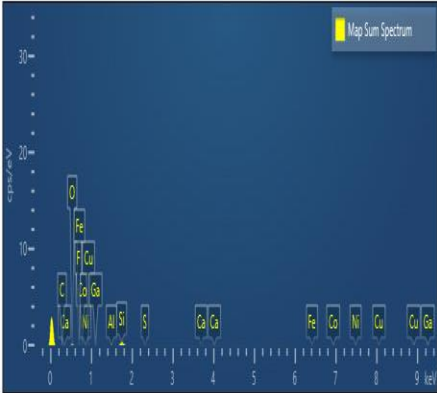
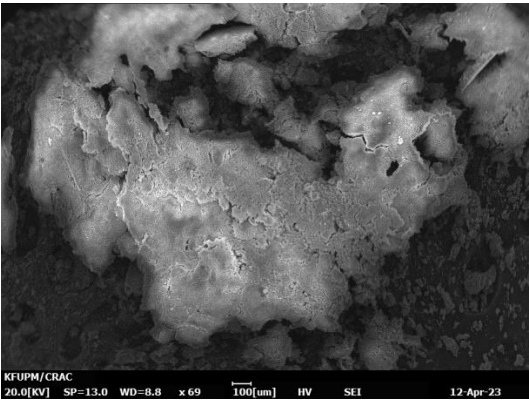
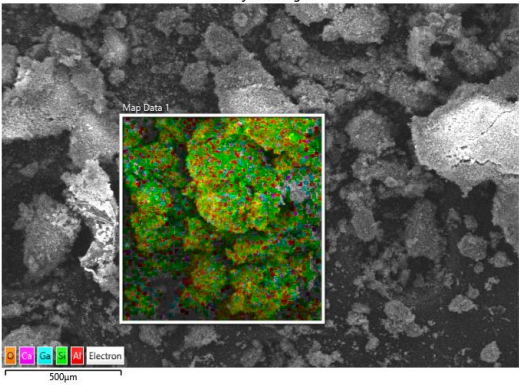
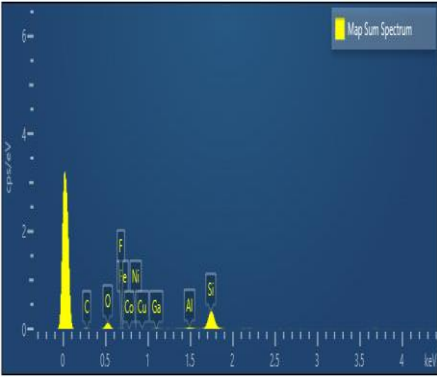
| Fresh Catalyst | SEM                                                                                | EDS                                                                                  | Map Sum Spectrum                                                                      |
|----------------|------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| Z3             |   |    |    |
| GZ3            |  |  |  |

