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UNIVERSITI TEKNOLOGI PETRONAS

DISSERTATION TITLE: EXPERIMENTAL STUDY ON PERFORMANCE OF MICROWAVE-METAL INTERACTION PYROLYSIS OF PLASTICS

by

HAROON ARSHAD

The undersigned certify that they have read and recommend to the Postgraduate Studies Programme for acceptance this thesis for the fulfillment of the requirements for the degree stated.

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EXPERIMENTAL STUDY ON PERFORMANCE OF MICROWAVE-METAL INTERACTION PYROLYSIS OF PLASTICS

by

HAROON ARSHAD

A Thesis
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PERAK

MAY 2020

DECLARATION OF THESIS

Title of thesis: Experimental Study on Performance of Microwave-metal Interaction Pyrolysis of Plastics

I HAROON ARSHAD

hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

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Date : 01-06-2020

Date : 8 June 2020

DEDICATION

To my late father, Mohammad Arshad…

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“Al lamal insaana ma lam y'alam” Allah taught men which he knew not **(Ch- 96 v- 5, Al-Quran)**

I feel great honor to express my deep and sincere gratitude to my respected research supervisor **Professor Dr. Shaharin Anwar Sulaiman**, Department of Mechanical Engineering, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia for his scholastic guidance, affectionate supervision and encouraging behavior.

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ABSTRACT

The microwave-metal interaction pyrolysis technique has proved to be an effective process for rapid recovery of useful hydrocarbons from waste plastics. An improved understanding of the process performance can help to develop the technology for potential benefits in the waste-to-energy research. However, the past studies on microwave-metal interaction pyrolysis were mainly focused on waste polystyrene (PS) and demonstrated the effectiveness of the process limited to a fixed power (700 W) of a domestic microwave oven to pyrolyze waste PS using a metal coil. The aim of this research, therefore, was to study the effect of microwave power on the oil yield, temperature, reaction time and composition of liquid oil fraction, and determination of optimal conditions for maximum oil recovery. The experiments were conducted using metal coil to pyrolyze different plastics selected as model materials. It was found that maximum heating occurred in the first five minutes of microwave exposure during microwave-metal interaction pyrolysis of each plastic comprising PS, polypropylene (PP) and low density polyethylene (LDPE), respectively. The iron coil was found to perform better than copper coil giving higher oil yield in lesser time. The increase in microwave power resulted in an overall rise of oil yield with a shorter reaction time. The oil yield was observed to be maximum for PS at 88.7 wt.% followed by PP (54.65 wt.%) and LDPE (30.15 wt.%), respectively. The oils recovered from PS were aromatic in nature and composed styrene as the most abundant compound. Contrarily, PP and LDPE produced aliphatic class of hydrocarbons that contained alkanes, alkenes, and cycloalkanes as the representative species. The study was also demonstrated for the plastic blends and waste PS (PSW). The optimal operating conditions with maximum oil recovery determined for each plastic using the central composite design model were found to be 87 wt.% at 2008 W and 25 minutes for PS, 57 wt.% at 2271 W and 31 minutes for PP and 43 wt.% at 2466 W and 32 minutes for LDPE, respectively.

ABSTRAK

Teknik pirolisis interaksi antara gelombang mikro dan logam telah terbukti sebagai proses yang berkesan untuk memperoleh kembali hidrokarbon berguna dari sisa plastik. Pemahaman yang lebih baik terhadap prestasi proses dapat membantu mengembangkan lagi teknologi tersebut untuk memanfaatkan penyelidikan penggunaan sisa kepada tenaga. Walau bagaimanapun, kajian lampau mengenai pirolisis interaksi antara gelombang mikro dan logam hanya tertumpu kepada sisa polistirena (PS) dan demonstrasi keberkesanannya hanya terhad kepada gelombang mikro berkuasa tetap (700 W) dari ketuhar gelombang mikro domestik menggunakan gegelung logam. Oleh itu, penyelidikan ini bertujuan untuk mengkaji kesan kuasa gelombang mikro kepada hasil minyak, suhu, masa tindak balas dan komposisi pecahan cecair minyak, dan keadaan optimum untuk mendapatkan hasil minyak. Ujikaji dijalankan menggunakan gegelung logam untuk mempirolisiskan plastik berbeza. Pemanasan maksimum berlaku di dalam lima minit pertama pendedahan gelombang mikro bagi setiap plastik yang terdiri daripada PS, polipropilena (PP) dan polietilena ketumpatan rendah (LDPE). Gegelung besi didapati berprestasi lebih baik daripada gegelung tembaga dengan hasil minyak yang lebih tinggi dalam masa yang lebih rendah. Peningkatan kuasa gelombang mikro menyebabkan kenaikan keseluruhan hasil minyak dengan masa reaksi yang lebih pendek. Hasil minyak maksima diperolehi untuk PS pada 88.7 wt% diikuti oleh PP (54.65 wt%) dan LDPE (30.15 wt%). Minyak yang diperoleh dari PS bersifat aromatik dan terdiri daripada stirena sebagai sebatian yang paling banyak. Sebaliknya, PP dan LDPE menghasilkan hidrokarbon kelas alifatik yang mengandungi alkana, alkenes dan sikloalkana sebagai spesis wakil. Kajian ini juga dibuat untuk campuran plastic dan sisa PS (PSW). Operasi optimum diperolehi untuk setiap jenis plastik menggunakan model reka bentuk komposit pusat adalah 87% pada 2008 W dan 25 minit untuk PS, 57% pada 2271 W dan 31 minit untuk PP dan 43 wt% pada 2466 W dan 32 minit untuk LDPE.

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NOMENCLATURE

Notation and Unit

Y	Yield [wt. %]
P	Power [W]
t	Time [s]
T	Temperature [°C]
ρ	Density [kg/m^3]
E	Energy [J]
η	Efficiency [%]
A	Constant
α	Axial point

Abbreviations

ANOVA	Analysis of variance
CCD	Central composite design
EPF	Expanded polystyrene foam
GCMS	Gas chromatography-mass spectroscopy
HDPE	High density polyethylene
HHV	Higher heating value
LDPE	Low density polyethylene
MAP	Microwave-assisted pyrolysis

MSW	Municipal solid waste
PCDD	Polychlorinated dibenzo para dioxins
PCDF	Polychlorinated dibenzo furans
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PSW	Waste polystyrene
PVC	Polyvinyl chloride
RSM	Response surface methodology
TGA	Thermogravimetric analysis
wt.%	Weight percentage

CHAPTER 1

INTRODUCTION

This chapter provides an overview of the research background highlighting the global issues associated with plastic waste disposal, existing recycling techniques, merits, and demerits of the microwave heating technology. The problem statement leading to the current research work undertaken is presented together with the prime and associated objectives required to accomplish the study. The later section covers the scope and significance of the research work with a brief outline of the thesis.

1.1 Global Issues with Plastic Solid Waste

Plastics are included among indispensable items of modern times. Plastics have diverse applications due to its many excellent properties. Common types of plastics found in municipal solid waste (MSW) comprise high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene- terephthalate (PET) and polyvinyl chloride (PVC) [1], which are the principal contributors to the non-biodegradable class of solid waste. Some of the important properties of different plastics used commercially is presented in Table 1.1.

The identification codes [2] of common plastic resins is highlighted in Fig. 1.1 The identification codes usually found at the bottom of commercial plastic products gives information on the type of plastic used for production. Moreover, resin codes also makes waste sorting operation easier during the plastic recycling.

Table 1.1: Different plastics and its properties

Different plastics	Important properties
PS	Available as naturally transparent solid plastic; widely used in packaging under the name styrofoam
PP	It is semi-transparent, low friction surface, resistant to chemicals, good electrical resistance. High adaptability to manufacturing techniques makes it a widely used plastic with high demand.
LDPE	High ductility and low tensile strength; suitable for packaging.
HDPE	Stiff plastic with high tensile strength; used in robust applications like construction, solid containers etc.
PVC	Brittle, rigid and strong, although different variants of PVC are designed for flexible applications as well. Commonly used in electrical and plumbing applications.
PET	Extremely effective moisture barrier, shatterproof, widely used as fiber and water bottles.

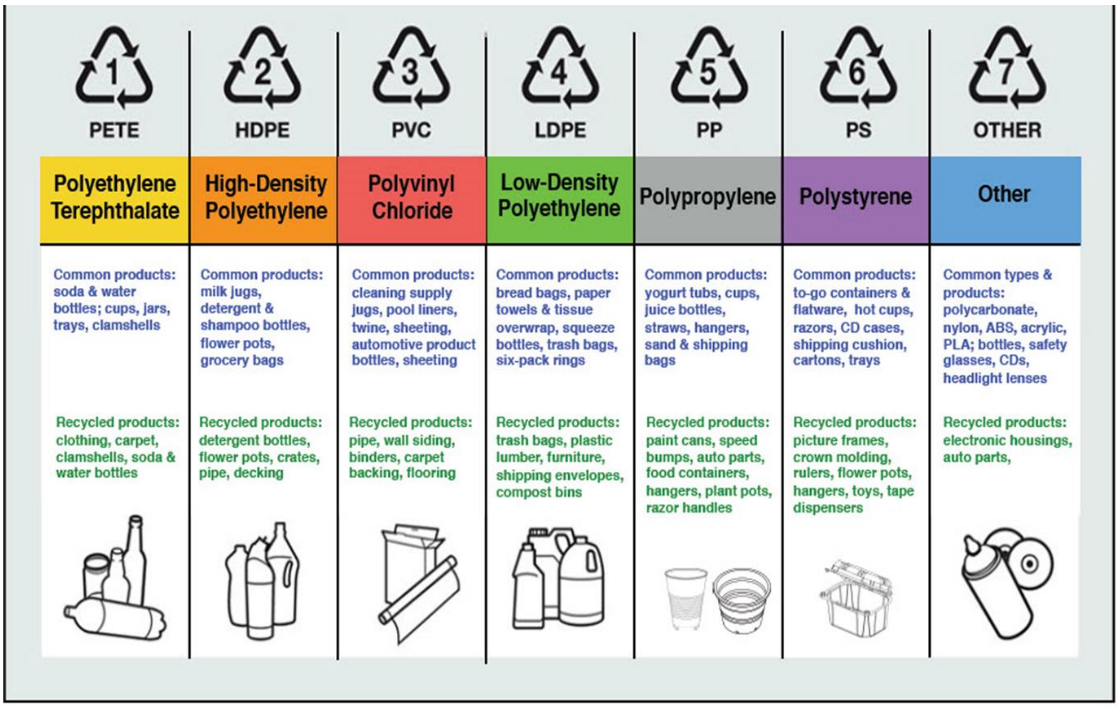


Figure 1.1: Plastic Resin Identification Codes [2]

With rapid growth in the world population, there has been a drastic increase in the use of commodity plastics dominant in packaging, clothing, beverage and trash containers, and numerous other household items. It was observed that the global production of plastics rose to 229 million tons in 2013 with a 4% gain over that of 2012 [3]. At the same time, there has also been huge accumulation of waste due to continuous rise in demand of plastics each year [4]. It was reported that the plastic waste reached to over 33 million tons in US according to a 2013 statistic [5]. Moreover, in Europe a study revealed that a total of 25 million tons of plastics went to the wastestream in 2012. Further, it was found that 38% of this waste was disposed to landfill, 26% were recycled and the remaining 36% was utilized for energy recovery [3] .

It was also reported that plasticizers (additives used to enhance plastic properties) found in some specific plastics like PVC can also leach out from improperly designed landfills and may contaminate groundwater which is caused by the production of phthalate esters or PAEs [6]. Further it was explored in a study that open dumping of municipal solid waste poses environmental hazards through the transfer of heavy metals to the soil which adversely affect our vegetation [7]. Another problem was identified associated with disposal of plastic waste into oceans which results in formation of soap and garbage patch like the great Pacific garbage patch posing risk to health of aquatic animals [8]. Today, the combustion processes called as incineration are widely applied as a thermochemical treatment of different wastes including the Municipal Solid Waste (MSW) [9]. However, incineration of plastic waste may lead to environmental pollution through the toxic emissions [10]. In most developed countries, incineration is considered to have limited potential for waste to energy technologies since it produces greenhouse gases and highly toxic pollutants such as polychlorinated dibenzo para dioxins (PCDD) and polychlorinated dibenzo furans (PCDF) [11].

Recent research has demonstrated the adverse effects of microplastics (<5 mm) present in the oceans [12]. It is well-known that a huge proportion of plastic waste is disposed into the oceans. The micro-plastics in water bodies interact with the aquatic life comprising the plant and animal species. These organisms ingest and absorb the micro-plastics that encourages accumulation of persistent organic pollutants (POP). Research has shown that marine organisms belonging to different sizes and trophic levels from zooplankton to mammals can transfer the microplastics from prey to predators [13]. The microplastics are also present as microbial biofilms in open ocean waters. These microplastics can therefore produce adverse ecological effects interfering with healthy sustenance of all forms of life.

In 2014, a study [14] was conducted on the status of waste management in Malaysia. It was found during the study that unsanitary landfill was the most dominant waste disposal method practiced in Malaysia. Fig. 1.2 highlights the percentages of various waste disposal methods that were used in the years 2002 and 2006 with predicted target for the year 2020. The application of incineration for energy recovery was absent before 2006. However, the targeted year 2020 would require zero practice of unsanitary landfill sites encouraging increased use of recycling, composting, inert landfill, and incineration techniques.

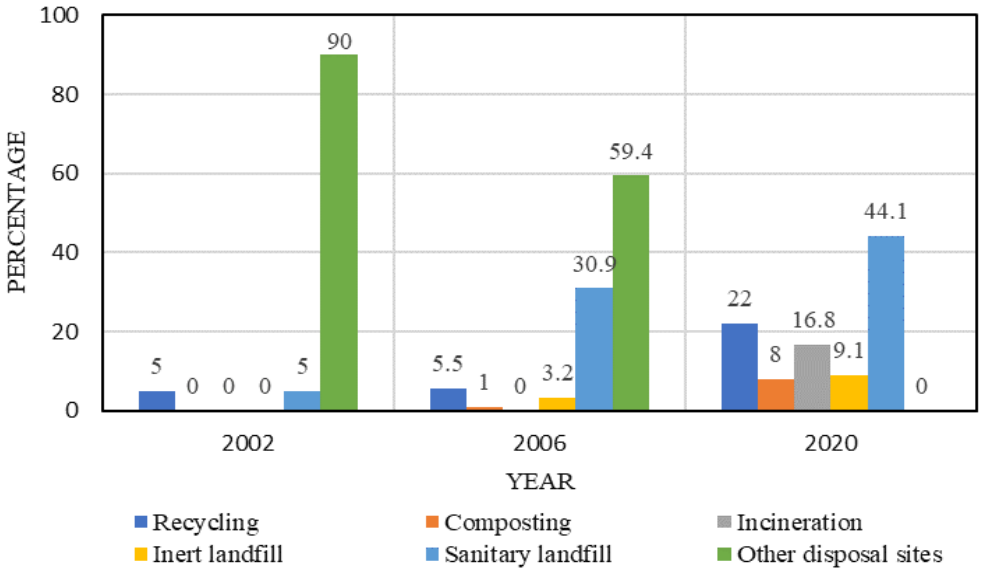


Figure 1.2: Waste treatment methods practiced in Malaysia [14]

In a 2009 study on characterization of municipal solid waste (MSW) generated in the capital city of Kuala Lumpur, the plastic waste generation rate was highest at 150,034 t/year with a recyclable component of only 24,747 t/year (Fig. 1.3) [14]. The second most abundant component was paper with a production of 86,305 t/year and a recyclable component of 14,235 t/year. The contribution of other waste components of municipal solid waste (MSW) were comparably very low as compared to plastic and paper wastes.

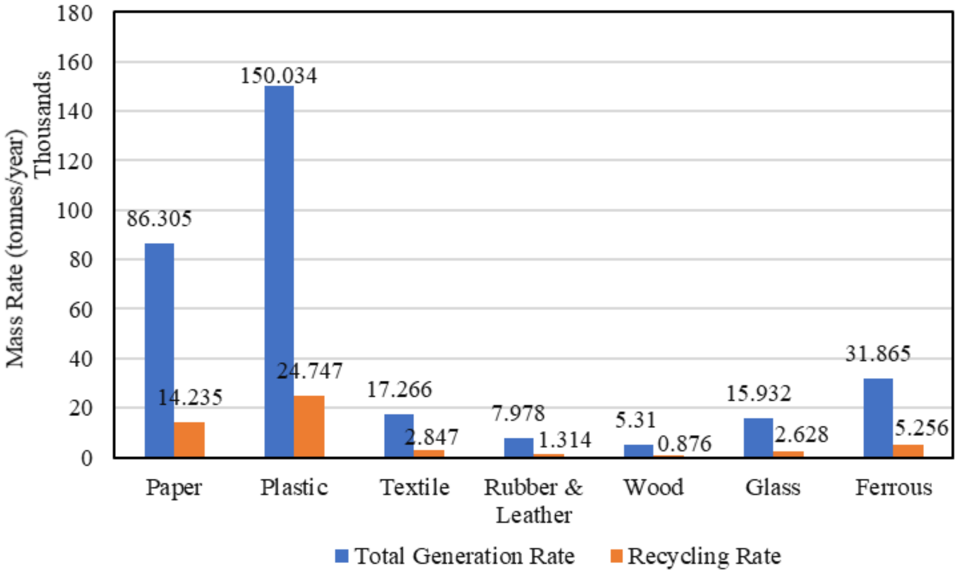


Figure 1.3: Recyclable components of Kuala Lumpur MSW in 2009 [14]

If waste recycling is encouraged in the country, it can reduce substantial volume of waste going to the landfills. This will also act as deterrent against the carbon footprint produced as a result of waste incineration plants. Currently, Malaysia is using small incinerators at small scale with only few of them capable of energy recovery. The largest incinerator plant in Malaysia belongs to Core Competencies Sdn Bhd (CCSB) Company, located in Selangor [14]. Generally, incineration is not a preferable option for the Malaysian waste as it has a high moisture content which limits its scope for energy recovery. Further, additional operations are required before the actual incineration that include separation of incombustible materials, moisture reduction, downsizing and palletizing of the waste.