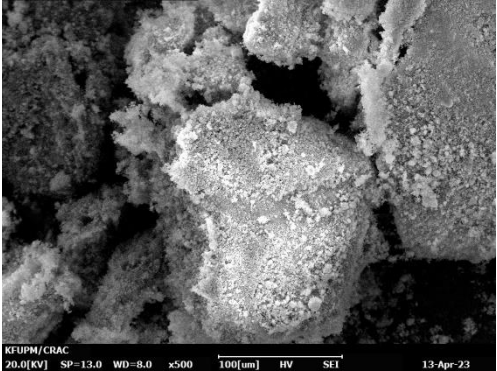
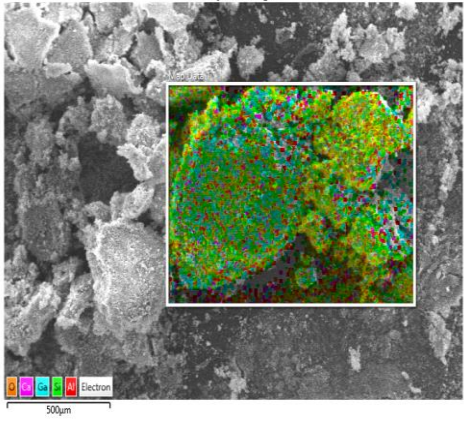
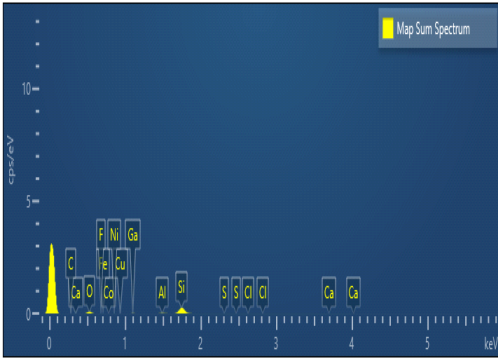
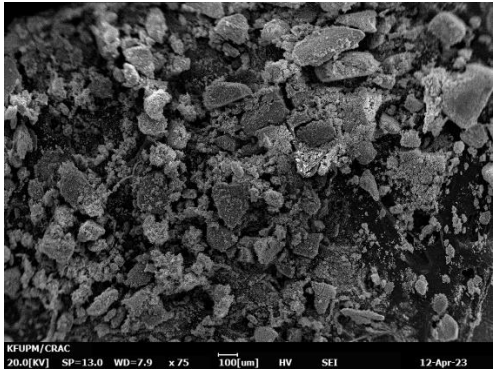
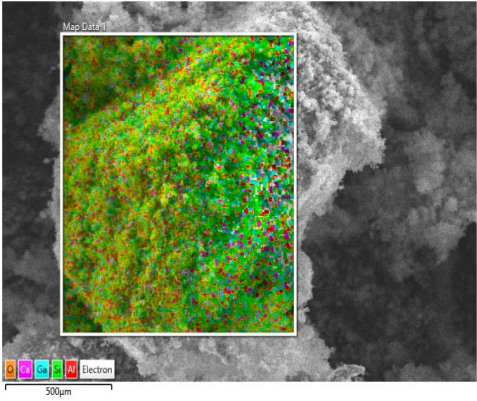
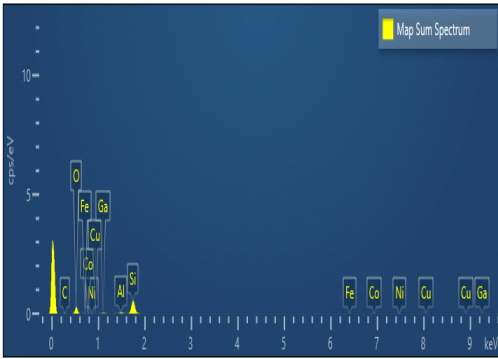
|       |                                                                                    |                                                                                    |                                                                                     |
|-------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| GNZ3  |   |  |  |
| GCoZ3 |  |  |  |

GCuZ3

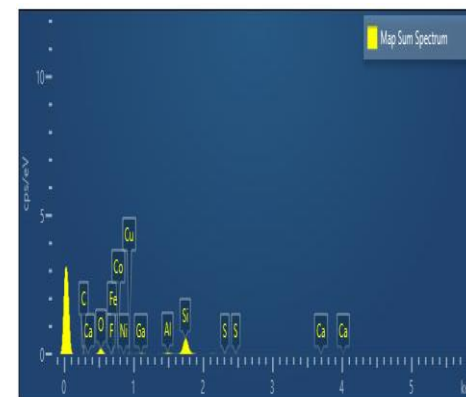
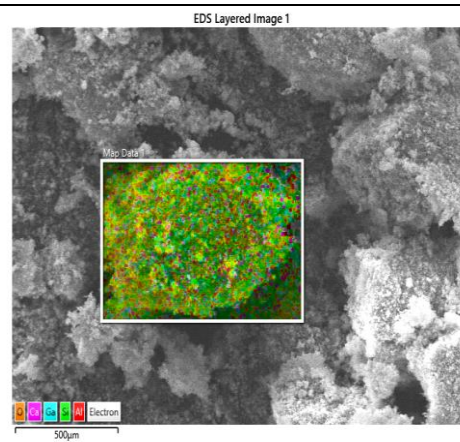
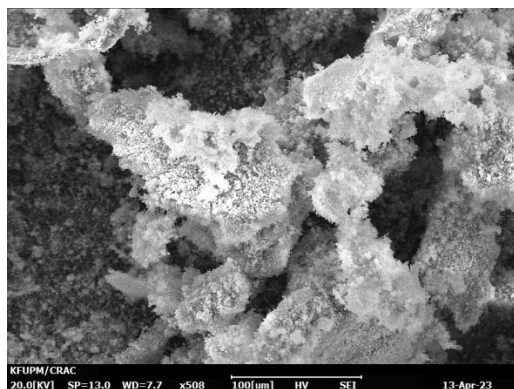


**Table 14 Spent Catalysts SEM and EDS**

| Spent Catalyst | SEM                                                                                | EDS                                                                                 | Map Sum Spectrum                                                                     |
|----------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| Z3             |   |   |   |
| GZ3            |  |  |  |

|       |                                                                                    |                                                                                                                |                                                                                      |
|-------|------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| GNZ3  |   | <p>EDS Layered Image 1</p>   |   |
| GCoZ3 |  | <p>EDS Layered Image 1</p>  |  |

GCuZ3



The morphology of the coke on the spent catalysts was studied by SEM analysis. SEM of fresh catalysts were also performed to understand the change. Along with SEM, EDS was also accomplished both for fresh and spent catalyst to determine the elemental composition of the samples.

The color of all spent catalysts was totally black after pyrolysis. This black color is the indication of coke deposition and deactivation [237–239]. The morphologies of Z3, gallium doped Z3, Ni/Co/Cu incorporation along with gallium doped Z3 are almost similar. These similar images show that the metal incorporation does not affect the crystallinity of the parent HZSM-5. This idea also aligns with the XRD results. However, metal doping shows high agglomeration compared to parent zeolite. Specially, bimetal incorporation increases the agglomeration rate which is noticeably clear from the SEM. On the other hand, mesopores which provides large surface area and volume for chemical reactions cannot be distinguished from SEM as the size of the mesopore varies from 2 to 50 nm where SEM images were taken with 100  $\mu\text{m}$  magnification. Disordered mesoporosity can form both inside and surrounding zeolite crystals due to clustering of small crystals of varying sizes that make up zeolite particles.

The presence of visibly rough outer surfaces indicates an increase in defect sites for the spent catalyst.

The EDS results of both fresh and spent catalysts are illustrated along with MAP Sum Spectrum from where elemental composition were analyzed. For fresh catalysts, Z3 contains almost no metal except Si (34.83 wt%) and Al (3.45 wt%). The gallium weight percentage in GZ3 was found 3.75%. The successive incorporation of Ni, Co and Cu metal

in GZ3 was found valid through EDS. Table 15 shows the elemental compositions analysis in detail in weight percentage unit. The findings agree with the notion that zeolite acts as a source of aluminum oxide and silicon oxide, thereby confirming the successful impregnation of gallium, nickel, cobalt, and copper onto the zeolite material.

**Table 15 Elemental Composition analysis of fresh and spent catalysts by EDS.**

| Element | Z3    |       | GZ3   |       | GNiZ3 |       | GCoZ3 |       | GCuZ3 |       |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|         | Fresh | Spent | Fresh | Spent | Fresh | Spent | Fresh | Spent | Fresh | Spent |
| O       | 60.6  | 57    | 59.86 | 58.95 | 54.49 | 55.54 | 61.5  | 63.64 | 54.58 | 55.72 |
| Si      | 34.83 | 32.93 | 33.82 | 34.03 | 34.59 | 31.91 | 29.71 | 28.04 | 34.62 | 32.18 |
| Al      | 3.45  | 2.1   | 2.34  | 2.14  | 1.94  | 2.52  | 1.97  | 2.34  | 2.14  | 2.12  |
| Ga      | -     | -     | 3.75  | 4.15  | 4.8   | 5.72  | 4.32  | 4.22  | 3.36  | 3.47  |
| Ni      | -     | -     | -     | -     | 3.94  | 3.64  | -     | -     | -     | -     |
| Co      | -     | -     | -     | -     | -     | -     | 2.23  | 1.47  | -     | -     |
| Cu      | -     | -     | -     | -     | -     | -     | -     | -     | 2.45  | 1.82  |

All the parameters' values were expressed in wt%.