So far, public contribution through 3R (reduce, reuse, recycle) has been proven to be the best solution. Waste recycling campaigns were also launched by Ministry of Housing and Local Government of Malaysia in 1993 and 2000 to encourage recycling from households but the initiative proved to be ineffective [15]. As such focused studies are being conducted by the researchers to identify the possible causes for failure of such attempts. According to experts, educational awareness amongst the Malaysians can play a key role in waste management. The consumption behavior of public can be improved through environmental awareness. The educating methods may differ based on different locations, types of waste management systems and socio-economic factors [16].

The waste management cannot be handled by the government alone but demands sincere efforts on the part of private organizations. Privates must collaborate through Public Private Partnership (PPP) for development of waste management programs. Another alternative for waste management is the community based approach which has the potential to reach the unserviced areas where municipal authorities are not active. The community driven waste management system is a combination of collection, transportation and waste diversion services [17]. Thus, it is believed that strategic and targeted management of waste can really contribute towards a sustainable development.

The Malaysian imports of plastic waste from developed countries has been of growing concern over the past years, particularly after China's ban on plastic waste imports effective from Jan 1, 2018. Fig. 1.4 highlights the exports of other plastics (e- plastics, mixed plastics etc.) from U.S. to other countries during Jan-Sept 2017 and Jan-Sept 2018 [18].

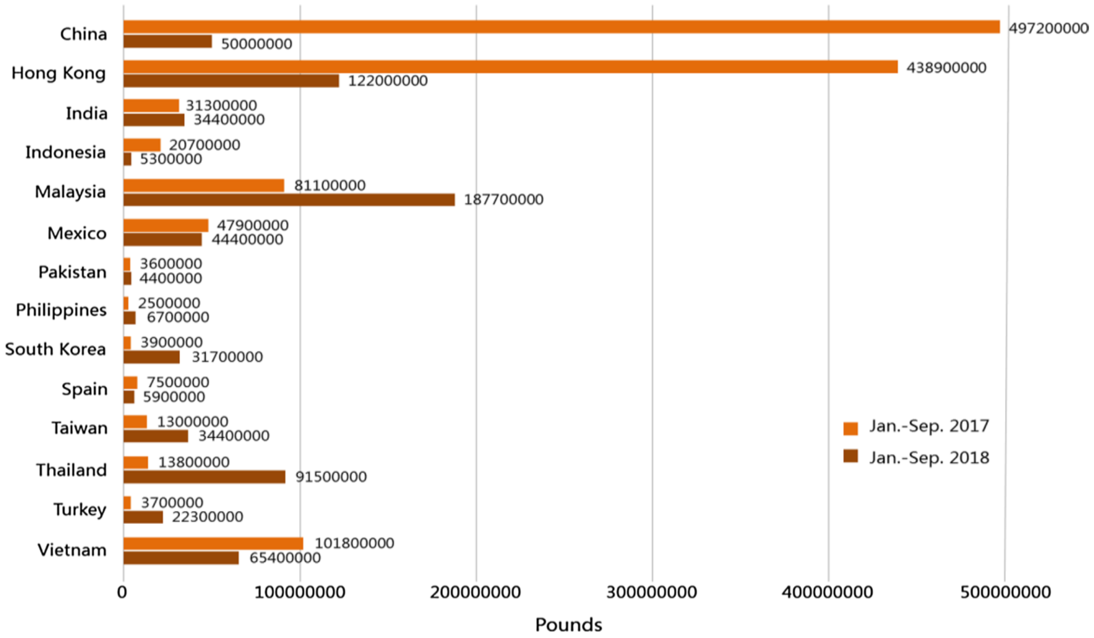


Figure 1.4: Exports of other plastics (e-plastic, mixed plastics etc.) from U.S. to other countries during Jan-Sept 2017 and Jan-Sept 2018 [18]

China has been the largest importer of plastic waste from developed countries, however, the imposed ban led to a drastic fall in the plastic waste imports reduced to over one-tenth from 2017 to 2018. The impact of plastic ban by China adversely affected Malaysia due to shift in plastic waste export trends from developed countries. The UK government was forced to divert the exports to other Asian countries after the China's ban in 2018 which caused the Malaysian imports figure to rise by over 42000 tons from 2017 to 2018, making Malaysia as the leading plastic waste importer. According to a survey by US Census Bureau and International Trade Commission, the exports of plastic waste from U.S. to China reduced significantly from 900,000 tons in 2017 to 120,000 tons in 2018 [18]. As a consequence, Malaysia became the largest importer of plastic waste exceeding China by 192,000 tons in the first 10 months of 2018. Additionally, Thailand imports of plastic waste also increased significantly during this period. According to CNBC reports published on Jan 25, 2019, the Malaysian government has announced to ban the plastic scrap imports in a similar move as initiated by China. The government would also take necessary steps to crack down the illegal plastic waste processing facilities operating within Malaysia.

1.2 Current Plastics Recycling Techniques

1.2.1 Mechanical Recycling

The method of mechanical recycling involves the reprocessing of waste plastic to produce new products with similar application. The technique can be considered to be a type of primary and secondary recycling where the homogenous plastic waste is converted to intended items, generally of lower quality standards as compared to original product [11]. Although, the method seems to be a green alternative for recycling of waste plastics, but the re-processing operation is not cost effective due to high input of energy required for the cleaning , sorting, transportation and processing with an extra cost of additives used to provide a usable product [19]. The heterogenous nature of mixed plastic waste with contamination caused by the presence of biological residues, makes the reprocessing operation practically challenging. Though the method is widely applied but is not recognized as a desirable option when product quality and ecological concerns are considerably important.

1.2.2 Thermal Recycling or Incineration

Incineration of plastic waste is a thermal recycling technique used for energy generation through the combustion process. This alternative is particularly beneficial to local authorities for getting financial gain by selling waste plastics as a fuel [20]. However, the practice of the method is discouraged in the developed countries at the present stage as it releases greenhouse gases and toxic pollutants like dioxins and furans [8], [10].

1.2.3 Chemical Recycling

The chemical recycling technique also known as feedstock recycling or tertiary recycling is used to convert the waste polymer into original monomers or other valuable chemicals. The chemical recycling incorporates a range of processes such as depolymerization, gasification (partial oxidation of hydrocarbons into synthesis gas, $H_2 + CO$) and pyrolysis (thermal and catalytic cracking of higher weight molecular compounds to lighter hydrocarbons) [11].

The process of pyrolysis involves thermal breakdown of complex polymers into simpler or lower weight hydrocarbons at elevated temperatures between 350-900°C in oxygen free environment [11]. The products of pyrolysis comprise oil, gas, waxes, and char. The process can be optimized to maximize the production of any of the constituent fractions by suitably controlling the pyrolysis temperature and residence time of the feedstock [21]. For instance, a high temperature and high residence time promotes gas production; high temperature with low residence time favors the release of condensates; while a low temperature and heating rate increases char formation [22]. Pyrolysis produces a range of valuable hydrocarbons that can be used directly as feedstock chemicals or transportation fuels through further treatment in the petrochemical refinery.

The application of catalysts during pyrolysis has been demonstrated to produce a narrower range of hydrocarbon fractions [23]. Further, the use of catalysts also produces a significant reduction in the pyrolysis temperature and reaction time [24]. Catalysts like zeolite and alumino-silicates have been used effectively during plastic pyrolysis to yield light hydrocarbon fuels through cracking of long polymeric chains [23].

1.3 Microwave Heating Technology

The microwave heating has been applied to a diverse range of technological and scientific applications that comprise food processing, sintering of metals and ceramics, pollution control, plasma processing, activated carbon regeneration, polymer processing, synthesis of functional materials, pyrolysis reactions and many other fields [25]–[32].

1.3.1 Advantages of Microwave Heating

The unique nature of microwave heating has several advantages over the conventional heating methods that includes:

- Non-contact heating enables the heat transfer to the sample without any physical contact unlike conventional heating [33], [34].
- Rapid heating with high temperatures can be achieved within a short time interval as a result of high power densities of the microwave field which increases the production speed with reduced costs [35].
- Selective material heating targets the specific material being receptive towards the microwaves. As such, it is possible to establish a uniform temperature profile across the focused region [36], [37].
- Volumetric heating achieves heating throughout the sample volume and in bulk with even distribution of temperature. This is possible due to the pervasive nature of the microwave field without depending upon any conductive or convective modes of heat transfer [38].

- Enhanced product yield due to efficient conversion of energy targeting specific material [39].
- Electronic control of the process helps in quick start-up and stop, automated, precise and safe operation [40].
- The magnetrons are easily available in all sizes and power outputs which would facilitate development of the technology for commercial applications.

1.3.2 Disadvantages of Microwave Heating

Despite many advantages of the microwave heating over conventional heating methods, there are also some limitations of the technology:

- The microwave heating can only heat the materials that are microwave receptors, also known as absorbents. Contrarily, heating of substances that do not respond to microwaves require additional use of microwave absorbents mixed with the sample.
- The conversion of electrical energy to microwave energy also known as transmission efficiency is not 100%. With modern equipment, a conversion efficiency of up to 90% can be achieved; the material losses during the energy transmission (waveguides, bends etc.) are responsible for the drop in efficiency [41].
- The construction of microwave reactor is based on a limited choice of materials that are not sensitive to microwaves. The use of metals inside microwave field can cause sparks or arcing [42], and therefore is avoided; only the microwave chamber walls are made of metal for the containment of microwaves.
- The components of microwave system comprising magnetrons, waveguide, applicator etc. are expensive and therefore makes it costlier that the conventional set-ups. Further, the scale-up of microwave system demands extra incurred cost than the relatively smaller units.

1.4 Microwave Assisted Pyrolysis of Plastics

Microwave assisted pyrolysis is a recent development over the conventional pyrolysis technique which was initially developed by Tech-En Ltd. (Hainault, U.K). The process involves mixing the plastics with a highly microwave-absorbent material, particularly carbon which when exposed to microwaves, can reach high temperatures of up to 1000°C within few minutes [43]. Microwave assisted pyrolysis has demonstrated [44], [45], the capability to efficiently convert plastic waste into value added chemicals. An alternative method based on microwave-metal interaction rather than the use of dielectric material as microwave absorbent, has been found to be effective in the pyrolysis of plastics but has not been explored widely [46]–[49]. The following section elaborates this new trend in microwave assisted pyrolysis of plastics based on microwave-metal interaction.

The microwave-metal interaction pyrolysis is a recent variant of microwave assisted pyrolysis where the essential heat required for the pyrolysis reaction is not produced through the use of microwave absorbent but instead a metal antenna is used as the heat generating medium. As demonstrated in the past study [46], microwave- metal interaction pyrolysis generates heat up to the melting point of metal (>1000°C) within a short time interval with efficient recovery of useful hydrocarbons. So far, the studies on microwave-metal interaction pyrolysis have been focused on waste PS. The effect of shape and size of metal antenna on the reaction time and oil yield was also investigated in the past [49]. Different shapes of metal antenna comprising cut-out metal strips, cylinder and tightly coiled wires were tested for the heating efficiency. The effect of thickness of coil wire was also evaluated to observe its influence on the oil yield. Metal antenna made of aluminum, iron and copper have been used in the previous studies [46]–[49] to evaluate the performance of microwave-metal interaction pyrolysis.

Based on the aforementioned studies, the available literature on microwave-metal interaction pyrolysis of plastics does not account for the effect of microwave power on the liquid oil yield, reaction time and chemical composition of the liquid fraction. Further, there is no optimization study on the process performance based on controlling the microwave power for liquid oil yield maximization. As such, the current study undertakes the stated work with the aim of developing better understanding of the performance of microwave-metal interaction pyrolysis of plastics.

1.5 Problem Statement

A recent advancement in MAP was the use of microwave-metal interaction pyrolysis where metal antenna was used to generate heat instead of dielectric materials. The method was first demonstrated in a published study [46] on microwave-metal interaction pyrolysis of waste PS, which proved to be rapid process for the recovery of useful hydrocarbons. Few studies had been published since then, based on microwave- metal interaction pyrolysis [46]–[50].

The previous studies on microwave-metal interaction pyrolysis were chiefly engaged in investigating the effect of shape, size, and form of metal antenna on the oil yield and composition of liquid fraction. Here, the heat generating medium in the form of metal coil provided essential heat for pyrolysis by focusing the microwaves on the sample as well as generating high temperatures in the range of 1100-1200°C. The majority of these works [46]–[49] demonstrated the effectiveness of the process limited to a fixed power (700 W) of a domestic microwave oven to pyrolyze waste PS using a metal coil. Further, the available literature reported only the peak value of the coil temperature (up to 1200°C), confirmed by the melting of wire tip, without monitoring the entire pyrolysis reaction. As a result, the effect of microwave power on oil yield, temperature, reaction time and composition during microwave- metal interaction pyrolysis of plastics is still unknown. Hence, further experimental investigation of the process performance is required to fill this knowledge gap. Also, there has been no study to date, on optimization of microwave- metal interaction pyrolysis process with liquid oil yield maximization. The current study is therefore, expected to provide sufficient advance to the understanding of microwave- metal interaction pyrolysis process that can help in future developments.

1.6 Research Objectives

The current work endeavors to provide insight into the performance of microwave- metal interaction pyrolysis of plastics which can address the research questions associated with this new alternative technique of microwave assisted pyrolysis.

The prime objective of this experimental work was to study the performance of microwave-metal interaction pyrolysis of plastics using a metal coil which was achieved based on the following specific objectives:

1. To study the effect of microwave power on the oil yield, temperature, reaction time, and composition during microwave-metal interaction pyrolysis of plastics.

2. To investigate the effect of coil gauge size and metal type on the oil yield, temperature, and reaction time of pyrolysis at different microwave powers.

3. To determine the optimum operating conditions of the experimental set-up with liquid oil yield maximization for individual plastics (PS, PP, LDPE).

1.7 Scope of the Experimental Work

The information on microwave-metal interaction pyrolysis of plastics in the existing literature is accurate but insufficient to provide adequate understanding of the process performance. The following points briefly highlight the scope of the present work:

1. The study investigated the temperature profiles of the iron and copper coils, effect of microwave power on oil yield, pyrolysis temperature, reaction time and composition of pyrolytic oils recovered from virgin plastics comprising PS, PP, and LDPE. The iron and copper wires were available as cheap materials with high melting point above 1000°C (microwave-metal interaction pyrolysis is a high temperature process and can easily damage coil fabricated from a metal such as aluminum with a low melting point of 660°C).

2. The virgin plastic is less contaminated as compared to waste plastics (presence of biological residues), and therefore, more suitable for initial investigations of the process. Further, the three plastics selected (PS, PP, LDPE) have a high volatile content above 95% which is important for high oil yield during pyrolysis. The model plastic types used also represent a significant portion of the plastic waste found in the MSW.

3. The study was also demonstrated for plastic blends and waste PS (post- consumed plantation cups) to investigate the variation in trends of oil recovery and reaction times.

4. The effect of coil gauge size and type of metal on the oil yield and reaction times was also evaluated.

5. The efficiency of the microwave- metal interaction pyrolysis process achieved by the current set-up was determined.

6. The study on optimization of microwave-metal interaction pyrolysis process was based on the central composite design model of experiments. The hypothesized model developed for PS, PP and LDPE, respectively, was tested for significance and qualification of model assumptions. The predicted response of the model was checked for adequacy within the experimental range of study. The models developed represented the optimum operating conditions for maximum oil recovery achieved by the experimental set-up.

1.8 Significance of the Work

The potential of microwave assisted pyrolysis of plastics has been of growing interest in the research community due its outstanding performance marked by efficient heat and mass transfer profiles in contrast to conventional methods of pyrolysis. The current technique of microwave-metal interaction pyrolysis enables quick release of volatiles with improved oil yields and shorter reaction times. The conversion of waste plastics to useful chemicals and fuels not only addresses the waste disposal problem but also serves as an alternative to conventional fossil derived fuels like petrol and diesel in solving the energy crisis. In this regard, the microwave-metal interaction pyrolysis process offers a simple procedure for recovery of valuable hydrocarbons showing great promise for future developments. A successful application of the technology would require deeper understanding of the microwave systems that comprise design of the microwave cavity, proper control of radiation time and microwave power and material throughput in order to achieve a desired treatment.