### 3.5.5 Challenges and opportunities

The following challenges and opportunities can be addressed from the experimental work.

1. Quartz/ borosilicate reactor, connectors and condensing line cannot be run at high pressure where the product formation significantly varies while operating at high pressure. Non-microwave resistant reactants holder like alumina could be used to operate at high pressure.
2. Only 15 g of LDPE sample was analyzed at once in batch mode. Continuous mode operation could be developed to increase the plastic treatment capacity. Furthermore, it was performed in in-situ mode where catalyst, absorbents and feedstock were mixed together. Ex-situ mode operation is recommended to ease the catalyst regeneration. To accomplish it, external catalyst bed should be developed where the temperature could be increased until  $500^{\circ}\text{C}$  to activate the catalyst.
3. Virgin LDPE was used to rather than waste LDPE product in this study. Waste plastic products, mixture of different grades of plastic products could be analyzed to make the challenge more real life inclined. Mixture of biomass along with plastic could be approached to get the synergistic effect on product quality.
4. Only Silicon carbide ball was utilized as microwave absorbents in this research. Different biomass derived activated carbon/charcoal, graphite, alumina could also be implanted as MW absorbents. Mixture of these absorbents could also open a new window in absorbent study.

5. Ni, Co, Cu metal addition to Ga doped Zeolite was explored. Transition metals like Zn, Fe on zeolite support can also be explored. Also, silica fibrous zeolite can also be studied along with different transition metals as it has significantly high surface area. Different metal oxides as catalysts are also a prominent area for the pyrolysis of the waste plastic.

## CHAPTER 4

### CONCLUSION

LDPE could be converted into valuable aromatics by catalytic microwave pyrolysis in the presence of zeolite and metal doped zeolite. The products distribution of the aromatic hydrocarbons was correlated to the type of the metal and amount of metal doped to the zeolite support. Specially, dual-metal addition changed the product quality significantly. Gallium doped zeolite (GZ3), Nickel, Cobalt & Copper impregnation on gallium doped zeolite (GNiZ3, GCoZ3, GCuZ3) were studied to understand the effect of second metal addition on product quality.

The following concluding remarks are highlighted from the experimental results.

1. Maximum oil yield could be attained from gallium doped zeolite catalyst (GZ3) where copper incorporation along with gallium doped zeolite catalyst (GCuZ3) scored the second highest.
2. Pyrolysis oil using Z3 catalyst contained the highest amount of gasoline fraction where the oil from cobalt impregnated gallium doped zeolite (GCoZ3) contained maximum heavy fractions (SimDist Data).
3. Pyrolysis derived oil using GCuZ3 contained 90% of C9-C12 aromatics which are mostly benzene derivatives proved it as a potential feedstock for the production BTX as a building block in petrochemical industries.

4. The reasonable peaks for aromatic hydrocarbon were found by the analysis of chemical shift region of  $^1\text{H}$ NMR that aligned with GC-MS data.
5. GCuZ3 catalyst facilitated the production hydrogen in pyrolysis gas. The total production of other alkane ( $\text{C}_1\text{-C}_5$ ) and alkene ( $\text{C}_2=$ ,  $\text{C}_4=$ ) range gases were also achieved maximum by the utilization of GCuZ3 catalyst.
6. Analysis of the textual properties (Nitrogen adsorption-desorption) suggests the following order  $\text{GZ3} > \text{GCuZ3} > \text{Z3} > \text{GCoZ3} > \text{GNiZ3}$  for the calculation of  $S_{\text{BET}}$ ,  $S_{\text{micro}}$ ,  $S_{\text{extr}}$ . While comparing the fresh and spent catalyst properties for surface, micro and external area, the reduction of these parameters was minimum for GCuZ3 catalyst which signifies its less catalytic deactivation.
7. Maximum amount of hard coke was found in spent GCuZ3 catalyst as the aromatic in liquid and hydrogen in syn gas production were maximum which left the highest hard coke.
8. Crystal phase (XRD) analysis reveals the well crystalline behavior before and after metal doping on zeolite catalyst. GCuZ3 shows high agglomeration in SEM image and metal addition found valid for all metal doped catalyst through EDS.

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