1.9 Thesis Outline

Herein, the conducted research work is presented in a brief and systematic way. The dissertation is organized into 5 chapters. The first chapter gives an overview of the research background, problem statement, research objectives, scope, and industrial significance of the work. Chapter 2 presents the literature review of the relevant works conducted in the past. Chapter 3 deals with materials and methods developed to meet the research objectives. Chapter 4 gives a detailed analysis and discussion of the results collected during the entire study that involves investigation of the process parameters. Chapter 5 covers the concluding remarks and recommendations for future works.

CHAPTER 2

LITERATURE REVIEW

This chapter presents a review of various studies conducted in the field of microwave assisted pyrolysis of plastics. The opening section sheds light on the technical understanding of the fundamentals of microwave heating. The later section elaborates the pyrolysis process, its types and important factors influencing the process. The major contributions in the field of microwave assisted pyrolysis of plastics are then discussed in detail classified according to the type of microwave receptors (absorbents/catalysts, metal antenna). The application of metal antenna for conducting pyrolysis of plastics is highlighted being the focus of the current study. The literature also provides a brief discussion on other important applications of microwave assisted pyrolysis and the process variables of interest. The chapter ends with a review of the major limitations of microwave assisted pyrolysis justifying the need for extended studies followed by a summary of key works.

2.1 Fundamentals of Microwave Heating

Von Hippel developed the basic understanding of macroscopic microwave interactions with matter for the first time [51]. Since the mid-nineties, microwave heating has been applied over a diverse range of technological and scientific fields that includes: sintering of metals and ceramics, food processing, activated carbon regeneration, plasma processing, solution treatment, polymer processing, synthesis of functional materials, pollution control, pyrolysis reactions and a multitude of other physical and chemical applications [25], [27]–[32], [52]–[54]. This technique not only has the potential to reduce energy consumption and processing time but is also capable of producing a new chemistry (phenomenon associated with microwave internal heating). Further, it can also improve the overall quality of production [55], [56].

Microwave is an electromagnetic form of energy found in the range of wavelengths of 0.001 to 1 m operating at a frequency band of 0.3-300 GHz. Most of the common microwaves used, particularly, the domestic ovens operate at frequency of 2.45 GHz. The electromagnetic field of microwaves is made up of two mutually perpendicular components, namely electric and magnetic fields as shown in Fig. 2.1 [39]. When electromagnetic waves encounter a medium, the waves can be reflected, absorbed, transmitted or a combination of any three of these interactions. Based on the nature of interaction with the microwaves, materials can be broadly classified as: (a) insulators or microwave transparent materials which readily allow the microwaves to pass through them without any losses like quartz, plastic etc. (b) conductors where the microwaves are readily reflected without any penetration like metals, and (c) absorbers where the microwaves are absorbed by the materials like water, polar solvents etc. The materials which can absorb the microwaves are known as dielectrics, and the associated heating is commonly referred to as dielectric heating.

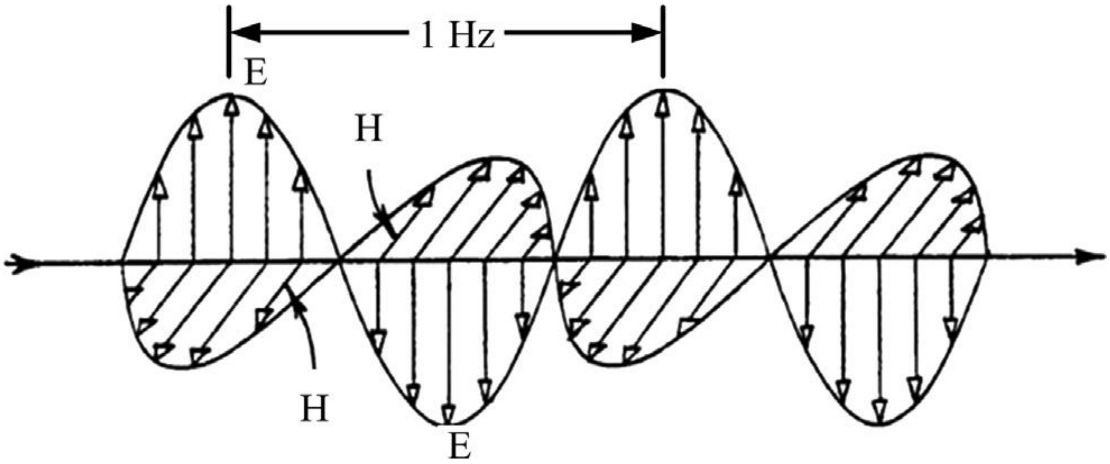


Figure 2.1: Electric (E) and magnetic (H) field components in microwave field [39]

The microwave matter interactions occurs through various mechanisms based on dielectric losses, conductive losses and magnetic losses, responsible for distinct types of heating known as dielectric, Joule, and induction heating, all of which depend upon the electromagnetic field and material properties [57][58]. Fundamentally, the microwave heating is a result of energy dissipation due to internal friction of atoms/molecules, charges or defects present in the material exposed to microwaves [59]. Heating caused by the interaction of individual components of electromagnetic field of microwaves, that is, electric and magnetic field, is discussed in the following section.

2.1.1 Microwave Electric Field Heating

The dielectric heating of materials is caused by the electric field component of microwaves. This heating effect is produced through two mechanisms, namely dipolar polarization, and ionic conduction. When dielectric materials like water or polar solvents encounter microwave irradiation, the dipoles being sensitive to the electric field, attempt to align itself to the frequency of microwave electric field. Due to high frequency of electric field, dipoles fail to adjust and produce a phase lag which renders the dipoles to collide with each other resulting in the generation of heat within the material. This effect is known as dielectric loss heating. In case of conductive heating of materials, the charge carriers (electrons or ions etc.) undergo back and forth movements due to the electric field causing the flow of induced currents. These currents are subjected to electrical resistance which generates heating in the material. However, it must be highlighted that the pure conductors (eg. metals) and insulators (eg. plastics), are not influenced by the microwave electric field since the microwaves either simply pass through the material or reflected at the surface.

2.1.2 Microwave Magnetic Field Heating

The principal mechanisms governing the magnetic field induced microwave heating is a consequence of the magnetic field losses classified as: (a) eddy current losses produced by the relative motion between conductor and magnetic field (b) hysteresis losses caused by the irreversible magnetization [60], occurring only in magnetic materials like ferrous materials, steel, nickel etc. (c) magnetic resonance losses caused by the resonance caused in metal oxides like ferrites and other magnetic materials [40].

2.1.3 Power Loss due to Microwave Heating

The power dissipated or heat generated into the material per unit volume caused by direct conversion of microwave energy when microwaves interact with the sample material. This power loss is a function of both the electric and magnetic field components of the microwaves. The power loss per unit volume (P) is a combination of electric field loss and the magnetic field loss defined as [61]:

$$P = \omega\,(\mu_o \mu''_{eff} H^2_{rms} + \varepsilon_0 \varepsilon''_{eff} E^2_{rms}) \qquad \text{Eq. (2.1)}$$

This equation describes the power dissipated as sum of the magnetic field loss (first term) and the electric field loss (second term). The notations are expressed as: ω as the angular frequency of incident microwaves, μ_o is the vacuum magnetic permeability, μ''_{eff} described as the imaginary part of the effective magnetic permeability (a combination of hysteresis loss, eddy current loss and residual loss), H_{rms} and E_{rms} are the local magnetic and electric field strength, respectively, $\varepsilon_0$is the permittivity of free space and ε''_{eff} is the effective dielectric loss factor.

2.1.4 Effects of Microwave-Metal Interactions

The microwave interaction with the conductive metals is limited to the surface penetration depth (or skin depth) only. Penetration depth is a measure of the depth of microwave penetration in a material which is defined as the distance from the surface to the place at which the magnitude of the field strength drops to e^{-1} (=0.368) of its value at the surface The skin depth is a function of microwave frequency, electrical conductivity, magnetic permeability etc. [62]. The consideration of skin depth is of paramount importance when dealing with metallic conductors to achieve efficient and uniform microwave heating. The proceeding section elaborates the effects of microwave-metal interaction which is critical to the concept of microwave heating involved in the present study.

2.1.4.1 Reflection Effect

Bulk of the metals readily reflect the incident microwaves due to the skin-effect allowing only shallow penetration of microwaves into the surface since no electric field is induced inside the metals. Despite the reflection, the constructive and destructive interferences of the travelling waves and reflected waves can alter the spatial distribution of microwave field intensity leading to changes in the spatial power absorption patterns within the surrounding medium.

Basak [63], [64] conducted studies on 2D samples with metallic plates or supports of different shapes to investigate the role of various shapes in controlling the focus of microwaves in an efficient way to achieve larger power absorption within the material. It was confirmed in a study [64] on bread and beef sample that different shapes of metallic annuli can be used to optimize the heating effects with enhanced power absorption or higher heating rates. The spatial power absorption pattern is also influenced by the type of microwave cavity which is broadly classified as:

(a) Single mode cavity— It supports only one mode of microwaves and produces predictable microwave field patterns with higher field strength. Single mode cavity, also offers convenient control in achieving the desired heating strength.

(b) Multi-mode cavity— This type of cavity is more complicated as compared to single mode cavity. It produces multiple modes of microwaves generating different spatial field configurations. Further, multimode cavities have all the dimensions comparably much larger than the incident wavelength. Here, the final electromagnetic field distribution is a resultant of the superimpositions of multiple reflections from the cavity walls. Many experiments have been performed in multimode cavity, usually, as modified household ovens [40].

2.1.4.2 Heating Effect

The heating effect in metals is strongly dependent on the skin depth of microwaves, which defines the upper limit of the thickness of metal that can be heated by the microwaves directly. Generally, in the case of metals, the skin depth is relatively small producing only a superficial heating effect. However, this effect plays a critical role in the treatment of microscopic sized metallic powders where the effective skin is sufficient to produce significant heating [65].

2.1.4.3 Discharge Effect

This effect is caused in conductors when the microwaves interact with sharp edges, tips and microscopic irregularities, that results in the electric arc or discharge. This phenomenon, sometimes, become more intense and results in the generation of high temperature hotspots. These hotspots release considerable amount of heat as the effect is transient and concentrated. The high temperature hotspots can melt the metal terminals as shown in Fig. 2.2 [66]. The microwave metal discharge can also alter the chemical reaction process and product composition [67] which makes this effect important in numerous other applications.

Figure 2.2: Morphology of the metal strips after discharge [66]

2.2 Microwave and Conventional Heating

The microwaves have the ability to penetrate through the solid material which allows volumetric heating in contrast to conventional form of heating where only surface heating is achievable. The heat flow patterns showing the temperature distribution produced during the two heating schemes is illustrated in Fig. 2.3 [68].

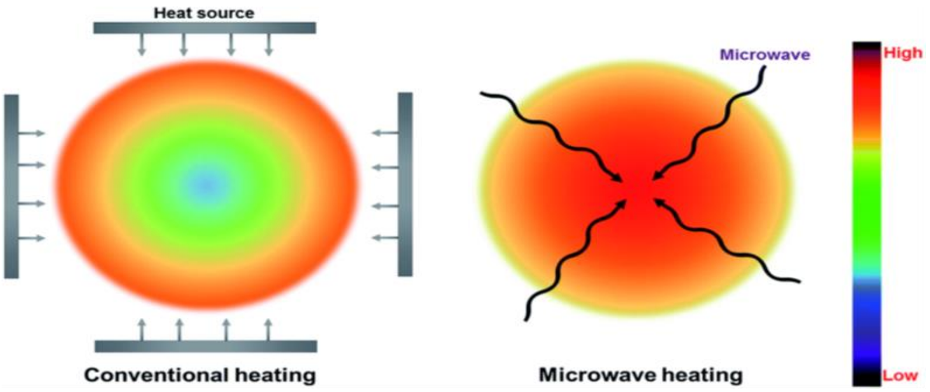


Figure 2.3: Microwave and conventional heating patterns [68]

In the case of conventional heating, heat is transferred from outer surface towards the inner core of the material whereas heat is induced within the material during microwave heating. Further, the temperature distribution within the material during microwave heating is uniform unlike conventional heating. The major difference between the microwave and conventional heating is the heat transfer mechanism. Conventional methods utilize furnaces to initially heat the surface, before any conductive heat transfer towards the inner core of the material takes place [69].

In case of microwave assisted pyrolysis of plastics, additional use of dielectric material called as absorbent is required. A study conducted on pyrolysis of plastic waste utilized carbon black as absorbent for conversion of microwave energy into heat required for pyrolysis [70]. Contrarily, conventional heating does not need any absorbent due to direct mode of heat transfer to the material. Another criterion used to differentiate between microwave and conventional pyrolysis techniques is the distribution of products. An investigation led by Khaghanikavkani [71] on variation in product composition was carried out for pyrolysis of plastics using microwaves and conventional method. The results revealed a very similar distribution of pyrolysis products. However, the heating uniformity was found to be considerably improved in contrast to conventional method as a result of microwave volumetric heating leading to faster pyrolysis. In case of plastics at a suitable scale (0.5 kg), the microwave heating has proved to be an efficient and cleaner process with faster and easier control [71].

There are several benefits of microwave heating in addition to volumetric heating [55], [72]. Selective material heating is a unique advantage of this technology that targets the specific material. In this process, the magnitude of heating strongly depends on the dielectric strength of the material. Since plastics have poor dielectric strength, they are mixed with dielectric absorbents like carbon which has been observed to convert microwave energy into thermal energy in a short span of time [73]. Thus, heating efficiency may vary for different materials which has also been a great challenge to industries [74]. Here, rapid heating can be easily promoted. It was pointed out that decomposition temperature up to 450°C in solid organic polymers can be achieved in a fraction of the time taken in conventional pyrolysis [75]. High temperatures can be reached in few minutes rather than hours in most cases, when the materials are heated at higher heating rates [75]. Another unique feature of this method is the non-contact heating. If microwaves can be controlled properly, it has the potential to treat the material without any physical contact with the heated sample [75]. Additionally, the control of the process is also simple. Plastic pyrolysis was achieved through efficient coupling and easy control of temperature by tuning and power control [71]. Microwaves have also been found to be effective for the upgrading of in-situ pyrolytic vapors into enhanced bio-oils, during biomass pyrolysis [22], [76]. Many studies have reported faster heating and in situ treatment of waste [26], [39], [73], [77]. The flexibility of operation and portability of equipment are the noted benefits of microwave technology [39], [78].

2.3 Pyrolysis of Plastics

Pyrolysis is a tertiary recycling technique in which organic polymers are converted to oil, gas and char at high temperatures in the absence of oxygen. The pyrolysis studies were conducted in the temperature range 300-900°C, however, in the case of plastic waste, the typical optimum temperature range of pyrolysis was around 500-550°C [79]. The pyrolysis of plastic waste was carried out at different temperatures and heating rates by various workers. For example, Kumar and Singh [80], conducted pyrolysis of HDPE in a semi- batch reactor at different temperatures in the range 400-550°C, and found that increasing the temperature reduced the retention time e.g. time e.g. 760 min

(400°C), 290 min (450°C), 68 min (500°C) and 54 min (550°C). In addition, pyrolysis of plastic waste was also performed at different heating rates 4 °C/min [81], 20– 25 °C/min [82] and 10 °C/min [83]. Lopez et al. [84] carried out pyrolysis of plastic waste at different retention times of 0-15, 30 and 120 min. Further, Buah et al. [83] used 40-70 min retention time while Velghe et al. [81] used 120 min. Thus, the pyrolysis process offers the potential to optimize the overall efficiency through suitable control of temperature and retention time. Fig. 2.4 presents a comparison between thermal and catalytic pyrolysis processes [85]. The process of pyrolysis can be achieved via thermal and catalytic methods.

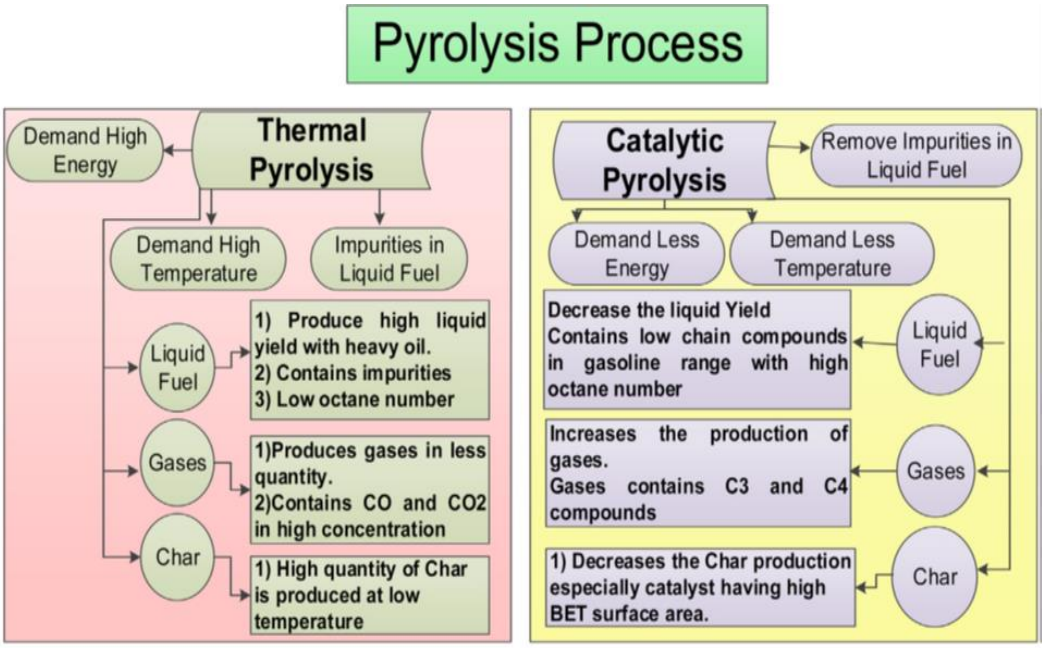


Figure 2.4: Pyrolysis process [85]

2.3.1 Thermal Pyrolysis

The thermal or non-catalytic pyrolysis of polyolefins is a high energy endothermic process that requires heating temperature in the range 350-500°C [86], [87]. This temperature may vary from 700-900°C if desirable product yields are required [21], [88]. The thermal pyrolysis of different types of plastics has been carried out extensively in the past that includes PE [89], [90], PP [91], [92] and PS [87], [90]. However, only few studies were conducted on PVC, PET, polymethyl methacrylate and polyurethane [93], [94]. It is to be noted that pyrolytic oil recovered through thermal pyrolysis contains long carbon chains [95], and low octane number, presence of solid residues [91], and impurities such as sulphur, chlorine, nitrogen and phosphorous [96].

2.3.2 Catalytic Pyrolysis

The catalytic pyrolysis is based on thermal breakdown in the presence of a catalyst. The use of catalyst in the conversion of plastics, add uniqueness to the process with reduced degradation temperature and residence time, and improved quality of liquid oil. A variety of catalysts have been used in the past studies such as FCC [97], spent or used FCC [98], HZSM-5 [99], ZSM-5 [96], and Cu-Al_2O_3 [100], all of which enhanced the yields and mechanisms of catalytic pyrolysis.

2.3.3 Factors affecting Pyrolysis

There are many important factors that can influence the pyrolysis of plastics waste such as temperature, retention time, feedstock composition, catalyst type, moisture content, heating rate and particle size. The most important factors are discussed in the following sub-sections.

2.3.3.1 Temperature

It is one of the most weighed factors in the pyrolysis process since it can determine the quality and quantity of the pyrolysis products [95], as it influences the cracking reactions that are responsible for variation in the yield of liquid oil and gas. Low temperature produces long hydrocarbon chains whereas high temperature gives shorter chains due to cracking of C-C bonds.

2.3.3.2 Retention time and Feedstock Composition

The effect of retention time is not much strong on the nature of pyrolysis products In a study conducted by Lopez et al. [84], same yield of liquid oil was observed at 30 min and 120 min retention times. Similar observation was made by Lee and Shin [101], where the aromatic compounds present in the oil at different retention times and same temperature were of similar nature. As regards the feedstock composition, it was found that PE and PP require higher temperatures for degradation as compared to PS due to its complex structure [96]. However, more detailed investigations are required to study the role of feedstock composition in pyrolysis [102].

2.3.3.3 Use of Catalyst

The role of catalyst in pyrolysis process is to improve the quality of pyrolytic products as well as reducing the temperature and retention time. The characteristics of the catalysts such as BET surface area, pore size, pore volume and acidity [103], are the critical factors that can affect the catalytic activity of any catalyst in the pyrolysis process.

2.4 Microwave Assisted Pyrolysis of Plastics

This section presents a review of studies conducted on microwave assisted pyrolysis (MAP) of plastics. The works are broadly divided into two types based on the microwave heating techniques. The first one involves the use of microwave absorbents and/or catalysts which has been most widely applied in the literature. The second type of MAP of plastics is a recent development and subject of the current study, which is based on microwave-metal interaction pyrolysis using metal antenna as the heat generating medium.

2.4.1 Using Absorbents/Catalysts

Ludlow-Palafox and Chase [43] demonstrated for the first time microwave-induced pyrolysis of HDPE and aluminum-plastic laminates (toothpaste tube) separately in a semi-batch bench scale apparatus. The experiments were performed using a modified microwave oven with continuous wave mode rather than on-off cycle operation. A maximum power output of 5 kW was produced using 4 magnetrons. Particulate carbon collected from the bottom residues of distillation towers was used as the microwave absorbent that constituted the carbon bed reactor. The reactor was also equipped with a stirrer with maximum speed of 6 rpm. The degradation of 50 g of polyethylene sample was carried out between 500°C and 700°C. The results indicated similar values of yield of oil and gas at around 80% and 20% respectively. As the temperature was increased from 500°C to 600°C, only small variation was observed in the yield of oil and gas, which was attributed to the effect of rise in temperature being counterbalanced by reduction in the residence time. Most of the hydrocarbons present in the oil and gas were primarily linear aliphatics comprising alkanes, alkenes, alkadienes with minimal aromatics (<2%). In the case of toothpaste waste, the microwave-assisted pyrolysis was found to be an effective method to recover high quality aluminum along with valuable hydrocarbons similar to those recovered from the pyrolysis of HDPE pellets. It was confirmed in the study that microwave induced pyrolysis has a great potential for the treatment of problematic waste like toothpaste tubes.

Microwave assisted pyrolysis of virgin HDPE plastic was carried out by Russell et al. [104] using an activated carbon bed and a traditional coke bed as the microwave absorbent. The batch-scale experiment was conducted using a magnetron rated 3 kW and 2.45 GHz to pyrolyze 100 g of HDPE load in a stirred-bed reactor. During the study, the temperature of the reactor was maintained between 400 and 600°C. The liquid oil recovered using the activated carbon bed was found to resemble carbon chain structure similar to diesel and petrol. Further, it was observed that the carbon bed played a catalytic role during pyrolysis through in- situ upgrading of reaction intermediates that produced a narrower range of hydrocarbons in contrast to the use of traditional coke bed.

Khaghanikavkani et al. [71] conducted microwave assisted pyrolysis of HDPE pellets for recovery of fuels and other useful hydrocarbons. Carbon blocks and silicon carbide were used as microwave absorbents in separate experiments. The experimental set-up was developed based on the simulated results of microwave electromagnetic field using Microwave Studio (MWS) software. A multimode batch-scale microwave reactor was used that operated at a maximum output power of 6 kW and frequency of 2.45 GHz. The reactor was designed to operate both in the stationary mode and rotation mode. A total of 10 experiments were conducted with first 8 in the stationary mode and last 2 in rotation mode. The pyrolysis reactor was heated between 400- 550°C in all the experiments. The total yield of oil/wax in the pyrolysis with stationary mode reactor was found to be 60% and 40%, using carbon and silicon carbide as microwave absorbents, respectively. However, the yield increased to 73% when silicon carbide was used in the rotating reactor. The most abundant hydrocarbons recovered were in the range C_8 to C_{35}. However, under optimized conditions the range was reduced from C_8 to C_{20} that could be used as fuels. The study also confirmed the feasibility of the MAP process on a reasonable scale in the proposed design. Further, the use of silicon carbide as absorbent was preferred over carbon blocks due to its better receptivity towards microwave, higher thermal conductivity, and higher density causing less dust in the reactor.

Undri et al. [45] applied microwave assisted pyrolysis (MAP) for efficient disposal of waste polyolefins using tires and carbonaceous char as the microwave absorbents. High density polyethylene flask, polypropylene container and a commercial tire were used as raw materials in the study. A batch laboratory scale microwave oven was used operating at 2.45 GHz, variable power output of up to 6 kW, and an additional fractionating column connected to the pyrolysis oven. Two experimental set-ups were used: A simple oven as reported in previous paper [105], here called set-up A, and set- up B [106] with a fractionating column between oven and liquid collection system.

The microwave assisted pyrolysis of HDPE and PP was investigated based on three parameters namely, the microwave power, microwave absorber and the experimental set-up used. The pyrolysis of HDPE produced a low viscosity oil at low microwave power but was not pyrolyzed completely. However, PP was always converted to low viscosity oil at low powers with complete pyrolysis. Liquid fraction from HDPE was composed of linear alkanes and 1-alkenes with negligible amount of branched, cyclic or aromatic content, while PP produced a mixture of methyl-branched alkane and alkenes or sometimes an aromatic fraction. It was also observed that the use of tire and carbon as microwave absorbents did not affect the progress of pyrolysis. Thus, the method proved to be an efficient way for disposal of waste polyolefins along with recovery of useful chemicals.

In a similar investigation by Undri et al. [107], MAP was applied to waste multilayer packaging (WMP) beverage to recover useful chemicals and fuel. WMP is a composite material synthesized using layers of paper, polyethylene (PE) and aluminum (Al). The apparatus used was same as reported in [45]. The experiments were carried out using different microwave absorbers (none, chopped tire, iron, and carbon). It was found that iron promoted better pyrolysis as compared to other absorbers. The PE component of the waste produced high viscous liquid except when fractionating set-up B was used, where lighter liquids were released comparable to fuels. The use of fractionating column or set-up B increased the residence time of pyrolysis which favored higher char formation and lower weight organic liquids. The organic liquid from WMP was mainly composed of hydrocarbons consisting of alkanes, alkenes and aromatics when set-up B was used. However, in the previous work [45], aromatic fraction was negligibly small. Further, a heavier bio-oil fraction composed of oxygenated species was also released due to the presence of paper in MWP. The process, in addition, also recovered high quality Al which proved the economy of the MAP technology in waste valorization.

Research was carried out by Suriapparao and Vinu [42] on MAP of PP as model plastic, using six different susceptors or microwave absorbers comprising graphite, silicon carbide, aluminum, lignin, flyash and activated carbon. The effects of microwave power, susceptor type and PP to susceptor ratio on (a) temperature and heating rate profiles (b) overall oil gas and char yields (c) oil and gas composition and (d) heating value of oil were investigated. The pyrolysis experiments were conducted in a domestic multimode microwave reactor at different powers between 180-800 W. Under optimal conditions of 450 W and ratio of 100:1 wt./wt. of PP (5g): graphite, 48%

oil was recovered with a heating value of 44.45 MJ/kg and 50% of gaseous hydrocarbons. The scalability of the process was also tested using 50 g of PP, producing oil with an energy recovery of 83%. The oil was found to contain alkenes and cycloalkanes as the major fraction. The susceptors were found to play a catalytic role in addition to conversion of microwave energy to heat. The potential of the technique was also demonstrated for pyrolysis of commercial polyethylenes and polyisoprene.

In another study, Aishwarya and Sindhu [70] applied MAP to plastic mixture sample prepared from industrial plants waste streams and domestic plastic waste. The experiment was performed in a batch-scale microwave reactor using carbon black as the microwave absorbent. The microwave operated at 2.45 GHz with a maximum output power of up to 5 kW. The liquid oil recovered under optimal conditions of pyrolysis was found to be suitable for application as a fuel.

Zhang et al. [44] conducted the catalytic microwave-induced pyrolysis of low density polyethylene (LDPE) over ZSM-5 for the first time. The method was found to be effective in producing gasoline range hydrocarbons. The microwaves were applied to the LDPE sample placed inside a quartz flask reactor which was connected to another packed-bed catalysis reactor before the condenser. A central composite design (CCD) was used to study the effect of catalytic temperature and reactant to catalyst ratio on the pyrolysis oil composition and to maximize the oil yield. The optimum conditions produced (32.58 wt.%) oil at 450°C with a reactant to catalyst ratio of 2. The results showed that LDPE could be converted to useful aromatic hydrocarbons through the catalytic activity of ZSM-5 during microwave induced pyrolysis.

In another application of catalytic microwave pyrolysis, Ding et al. [108] used NiO and HY zeolite catalysts to enhance the yield and quality of gasoline range hydrocarbons recovered from LDPE pyrolysis. A two-stage pyrolysis-catalysis system was used to carry out in-situ and ex-situ reactions using NiO and HY catalysts, respectively. The maximum output power of the microwave was 1.8 kW at 2.45 GHz. In every experiment, the LDPE sample (15 g) was first mixed with NiO or HY catalyst and then blended with SiC (500 g) as microwave absorbent. The optimum temperatures of pyrolysis and catalysis were found to be 500°C and 450°C, respectively, with 56.53% oil fraction composed of 93.80% as gasoline-range products. It was concluded that the co-catalytic MAP of LDPE with NiO and HY catalysts can both produce high-yield and high-gasoline oil fraction.

2.4.2 Using Metal Antenna

Hussain et al. [46] introduced a novel technique of microwave-metal interaction pyrolysis to convert waste polystyrene (PS) into useful hydrocarbons. A metal antenna in the form cylindrical iron mesh was used as the heat generating medium to achieve essential heating for pyrolysis. A domestic (on/off) microwave with output power 700 W and frequency 2.45 GHz was modified to carry out the pyrolysis experiment (Fig. 2.5). Waste polystyrene sample of 20 g was placed inside the iron mesh to carry out the pyrolysis reaction. The microwave was applied with 2-min pulses for a duration of 10 min. The temperature of the coil reached around 1100-1200°C. The iron mesh performed two functions: focusing the microwaves on the sample and build-up of high temperature within the mesh. The waste PS was converted to 80% oil, 15% gas and 5% char residue. It was observed that the pyrolysis reaction completed in a shorter time than conventional pyrolysis. The useful hydrocarbons recovered were mainly aromatics composed of styrene, ethyl benzene and condensed ring aromatics.

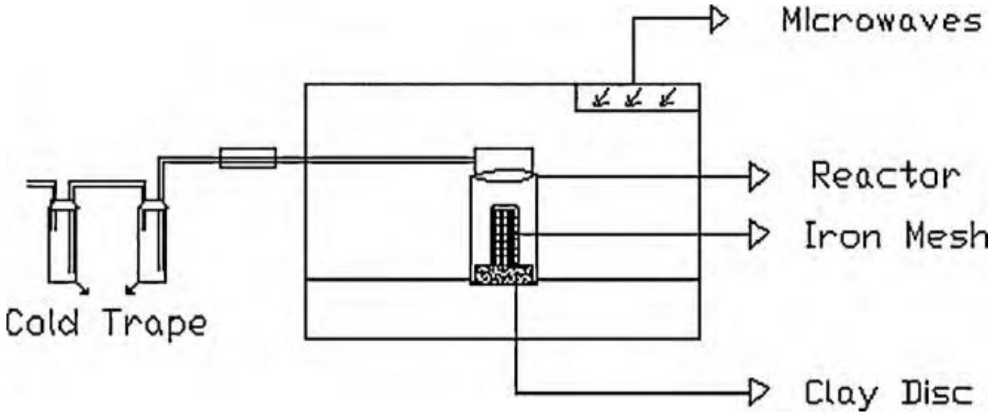


Figure 2.5: Schematic diagram of the experimental setup for the microwave–metal interaction pyrolysis of polystyrene [46]

In a later study, the effect of shape, size and nature of metal antenna during microwave- metal interaction pyrolysis of waste PS was investigated by Hussain et al. [49]. The experiment was carried out using aluminum as the metal antenna in the form of tightly coiled wire, strips, and cylinder. The experimental set-up used here, was the same as in the previous work [46], except the use of aluminum antenna in this study. It was found that the rate of reaction depended on the size, shape, and form of metal antenna. The pyrolysis reaction was observed to be faster in the case of coil, slower for the strips and negligible for cylinder. The faster reaction was observed due to rapid heating caused by largest exposed surface available in coil followed by strips, and least in case of cylinder. The properties of metal antenna comprising its nature, heat capacity, thermal conductivity, and reflecting power, were found to influence the reaction kinetics. The thickness of the wire was found to have a significant influence on the reaction time. It was concluded that the thicker wire had a better capacity to store larger amount of heat in contrast to a thin wire. The products of pyrolysis gave 88 wt.% oil, 9- 10 wt.% gases and char residue, at the optimum conditions of reaction. The nature of the recovered oil was aromatic consisting of substituted benzene in addition to other polycyclic aromatics and condensed ring aromatics.

The co-pyrolysis of waste PS with coal was carried out by Hussain et al. [48] using microwave-metal interaction pyrolysis. The experimental apparatus used was the same as in the past study [46], except the use of copper coil reactor in this study. The products of pyrolysis contained 66% oily liquid (mixture of oil and tar), 10% aqueous liquid mostly containing sulfides, 6% gases and 18% char residue. The co-pyrolysis of coal with waste PS using copper coil was found to be more efficient than the reported co- pyrolysis studies based on conventional heating. The oil products were found to be aromatic in nature. Overall, the method proved to be an efficient technique for disposal of waste polystyrene and recovery of useful chemicals.

Another study [47] was conducted on microwave-metal interaction pyrolysis using a copper coil. The waste PS recovered from packing material of Dell computers was used for the experiments. The experimental set-up used here, was the same as in the previous study [46] on iron mesh. The temperature achieved during the process was in the melting point range of copper (1000-1100)°C as was confirmed through the melting of wire tip. The rate of reaction was found to depend on the shape, size and nature of metal antenna which was also demonstrated in the past investigation [49] using aluminum coil. It was found that coil made of thicker wire increased the rate of pyrolysis reaction. The pyrolysis reaction was completed in 5-6 min when a 3 mm coil was used. However, when a coil of gauge size between 1-2 mm was used, the reaction period increased from 10-15 min. It was also observed that metal antenna with larger exposed surface produced higher quantity of heat that reduced the reaction time of pyrolysis. When the coil wire was replaced by a solid cylinder, the reaction time increased to 20 min whereas when the same cylinder was cut into metal strips, the reaction time decreased to 15 min. The pyrolysis products were found to contain 85% oily liquid, 10-12% gases, and char residue. The pyrolytic oil was found to contain substituted benzene in addition to polycyclic and condensed ring aromatics. The microwave-metal interaction pyrolysis was found to be an efficient technique for the recovery of useful hydrocarbons from waste PS.

The novel technique of microwave-metal interaction pyrolysis was also applied to biomass in a study led by Bashir et al. [50]. The study investigated the effect of metal type and gauge size on the product quality and composition using different coils made of iron, copper, and aluminum. The water hyacinth was used as the biomass feedstock. The microwave oven and reactor assembly was similar to the experimental set-up used earlier investigations [46], [48], [49]. The wire gauges used were 1, 1.5, 2 and 2.5 mm, respectively. The oil yield obtained from iron coil was found to be maximum followed by copper and aluminum coils for each gauge size. It was also observed that higher gauge size coil produced more oil than a coil of lower gauge. The hydrocarbon content of the pyrolytic oil for iron, copper and aluminum coils was found to be 13.189%, 7.87% and 14.7%, respectively. The composition of the bio-oils showed presence of only hydrocarbons, aromatic compounds, small quantity of furans with no water and acids. It was concluded that oil produced from microwave-metal interaction pyrolysis of water hyacinth can be used as a fuel after simple distillation without need of upgradation.

2.5 Other Applications of Microwave Assisted Pyrolysis Technology

2.5.1 Treatment of Problematic Waste

Microwave assisted pyrolysis has been successfully applied to treat some of the environmentally hazardous forms of wastes. The disposal of waste tires through microwave assisted pyrolysis is such an example. Undri et al. [109] used the MAP method to convert the waste tire into manageable products in the form of chemicals and fuels. The gaseous products of MAP of scrap tires [110] was also investigated in the past. The presence of carbon black in tires makes it a good microwave absorbent and therefore, is also a suitable material to conduct MAP.

The microwave assisted pyrolysis was also used to treat the used automotive engine oil which contains environmentally toxic compounds like heavy metals and polyaromatic hydrocarbons. Lam et al. [111] used microwave pyrolysis to convert waste engine oil into valuable gases (hydrogen, syngas) as a source of hydrocarbon energy. Around 41% gases were recovered in the process which belonged to aromatic and aliphatic class of compounds.

Sewage sludge is another harmful waste that must be treated to protect environment. Domingues et al. [112] investigated the microwave assisted pyrolysis of sewage sludge to recover bio-fuel in the form of hydrogen and syngas (H_2 + CO). The microwave irradiation was used to pyrolyze the sludge with improved gas yield as compared to conventional methods.

2.5.2 Biomass Waste

The microwave assisted pyrolysis has been applied to a wide variety of biomass for the recovery of bio-oils. The applications include MAP of coffee hulls [22], corn stover and wood [113] , oil palm shell [114], rice straw [115] and macro-algae [116]. In most of the studies , microwave absorbents were used where the source material was a poor microwave receptor. The microwave assisted pyrolysis converted the biomass material into gas and oil fractions with char residue. The products of biomass microwave pyrolysis were recovered as useful bio-oils and gases. The bulk heating characteristics of microwave assisted pyrolysis reduced the high energy consumption and cost involved in the grinding/shredding process. The rapid heating potential and in-situ upgrading of products proved the microwave induced pyrolysis as an efficient technique for the recovery of value-added products in comparison to conventional pyrolysis.

2.5.3 Upgrading of Natural Hydrocarbons

Microwave-induced pyrolysis has been applied to naturally occurring hydrocarbons for production of fuels. An important example is the conversion of oil shale using MAP. The reaction occurs at 700°C producing 6% aromatic oil and 10% gases [117]. The conversion of natural coal to useful hydrocarbons through MAP has been carried out in the past [118]. Co- pyrolysis of coal with waste PS was carried out [48] to recover improved quality of valuable hydrocarbons and simultaneous disposal of waste polystyrene. The process was based on microwave-metal interaction pyrolysis which involved the use of copper coil as the heat generating medium, since coal has poor reception to microwaves. The process was found to be effective in producing improved yield and quality of final products than the conventional techniques of coal pyrolysis.

2.6 Process Variables in Microwave Assisted Pyrolysis

The process variables of microwave assisted pyrolysis technology play a critical role in efficient conversion of the sample material into oil, gas and char. Suitable control of these variables can be used to optimize the process and improve the yield and quality of the final products. The following are the important factors of consideration in MAP:

1. Size and type of input material
2. Reaction temperature
3. Residence time
4. Microwave power output and cavity type (single-mode/multimode)

5. Reactor design
6. Nature of absorbent or metal antenna
7. Catalyst type
8. Type and rate of carrier gas

2.7 Limitations of Microwave Assisted Pyrolysis

The potential of dielectric materials called as absorbents or susceptors to be used in the pyrolysis of polymers and plastics has been explored widely [39], [73], [77]. However the specific role of susceptor in the energy transfer or catalyzing effect on pyrolysis reaction is still not well known [42]. Further, the absence of sufficient data required for quantification of dielectric properties of materials makes the application of microwave assisted pyrolysis even more difficult. It is to be pointed out that not all materials have the ability to absorb microwaves [75], and that, the efficiency of microwave heating depends strongly on the dielectric properties of the material. As a result, plastics which have a low dielectric constant if mixed with a suitable microwave- absorbent material such as carbon can significantly improve the conversion of microwave energy into heat in shorter time [73]. Therefore, heating efficiency may differ for different absorbents which makes industrial application of this process very challenging [74].

To date, macroscopic temperature measurement methods, can only measure the overall or average value of temperature of the heating medium due to detection limitation of measurement devices at temporal and spatial scales, and it has been very difficult to measure temperature of isolated hotspots [119]. With the use of advanced detecting instruments like high-speed camera and optical temperature probe, existence of hotspot effect has been confirmed [120], [121]. Another difficulty is faced during accurate measurement of temperature within the reaction mixture. In a study led by Undri et al. [109], on microwave assisted pyrolysis of silicon oil, a temperature lag was observed in IR-based sensors in contrast to conventional use of thermocouples. The temperature monitoring of the process becomes difficult since the temperature goes beyond 1000˚C and an instrument like thermocouple will melt down. In this scenario, there are two alternatives available for temperature measurement. One is the use of infrared thermometer and the other one being fiber optic thermometer. The infrared thermometer works without contact over a wide range of temperatures. But the IR thermometer sensors can only measure the surface temperature of the reactor which is lower than the temperature of the reaction mixture [42]. In this context only few studies have been able to measure the temperature within the reaction mixture [122]–[124]. On the other hand the use of fiber optic device is not possible since it can measure temperatures only up to 400°C [7]. But there is a new variant of optical fiber temperature probe which is made of sapphire crystalline fiber and has been used effectively in microwave pyrolysis [127]. In another published work, a thermocouple was used for temperature measurement inside a domestic microwave oven operating under low power of magnetron [42]. This facilitated measurement of temperature inside the reaction mixture during the off-time which is greater than the on-time period in contrast to high power microwave. It was pointed that conventional thermocouple may lead to sparks and trips due to reflection of microwave. Therefore, in this experiment, a chromel- alumel thermocouple was used as a modified version of conventional thermocouple.

Formation of hotspot or microplasmas is another limitation, that has been identified as a form of thermal instability associated with rapid heating in a microwave. According to a study, hotspot formation is a result of non-linear dependence of electromagnetic field on the thermal properties of the material [128]. The presence of such a hotspot may lead to non-uniform heating as materials not present in the hotspot region are not subjected to the same degree of microwave heating [129]. Further, it was reported that the design of microwave cavity plays a crucial role in the control or utilization of this hotspot for effective heating [130]. According to a simulation study on microwave design, uneven distribution of scattered hotspots within the sample may result in non-uniform heating [129]. A major problem is faced when dealing with microwave metal-discharge applications. Here, the main obstacle is that the discharge is highly unstable and difficult to sustain for a long time [119]. In microwave systems, discharge occurs when metals with sharp edges or tips are subjected to microwave irradiations. Spark discharge at the tip of metal electrode is an example where surrounding gas is broken down to conducting ions which may lead to formation of hotspots due to excessive generation of heat in the process. Another microwave-metal discharge effect can be observed in the use of thermocouples inside a microwave field, which can cause incorrect recording of temperature and may also damage the thermocouple in the extreme case of hotspots formation. Finally, application of microwave technology is still limited to only lab scale systems and is not effective at industrial scales. This drawback can be attributed to the limited understanding of microwave systems. Apart from material properties and characteristics, operating parameters such as radiation time and power, cavity design and material throughput have been found to determine the extent to which a successful treatment is achieved [75].

2.8 Summary of Key Works

The present Section 2.8 summarizes the relevant works in the field of microwave assisted pyrolysis using absorbents and metal antenna as the heat generating mediums.

Table 2.1: Summary of key works in the field of MAP

No.	Author	Application	Findings	Research gap
1.	Ludlow-Palafox and Chase, 2001 [43] Ind. Eng. Chem. Res.	MAP of HDPE and aluminum plastic laminates (toothpaste tube) using particulate carbon.	Recovery of valuable hydrocarbons (oil-80%, gas-20%), mostly aliphatic in nature in case of HDPE. In case of toothpaste tube waste, high quality aluminum was recovered.	Previous works mainly focused on pure plastics or homogenous waste rather than realistic materials with contaminants.

2.	Russell et al., 2012 [104] RSC Advances	MAP of Virgin HDPE using activated carbon bed and traditional coke bed.	Activated carbon bed produced oils similar to diesel and petrol. Further, activated carbon played a catalytic role in producing narrower range of hydrocarbons unlike traditional coke bed.	Traditional coke produced wide range of oils with a need for further treatment to be used as fuels.
3.	Khaghanikavkani et al. 2013 [71] Chemical Engineering & Process Technology	MAP of HDPE pellets using carbon blocks and silicon carbide as the microwave absorbents.	Oil/wax yield up to 60% and 40% for carbon blocks and silicon carbide. Hydrocarbons range was C8 to C35. Use of rotating reactor increased the yield to 73% for silicon carbide. Silicon carbide was found to be more efficient towards microwave heating.	Complex nature of microwave pyrolysis makes uniform heating hard to achieve in short time on a reasonable scale as compared to conventional pyrolysis.

4.	Undri et al., 2014 [45] Fuel	MAP of waste polyolefins (HDPE+PP) using chopped tires and char as microwave absorbents.	Recovery of useful hydrocarbons. PP always produced low viscosity oil, however, HDPE produced light oil only at low powers with incomplete pyrolysis. Use of tire and carbon did not affect the progress of pyrolysis. Efficient disposal technique.	Commercial application of MAP not feasible without implementation of MAP of PE and PP
5.	Undri et al., 2014 [107] Fuel	MAP of Waste Multilayer Packaging Beverage (paper + PE+ Al).	Paper converted to bio-oil, PE converted to high viscosity oil composed of alkanes, alkenes, cyclic and aromatics. Al recovered in good condition unscratched.	Products formed from different layers of the multilayer waste and the possible interaction between them unknown.

6.	Suriapparao and Vinu, 2015 [42] Journal of Analytical and Applied Pyrolysis	MAP of PP using graphite, silicon carbide, aluminum, lignin, flyash and activated carbon as MW absorbents.	The susceptors acted as catalysts. Under optimal conditions, oil produced was 48% from 5 g PP. At higher scale of 50 g, energy recovery in oil was up to 83%.	The specific role played by the susceptor in altering the energy transfer during pyrolysis reactions not clear.
7.	Aishwarya and Sindhu, 2016 [70] Procedia Technology	MAP of plastic waste using carbon as microwave absorber.	Fuel range liquid products were obtained on optimal pyrolysis of plastic waste mixture.	Need for more efficient heat transfer methods to optimize the process.
8.	Zhang et al., 2015 [44] Fuel	MAP of LDPE using ZSM-5 catalyst in a quartz flask reactor, no absorbent.	Optimal conditions explored were: 32.58% oil produced at 450°C and reactant to catalyst ration of 2. The upgraded oil was dominantly aromatic in nature.	The evolution of individual aromatic hydrocarbons in liquid phase derived from MAP of polyolefins over ZSM-5 remained unexplored.

9.	Ding et al., 2019 [108] Energy Conversion and Management	MAP of plastic waste over NiO and HY catalysts using SiC as MW absorbent.	Optimum pyrolysis and catalysis temperatures were 500 °C and 450 °C, respectively, with 56.53 wt% oil product and 93.80% gasoline-range fraction.	Recovery of gasoline fuel combined with high yield, high quality and specific carbon number has been a challenge.
10.	Hussain et al., 2010 [46] Journal of Analytical and Applied Pyrolysis	Microwave-metal interaction pyrolysis of waste PS using iron mesh.	Shorter reaction time than conventional methods, higher temperature range 1100-1200°C, lighter products, and higher yield with 80% liquid, 15% gas, rate of reaction dependent on shape and nature of antenna.	Limitation of non- selective nature and high temperature required during conventional pyrolysis.

11.	Hussain et al., 2011 [48] Journal of Analytical and Applied Pyrolysis	Microwave-metal interaction co-pyrolysis of waste PS with coal using copper coil.	The products of pyrolysis contained 66% oily liquid (mixture of oil and tar), 10% aqueous liquid mostly containing sulfides, 6% gases and 18% char residue. Oil was mainly aromatic.	Direct process of liquefaction of coal produces low quality oil with higher char formation.
12.	Hussain et al., 2012, [49] Fuel Processing Technology	Microwave-metal interaction pyrolysis of waste PS using aluminum coil, strips, and cylinder.	Products of pyrolysis gave 88 wt.% oil, 9- 10 wt.% gases and char residue, rate of reaction was found to depend on shape, size, and form of metal.	Development of more efficient technique of MAP of plastics for recovery of useful products required.
13.	Hussain et al., 2014 [47] Energy Sources, Part A: Recovery, Utilization, and Environmental Effects	Microwave-metal interaction pyrolysis of waste PS using copper coil.	Copper coil played a catalytic role, products yield- 85% oil, 10-12% gases and char residue.	Improvement in the efficiency of MAP of plastics for recovery of useful products required.

14.	Bashir et al., 2018 [50] Chemical Engineering & Processing: Process Intensification	Microwave-metal interaction pyrolysis of biomass using iron, copper, and aluminum coils.	Significant difference in the chemical composition of the bio- oils, produced with different metal coils was noticed.	Improvement in the efficiency of MAP of biomass for recovery of useful oil and gas products required.

CHAPTER 3

METHODOLOGY

This chapter describes the materials and methods used to achieve the research objectives of the study. Section 3.1 shows the research flowchart highlighting the steps undertaken during the entire research. Section 3.2 provides knowledge of the materials used during the experiments and metals used for fabrication of heating coils. Sections 3.3 to 3.6 elaborates on the development of experimental rig, temperature monitoring, experimental procedure and formulation used during the study. The equipment was designed, fabricated, and tested to meet the safety and operational requirements. Section 3.7 provides a concise explanation of GCMS technique used to identify the possible compounds present in the pyrolytic oils. Sections 3.8 and 3.9 describes the coil gauge size and type of metal used to conduct the microwave-metal interaction pyrolysis. Section 3.10 elaborates the method used for determination of energy efficiency of the process. The chapter ends with Section 3.11 presenting the central composite design model used to evaluate the optimum operating conditions with liquid oil yield maximization.

3.1 Research Scheme

The current research work was initiated with preliminary characterization of virgin plastics comprising PS, PP and LDPE, respectively, which is important for understanding the performance of microwave-metal interaction pyrolysis. Properties like thermal degradation temperature and volatile content of the plastic play a critical role in the recovery of products of pyrolysis. An attempt was made to address the raised research question by conducting an experimental investigation on the performance of microwave-metal interaction pyrolysis of plastics using a metal coil. The study was performed based on the effect of microwave power on the oil yield, temperature, reaction time and composition during microwave-metal interaction pyrolysis of PS, PP and LDPE, respectively. The performance was also evaluated for plastic blends and waste PS. The effect of wire gauge size and type of metal on process performance and process efficiency were also investigated. At the end, central composite design model was developed to determine the optimum operating conditions of the process with maximum oil recovery for each plastic comprising PS, PP and LDPE, respectively.

Figure 3.1 highlights the various steps that were undertaken during the entire study. The first step involved detailed review of the literature that led to identification of the research problem. The materials selected for the study comprising PS, PP, LDPE, and waste PS, respectively, were characterized as a part of preliminary investigation. The laboratory scale microwave pyrolysis system was designed and fabricated that comprised a microwave oven, metal coil and reactor assembly. The first experiments were then conducted to study the temperature profile of the heating coil. It was assured at each level of investigation that the study addressed the involved research question before moving on to the next level of study. In case of negative feedback, the investigation was relooked into or repeated to reach a conclusive evidence. The performance of microwave-metal interaction pyrolysis was evaluated for individual plastics (PS, PP, LDPE), plastic blends and waste PS (PSW). This was followed by the study on effect of coil gauge size and type of metal on the process performance. The GCMS characterization of recovered oils was also performed during the course of study. The next step involved determination of energy efficiency of the process. The last step in the study involved investigation on optimization of microwave-metal interaction pyrolysis process for maximum oil recovery.

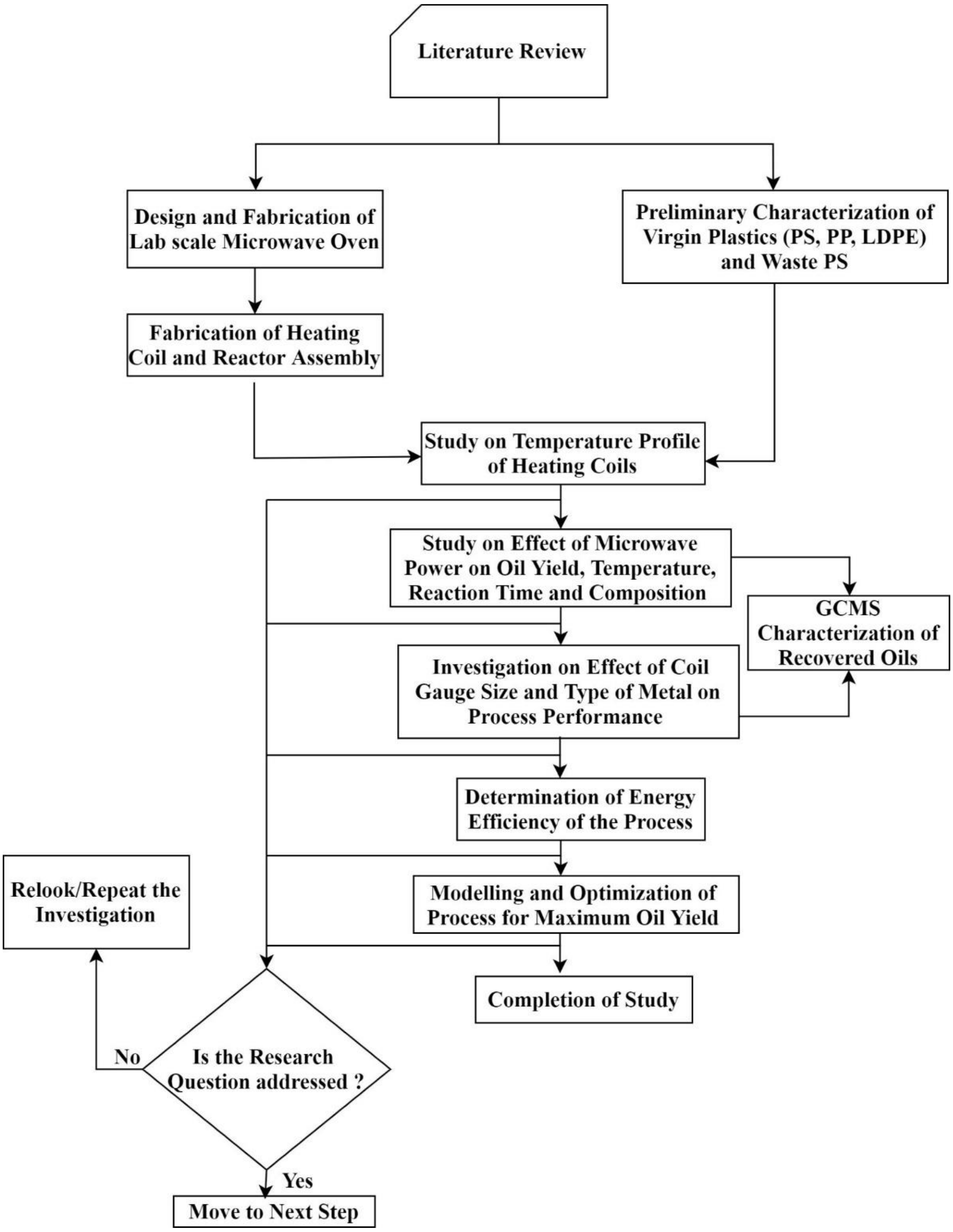


Figure 3.1: Flowchart of the steps undertaken during the research work

3.2 Materials

The knowledge of properties of different plastics used in the experimental study is provided. The sample materials used for pyrolysis comprised virgin plastics or non- commercial plastics (PS,PP, LDPE) and waste PS. Preliminary characterization of materials included determination of calorific value, elemental analysis, proximate and TGA (thermogravimetric analysis). The data obtained from aforementioned characterization tests is important to understand the behavior of pyrolysis for different plastics. The wires used for fabrication of heating coil are described based on the specifications provided by the manufacturer.

3.2.1 Plastic Samples and Preparation

Virgin plastic samples of PS, PP and LDPE were used as the model of waste plastics for this study. Fig. 3.2 shows the different plastic resins comprising PS, PP, LDPE, and waste PS (PSW).

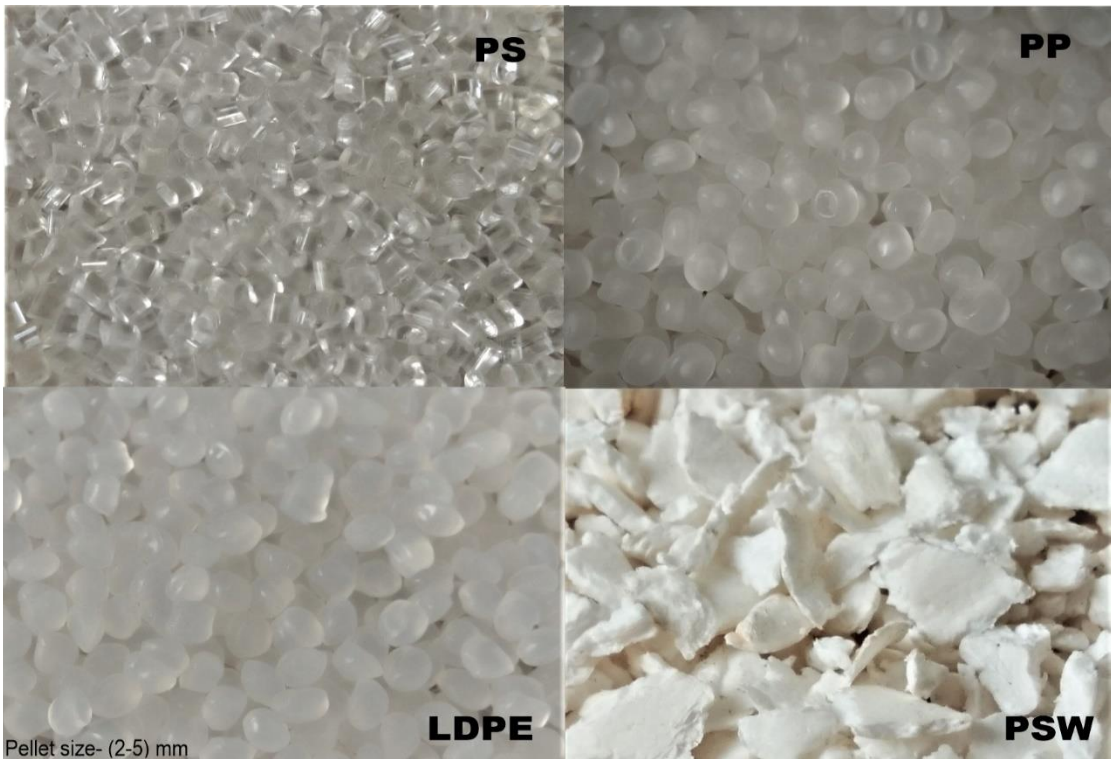


Figure 3.2: Material samples used during the study

The plastics are known as virgin since it is not used before in any commercial application. The plastic was purchased from Lotte Chemical Titan (M) Sdn. Bhd. available in the form of pellets of size in the range 2-3 mm. The waste PS was taken from the post-consumer plantation cups which is a type of expanded polystyrene foam (EPS). The cups were cleaned with water and dried in oven at 105°C for 10 min. These cups were then shredded into small pellets of size 2-5 mm using a mechanical grinder (Model- WSGP- 230, Wensui Plastics Machinery Group, China). The density of virgin plastic based on ASTM D1505 as provided by manufacturer was: PS = 1.04 g/cm³, PP = 0.9 g/cm³, LDPE = 0.921 g/cm³. The density of waste PS cups (EPF) from the manufacturer company MEGAFOAM Sdn. Bhd. was 0.05 g/cm³.

The preliminary characterization of the plastic samples was performed which is important in understanding the behavior of pyrolysis for different plastic samples, comparative analysis, and estimation of energy recovery in oil (%). This included the following analyses:

(i) Measurement of Calorific Value: The calorific value of the plastic samples was determined using the adiabatic bomb calorimeter (ASTM D7309).

(ii) Elemental Analysis: The elemental analysis was performed using ELEMENTAR model-vario Micro Cube based on ASTM D5373.

(iii) Proximate and Thermogravimetric (TGA/DTG) Analysis: The proximate and TGA Analysis was done based on ASTM E1131. The TGA experiment was conducted by the LABSYS EVO TGA apparatus. The plastic samples were weighed to around 20 mg. Thermocouple was used for the measurement of the furnace temperature. Nitrogen (N_2) was passed through the chamber to create inert atmosphere at a flow rate of 100 ml/min. The samples were dried to eliminate the effect of moisture by heating up to 110ºC and holding for 5 min. The sample was then heated from room temperature to a maximum temperature up to 950°C in the presence of N_2 gas and with a heating rate of 10 °C/min. At 950°C, nitrogen gas was switched to oxygen for proximate analysis. The TGA and DTG curves are shown in Figures 3.3 to 3.6.

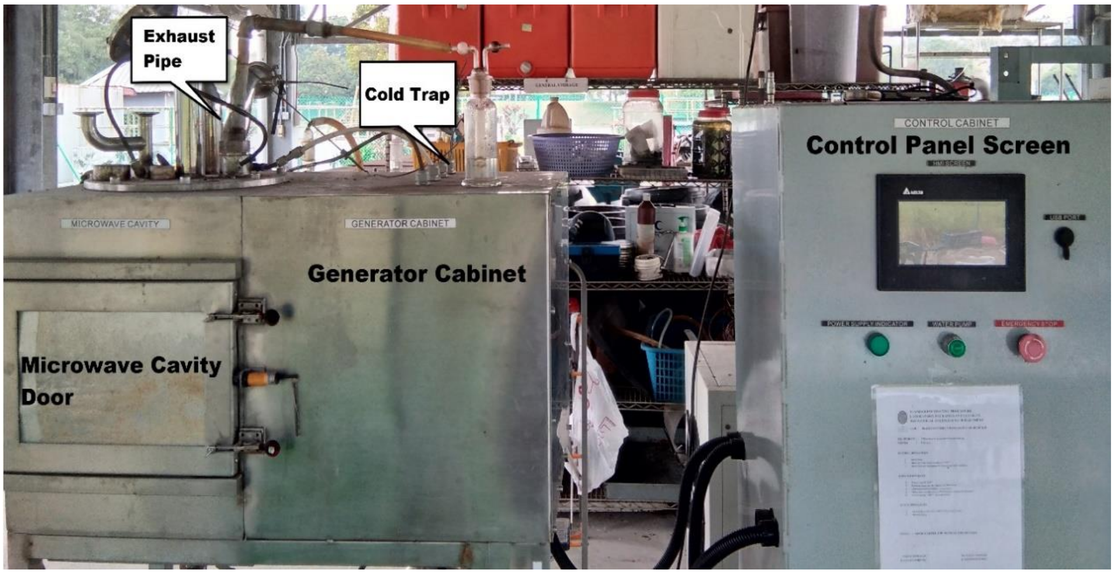
3.2.2 Metal Coils

The experimental study was carried out using coils made of iron and copper wires. The iron wire was purchased from a local market in Malaysia, commercially available as binding wire made of mild steel. The gauge of the wire was 1.5 mm and purity up to 99.8% as provided by the manufacturer. Three different gauges of iron wire were used to study the effect of gauge on the oil yield taken as: 1 mm, 1.5 mm, and 2.0 mm, respectively. The copper wire was also purchased from a local market with a gauge of 1.5 mm and purity up to 99.9% as provided by the manufacturer.

3.3 Operation and Testing of Microwave Apparatus

A custom-made microwave oven was used to carry out microwave-metal interaction pyrolysis. Fig. 3.3 illustrates the microwave pyrolysis system. The laboratory scale microwave oven was fabricated by Uni 10 Sdn. Bhd. The microwave operated at a frequency of 2.45 GHz in multimode with two magnetrons rated 1.5 kW each. The microwave power was variable and continuous in the range 250-2640 W. The microwave produced continuous heating based on pulse width modulation using invertor power supply which is different from previous works on microwave-metal interaction pyrolysis using pulse on-off cycle [46], [48], [49]. The dimensions of the chamber were width 40 cm, height 50 cm and depth 46 cm. The microwave cavity was used for placement of the sample. The generator cabinet contained the magnetrons which were cooled by an integrated chiller system. The control panel touch screen was used for adjustment of microwave power of each magnetron. The exhaust pipe was used to transfer the volatiles to the cold trap for oil collection. The microwave system was equipped with an emergency button that can be used to immediately stop the operation in case of an accident for operator safety.

The microwave system was tested using the leakage detector to ensure safe operation according to Safety Standard developed by US Federal and Drug Administration, FDA (21 CFR 1030.10). The microwave was found to operate within the safe limit (≤ 5 mW/cm^2) at a distance of 0.051 m from the microwave oven surface.



(A) Full view

(B) Close-up view integrated with cooling device (placed backside of control cabinet)

Figure 3.3: Microwave pyrolysis system

3.4 Installation and Operation of Reactor Assembly

Figure 3.4 shows a schematic representation of the experimental rig designed, fabricated, and used during the study. A galvanized iron (GI) pipe was used as a reactor chamber to place the sample. The GI pipe was installed from the top centre of the microwave chamber such that the base of the pipe was surrounded by the coil placed inside a clay pot (internal diameter = 6 cm, height = 8 cm) and the other end of the pipe was connected to the impinger bottle tube. The clay pot provided heat insulation to the reactor and can withstand high temperatures of up to 1000°C. The pot was raised to the centre of the chamber using a cylindrical metallic support.

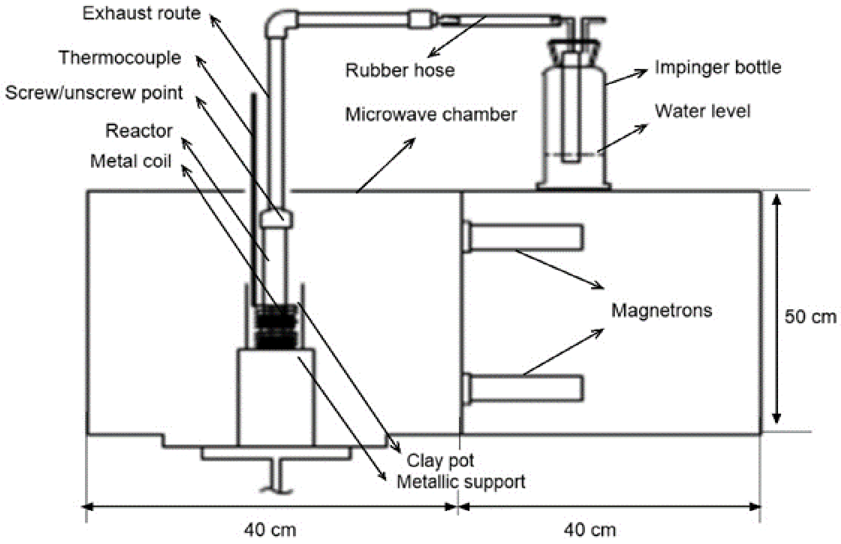


Figure 3.4: Schematic representation of the experimental set-up

Figure 3.5 gives a pictorial representation of the reactor assembly and the coils used for the experiments. The idea of using cylindrical metal support was to readily reflect the microwaves so that the essential microwave-metal interaction heating occurs only between coil and GI pipe. The outer diameter, inner diameter and height of the GI pipe reactor was 3.4 cm, 2.7 cm, and 15 cm, respectively. The bottom portion of the GI pipe around 5-6 cm contained the plastic sample and was surrounded by the iron coil of height = 5 cm and internal diameter = 5 cm. The coil was fabricated by tightly rolling the wire over a solid cylindrical object. A Type-K thermocouple was inserted through the top of the chamber touching the coil to measure the coil temperature. The thermocouple was movable along the vertical direction to provide flexibility of operation.

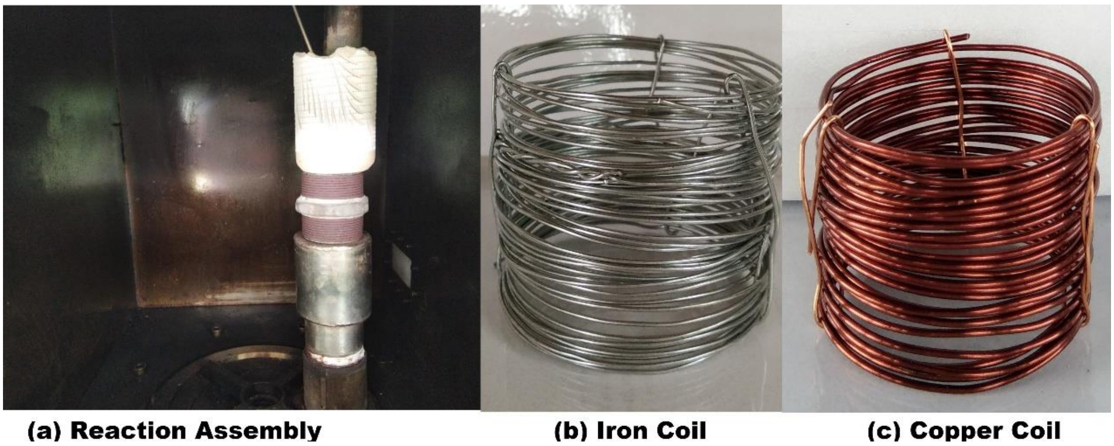


Figure 3.5: View of the reaction assembly and the fabricated coils

3.5 Temperature Monitoring during Microwave-metal Interaction Pyrolysis

A Type K thermocouple was inserted through the top of the chamber adjustable along the vertical direction and touching the coil to give temperature reading. The thermocouple probe was inbuilt in the customized design of the microwave system and the temperature reading was displayed at the control panel display screen. Heat generated through microwave-metal interaction using iron coil was used to pyrolyze the plastic samples. Temperature of coil was monitored for a total reaction time of 30 minutes at different values of microwave power in the range of 500-2500 W and for each plastic PS, PP and LDPE, selected for study. To investigate the consistency of heating process, average temperature attained by the coil during the entire reaction at a constant microwave power was determined and plotted against different values of microwave power in case of each plastic (PS, PP, LDPE).

3.6 Experimental Procedure for Microwave-metal Interaction Pyrolysis

The microwave-metal interaction pyrolysis was carried out to pyrolyze 20 ± 0.01 g of plastic sample. The performance of the microwave-metal interaction pyrolysis was investigated by measuring the oil yield and reaction time in each experiment, performed at different microwave powers varied from 500 to 2500 W with an increment of 200 W. The maximum oil yield with mass balance and conversion (wt.%) under optimal conditions was reported. The experiments were conducted on individual plastics comprising PS, PP and LDPE, plastic blends, and waste PS (Expanded Polystyrene Foam, EPF) . The blends were prepared with equal proportion of each plastic at a ratio of (1:1) for PS-PP, PP-LDPE, PS- LDPE and (1:1:1) for PS-PP-LDPE, respectively. In the case of experiments with EPF, sample size was taken to be 10 ± 0.01 g due to its extremely low density (0.05 g/cm^3) and was compressed to effective volume of GI pipe reactor utilized for pyrolysis reaction.

The temperature of the coil was recorded at different microwave powers during the experiments. However, there were fluctuations in the temperature due to trips and sparks, commonly encountered when metallic probes are subject to microwaves [42]. It must be mentioned here that the effect of degradation of coil was not accounted in the present study as this would require a reasonably accurate and precise system of temperature monitoring to detect subtle changes in performance of the process with heating fluctuations. In the present work, the use of conventional thermocouple provided an overall or average temperature of the heating medium (iron coil), also confirmed in a past study [59]. The pyrolysis temperature achieved at different microwave powers (temperature was recorded after microwave exposure of 10 minutes with minimal fluctuation) was assumed to be nearly equal to the coil temperature due to close proximity between coil and the GI pipe reactor (clearance = 8 mm). The plots of pyrolysis temperature versus microwave power were shown for the individual plastics (PS, PP, LDPE) and waste PS.

The essential heating required for the pyrolysis reaction to occur was provided by the microwave- metal interaction which caused thermal breakdown of the plastic sample. The volatiles produced in the reactor rise towards the exhaust passage and are collected in the impinger bottle (25°C) as an immiscible oil layer floating at the top. The non- condensates fraction (gas) was released into the environment and not monitored in the current study. The process of pyrolysis occurred in the absence of oxygen as the gas formed in the early phase of pyrolysis reaction replaced the traces of trapped oxygen inside the reactor. No purging gas was used in the entire experiment. Table 3.4 represents the formulas used for the calculation of conversion (oil + gas) , mass balance of pyrolysis products (oil, gas, and residue), oil density, energy recovered in oil, energy consumed and energy efficiency of the process.

Table 3.1: Different formulas used in the analysis

Eq. No	Formula used	Notations
(1)	$\text{Conversion (wt.\%)} = \frac{m_{\text{plastic feed}} - m_{\text{residue}}}{m_{\text{plastic feed}}} \times 100\%$	Mass (m) Volume (V) Yield (Y) Residue (R) Density (ρ) Higher heating value (HHV) Energy (E) Microwave power (P) Reaction time (t) Energy efficiency (η)
(2)	$Y_{\text{oil}}\ (\text{wt.\%}) = \frac{m_{\text{oil}}}{m_{\text{plastic feed}}} \times 100\%$	
(3)	$R\ (\text{wt.\%}) = \frac{m_{\text{residue}}}{m_{\text{plastic feed}}} \times 100\%$	
(4)	$Y_{\text{gas}}\ (\text{wt.\%}) = 100\% - (Y_{\text{oil}} + R)$	
(5)	$\rho\ (\text{g/cm}^3) = \frac{m_{\text{oil}}}{V_{\text{oil}}}$	
(6)	$E_{\text{oil}}\ (\%) = Y_{\text{oil}} \times \frac{HHV_{\text{oil}}}{HHV_{\text{plastic feed}}}$	
(7)	$E_{\text{oil}}\ (\text{J}) = m_{\text{oil}} \times HHV_{\text{oil}}$	
(8)	$E_{\text{consumed}}\ (\text{J}) = P \times t$	
(9)	$\eta\ (\%) = \frac{E_{\text{oil}}}{E_{\text{consumed}}} \times 100$	

The reaction time of pyrolysis was recorded when no further formation of oil drops could be seen in the cold trap glass tube. The oil collected in the impinger bottle was later transferred to a conical flask to measure the oil volume and weight was recorded using the weighing balance. The residue was left as solid char and sometimes as a thick waxy liquid (solid at room temperature) at the bottom of the reactor. The residue was removed from the reactor after dismantling the reaction assembly. The wax could be easily separated as a hot liquid and the char deposits were removed later for measurement.

3.7 Identification of Chemical Composition of Pyrolytic Oils

The pyrolytic oil samples (Fig. 3.6) were analyzed using Agilent G7035A GC- MS system. Agilent 122-5532 MS column of 30 m length, 0.25 mm internal diameter and film thickness of 0.25 µm was used for separation of oil fractions. The stationary phase composition of the column was (5% diphenyl) dimethyl poly-siloxane. Helium was used as a carrier gas with a flowrate of 1.2 mL/ min. The syringe size was 10 µL while the oil sample injected quantity was 0.2 µL. The temperature of hot GC injector tube was fixed at 325°C while the separation column was initially held at 60°C for 1.26 min and then heated up to 325°C at the rate of 7 °C/min.

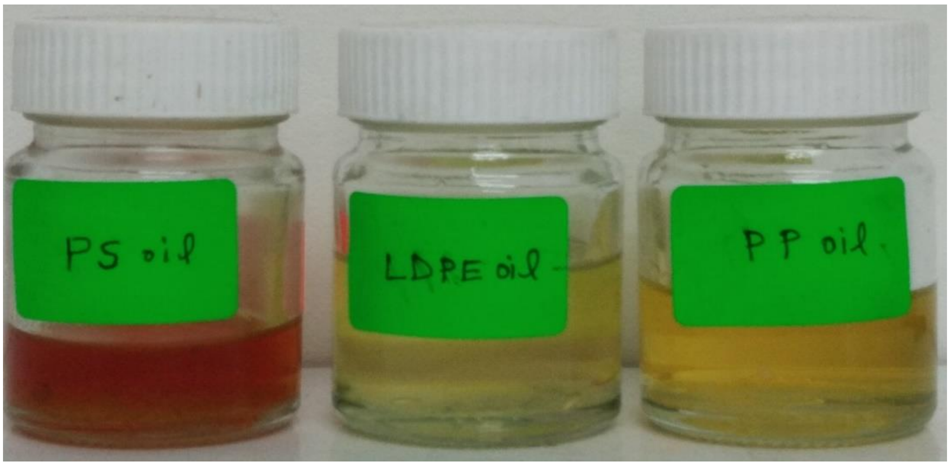


Figure 3.6: Pyrolytic oil samples from different plastics

The identification of the most abundant possible compounds present in the oils was established using total ion chromatograms matched to spectral library NIST-14. The most abundant compounds with distinct peaks were tabulated based on the peak number, retention time, peak area/relative concentration, compound name and chemical formula.

3.8 Effect of Wire Gauge on Oil Yield

To investigate the effect of wire gauge size on the liquid oil yield, iron wire gauge sizes of 1 mm, 1.5 mm, and 2.0 mm, respectively, were used for conducting the experiments with a sample size of 20 g of PS. The microwave power was varied from 1500 to 2500 W to measure the oil yield, temperature, and reaction time for each coil. The oil recovered during each run was collected and the oil yield was determined using Equation (2) (refer Table 3.4) . The oil yield, temperature and reaction time of pyrolysis was plotted as a function of microwave power for coils of different gauges to reveal the effect of gauge.

3.9 Effect of Type of Metal on Process Performance

The iron and copper coils of gauge 1.5 mm, height = 5 cm, and ID = 5 cm, were used to pyrolyze 20 g of PS. The comparison of performance of the two coils was evaluated based on the observations of oil yield, temperature, and reaction time at different microwave powers between 1500 and 2500 W. The first set of experiments were carried out on the iron coil to measure oil yield, temperature, and reaction time at different microwave powers. The same experiments were repeated with the copper coil. The plots of oil yield, temperature, and reaction time as function of the microwave power were used to compare the performance of the two coils.

3.10 Evaluation of Energy Efficiency of the Process

The efficiency of the process was determined using Equations (7) to (9) (refer Table 3.4). The maximum oil yield and corresponding value of the microwave power and reaction time for each plastic was taken as the optimal values. The energy output was the energy recovered in the form of oil while energy input was the electrical energy consumed in the process. The electrical energy consumed is the product of microwave power applied and the time of reaction. The ratio of the energy in oil to input electrical energy determined the efficiency of the process. The energy efficiencies of the plastics (PS, PP, LDPE) were compared to reveal the energy potential of each plastic for the microwave-metal interaction pyrolysis process.

3.11 Process Optimization for Maximum Oil Recovery

A central composite design (CCD) model was used to optimize the performance of microwave-metal interaction pyrolysis of individual plastics comprising PS, PP and LDPE, respectively. The Minitab Software package was used during the optimization study. The CCD model was chosen as it is best suited when unknown optimum conditions are to be determined and possible presence of quadratic effects. The loading for each plastic was taken to be 20 g. The independent variables selected were microwave power (P, W) and reaction time (t, min). The dependent variable used for response analysis was taken to be liquid oil yield (Y, wt.%). A total of 13 experiments were carried out for each plastic. The parameters of design of experiment (DOE) are presented in Table 3.5.

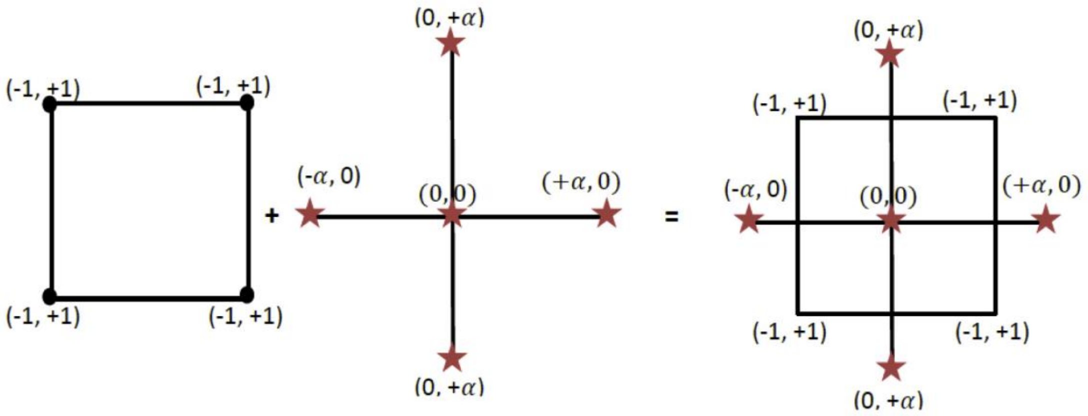
The design points of the model are presented in Fig. 3.7 while design boundaries for PS, PP and LDPE are shown in Tables 3.6 and 3.7, respectively. The corner points gives an estimate of the linear and interaction effects, centre points measure the effect of curvature and axial points measures the quadratic effects. The levels of microwave power and reaction time for each plastic were selected based on the performance of the experimental set-up. The microwave power level (P) was varied between 1500- 2300 W for each plastic selected as the low and high levels of the cube points. The level range of reaction time (t) for individual plastics was taken as: 15-25 min for PS, 20- 30 min for both PP and LDPE, respectively. Based on the statistical model used, the response was predicted using the following regression equation:

$$Y = A_0 + A_1 P + A_2 t + A_{11} P^2 + A_{12} P t + A_{22} t^2 \tag{3.10}$$

where: A_0 is the offset term; A_1 and A_2 represent the linear effects, A_{12} is the interaction term; and A_{11}, A_{22} are the squared effects, which are all regression coefficients. It must be noted here that

Table 3.2: Central composite design parameters.

Factors	2	
Base blocks	1	
Centre points in cube (replication)	5	
Axial points	4	
Centre points in axial	0	
α-value	1.41421	
Total runs performed for each plastic	13	
Display units	Uncoded	
Factor Levels	Low	High
Microwave power (P, W)	1500	2300
Reaction time (t, min) for PS	15	25
Reaction time (t, min) for both PP and LDPE	20	30



(a) Corner points (b) Middle and extended axial points (c) CCD design

Figure 3.7: CCD model design

Table 3.3: Boundaries of the CCD design for PS

Factor	Code	Unit	Levels				
			-α	-1	0	+1	+α
Microwave power	P	W	1334	1500	1900	2300	2466
Reaction time	t	min	13	15	20	25	27

Table 3.4: Boundaries of the CCD design for both PP and LDPE

Factor	Code	Unit	Levels				
			-α	-1	0	+1	+α
Microwave power	P	W	1334	1500	1900	2300	2466
Reaction time	t	min	18	20	25	30	32

CHAPTER 4

RESULTS AND DISCUSSION

This chapter opens with the preliminary characterization of model materials in Section 4.1. Section 4.2 presents the study on effect of reaction time and microwave power on the performance of iron coil. The effect of type of metal on coil temperature is discussed in Section 4.3. Sections 4.4-4.6 discuss the effect of microwave power on oil yield, reaction time and oil density for virgin plastics comprising PS, PP and LDPE, respectively. Section 4.7 presents the identification of chemical composition of liquid oil fraction for each plastic. The effect of microwave power on nature of liquid product distribution is discussed later in Section 4.8. The effect of microwave power on oil yield and reaction time in the case of plastic blends is demonstrated in Sections 4.9 and 4.10. Section 4.11 presents the chemical composition analysis for pyrolytic oils recovered from plastic blends. Sections 4.12 to 4.15 are devoted to investigation of effects of process parameters for waste PS (PSW) including comparison with virgin PS. The effect of coil gauge size and type of metal on process performance in case of individual plastics is discussed in Sections 4.16 and 4.17, respectively. Section 4.18 discusses the energy efficiency of the process for each plastic. The chapter ends with detailed study on process optimization for maximum oil recovery using response surface methodology.

4.1 Preliminary Characterization of Materials

The preliminary characterization was performed to study the properties of model materials that helped to understand the nature of pyrolysis for different plastics. The characterization involved the measurement of calorific value, elemental analysis, proximate and TGA/DTG analysis.

4.1.1 Determination of Calorific Value

The calorific values of PS, PP and LDPE, respectively, were found to be appreciably high between 40 and 47 MJ/kg and also close to the reported values [131] (Table 4.1). The heating value of LDPE and PP were found to be comparably higher at around 46 MJ/kg as compared to PS with a value of 40.9 MJ/kg. The high calorific values of these plastics make them a suitable choice to be used as a source of fuel.

Table 4.1: Comparison of the estimated calorific values of plastic samples with the reported values

Sample	Calorific Value (MJ/kg)	Calorific Value [131] (MJ/kg)	Difference (%)
LDPE	46.4	46.5	0.21
PP	46.7	45.2	3.31
PS	40.9	38.9	5.06

4.1.2 Elemental Analysis

The elemental analysis was used to determine the hydrocarbon content in PS, PP, LDPE and PSW and also possible presence of additives found in plastics. The percentages of carbon, hydrogen, nitrogen, and sulfur determined from the analysis are shown in Table 4.2. The carbon and hydrogen content for each plastic was between 84-87 wt.% and 4-11 wt.%, respectively, while nitrogen and sulfur were present in minor concentrations.

Table 4.2: Elemental analysis of the plastic samples

Sample	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)
LDPE	86.26	10.35	0.22	0.08
PP	84.51	9.71	0.24	0.12
PS	85.60	6.18	4.21	0.06
PSW	86.04	4.96	2.04	0.01

4.1.3 Proximate and Thermogravimetric (TGA/DTG) Analysis

The Table 4.3 shows the proximate analysis of the sample materials. The volatile content in PS, PP and LDPE, respectively, was found to be appreciably high in the range of 95-100 %. The values determined were found to be quite close to the reported values [131] with a difference observed in the range of 0-4%. The high volatile content of plastic indicated its promising potential to be used as a fuel.

Table 4.3: Comparison of volatile content of plastic samples observed in the proximate analysis with the reported values

Sample	Volatiles (wt%)	Volatile (wt%) [131]	Difference (%)
LDPE	96.80	99.98	3.18
PP	96.79	99.98	3.19
PS	99.16	99.57	0.41

The TGA curves for different plastic samples are shown in Figures 4.1 and 4.2 while the DTG peaks are highlighted in Figures 4.3 and 4.4, respectively. The thermal degradation temperature range of each plastic from TGA curve was found as: PS = (378- 439)°C, PP = (407-483)°C, LDPE = (420- 499)°C and PSW = (353- 438)°C. The DTG curves were used to determine the peak temperature showing the maximum mass loss rate for each plastic found as: PS = 422°C, PP = 469°C, LDPE = 477°C and PSW = 425°C. The above values play a critical role in understanding the thermal degradation behavior of different plastics affecting the oil yield, temperature, and reaction time of pyrolysis.

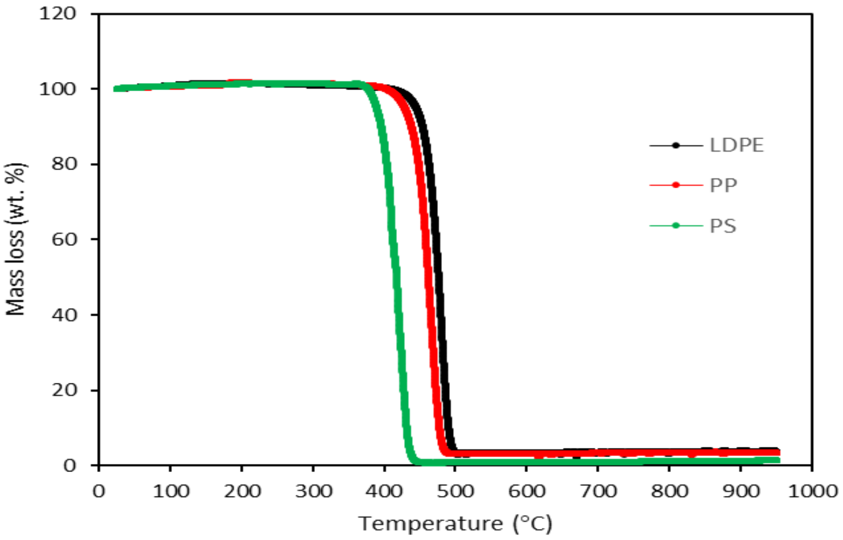


Figure 4.1: TGA curves of different plastic samples

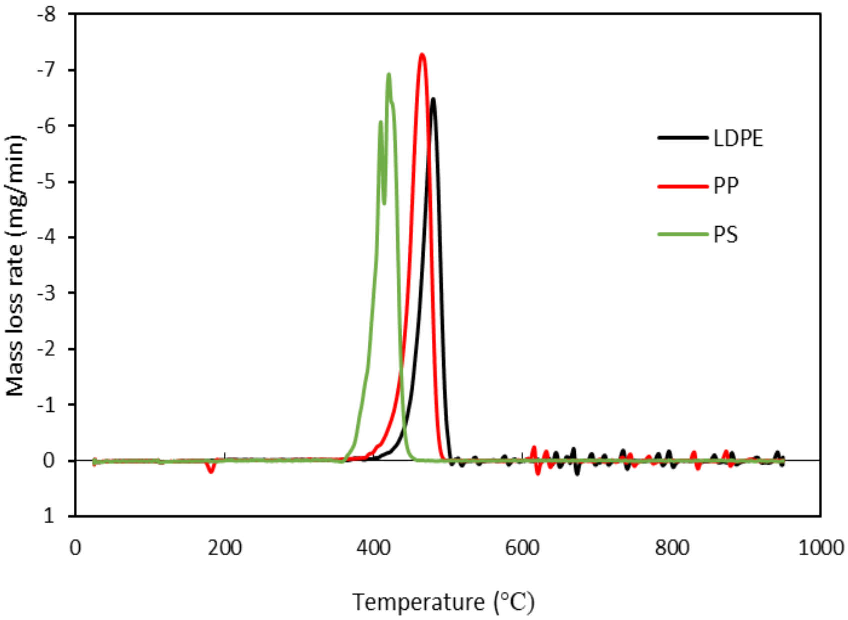


Figure 4.2: DTG curves of different plastic samples

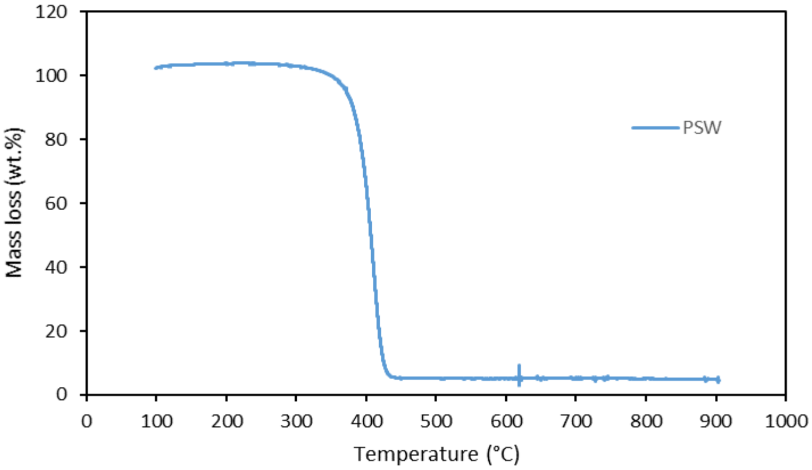


Figure 4.3: TGA curve of PSW

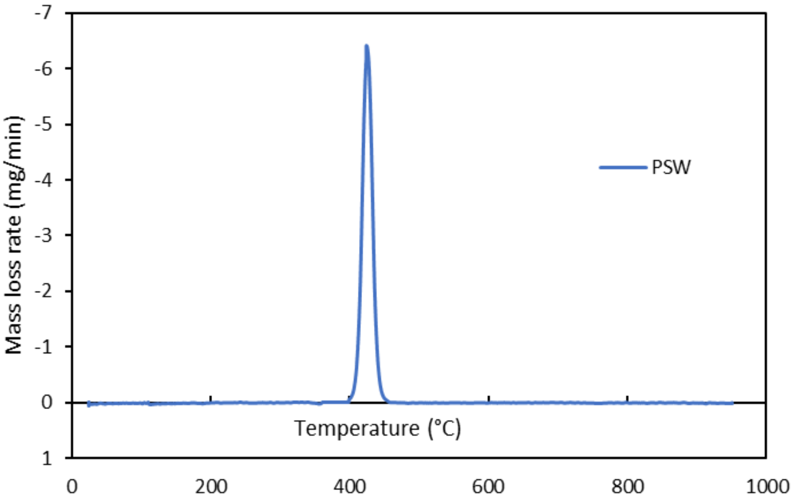


Figure 4.4: DTG curve of PSW

4.2 Effect of Reaction Time and Microwave Power on Coil Temperature

Figures 4.5 to 4.7 illustrate, variation of coil temperature with the reaction time and microwave power. Microwave power was increased from 500 to 2500 W to study the temperature distribution during pyrolysis of PS, PP and LDPE, respectively. The time limit was set to 30 minutes which was sufficient to observe the overall trend of the curve. During this time, the temperature stabilized with minor fluctuations apparent from the cluster of parallel lines. It was evident from the plots that heating rate was maximum in the first 5 minutes of microwave exposure and later stabilized with small fluctuations until the end of reaction period. This trend was observed in all the plastic samples.

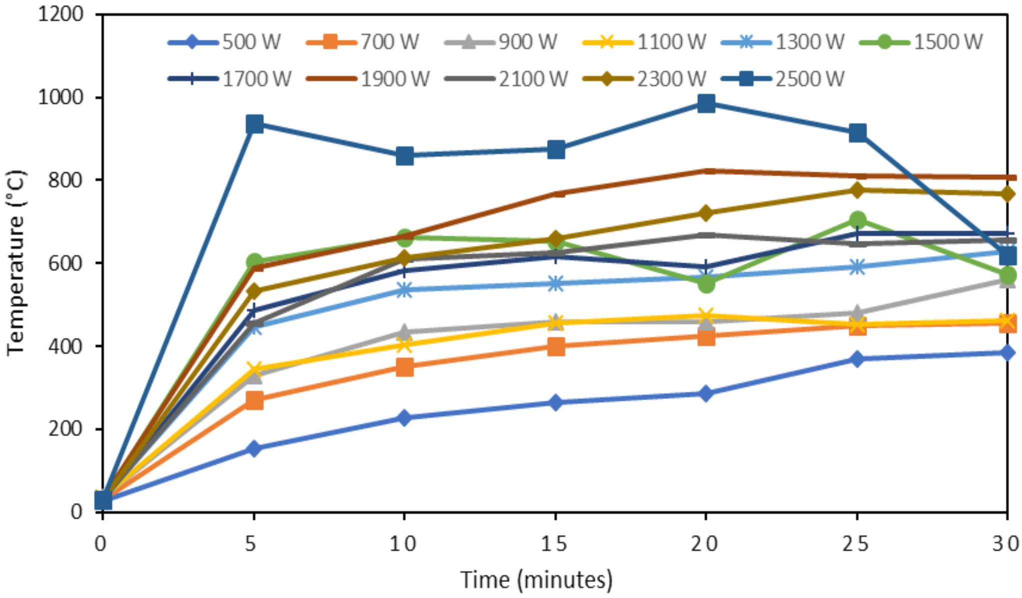


Figure 4.5: Variation of coil temperature with reaction time and microwave power during pyrolysis of PS

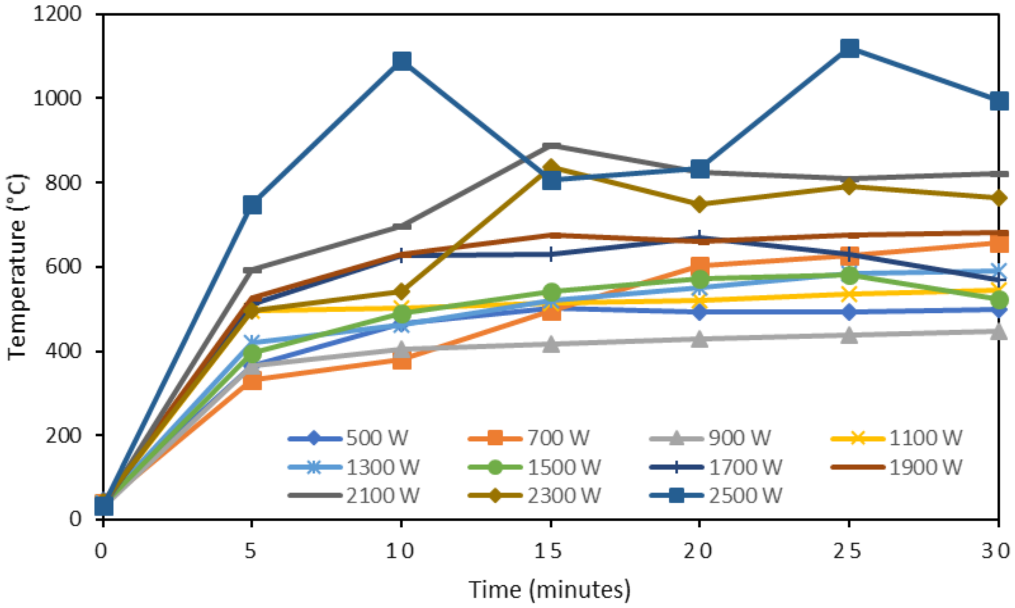


Figure 4.6: Variation of coil temperature with reaction time and microwave power during pyrolysis of PP

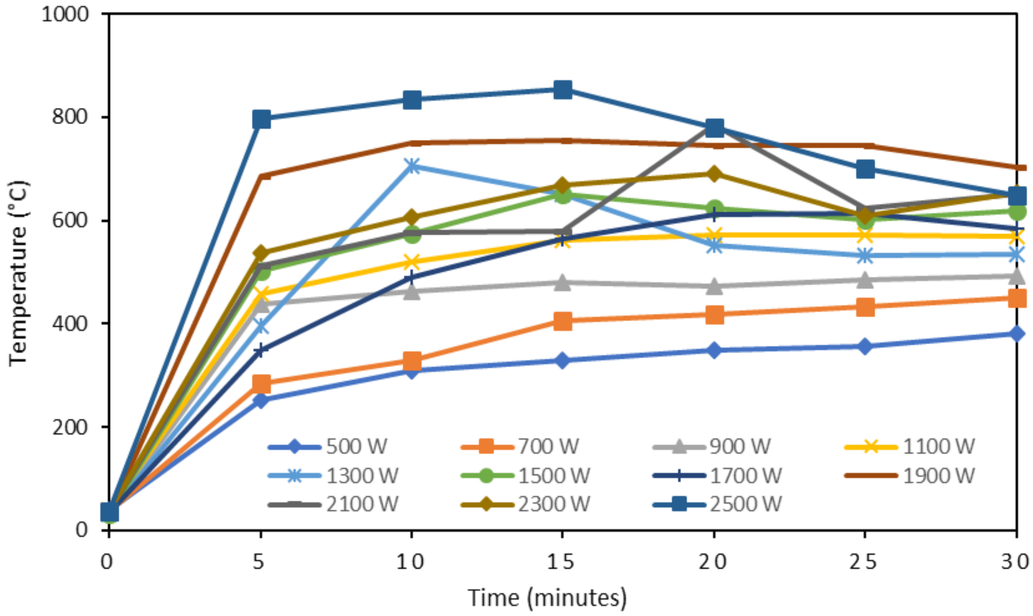


Figure 4.7: Variation of coil temperature with reaction time and microwave power during pyrolysis of LDPE

During the pyrolysis of PS, an increase in the value of microwave power, caused the slope or heating rate to shoot up rapidly. Similar behavior was observed in case of PP and LDPE. Results of variation in coil temperature at minimum and maximum microwave powers for each plastic are summarized in Table 4.4.

Table 4.4: Variation in coil temperature at minimum and maximum microwave powers for each plastic

Plastic sample	Rise in coil temperature (°C) after 5 minutes of microwave exposure	
	500 W (Min.)	2500 W (Max.)
PS	154	937
PP	365	748
LDPE	253	796

The significant variation in coil temperature at same powers of microwave heating in different plastic samples can be attributed to interaction of microwaves with metallic probe (Type K thermocouple) in addition to microwave interaction with iron coil. This is caused due to trips and sparks commonly encountered in microwave-metal interactions [42].

Repeated study on different plastics was carried out under the same conditions of microwave power and reaction time to reveal the distribution of fluctuations in the heating process. The production of oil during the process confirmed that temperature attained by coil was sufficient to breakdown the plastic. The process of thermal pyrolysis was carried out in the range of 300 to 700°C.

Variation in average coil temperature with microwave power is presented in Fig. 4.8. Average temperature rise was calculated at different powers in the range of 500 to 2500 W for PS, PP and LDPE. It was observed that average temperature was directly proportional to microwave power in case of each plastic. Slopes of average temperature versus microwave power were estimated as: PS = 0.24 °C/W, PP = 0.20 °C/W, LDPE = 0.18 °C /W, which represented similar values with insignificant deviation showing consistency of heating process for each plastic, achieved by the current set-up. Further, it was inferred that nature of plastic pyrolyzed had insignificant influence on coil temperature. This is also obvious to the fact that plastic was not in direct contact with the coil but was heated inside the GI pipe used in the current set-up.

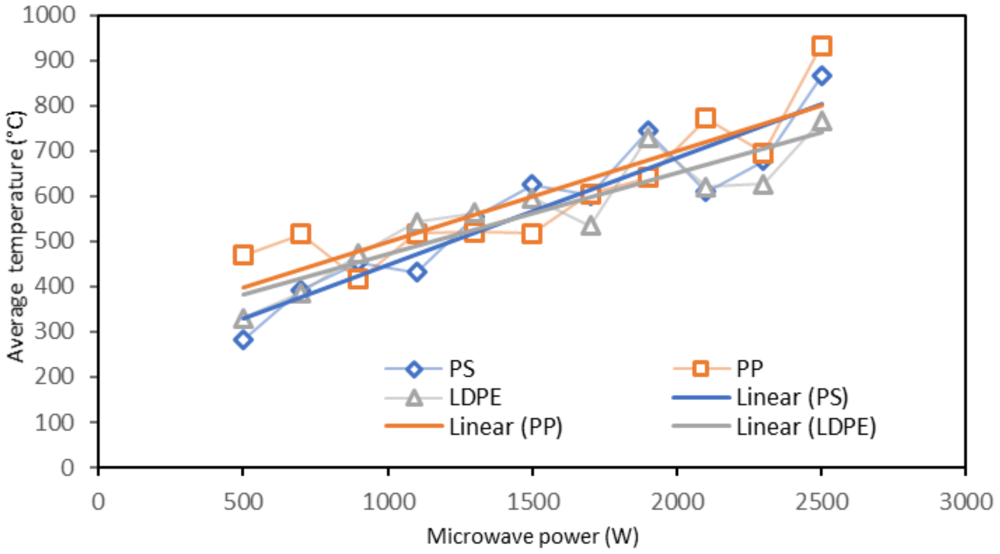
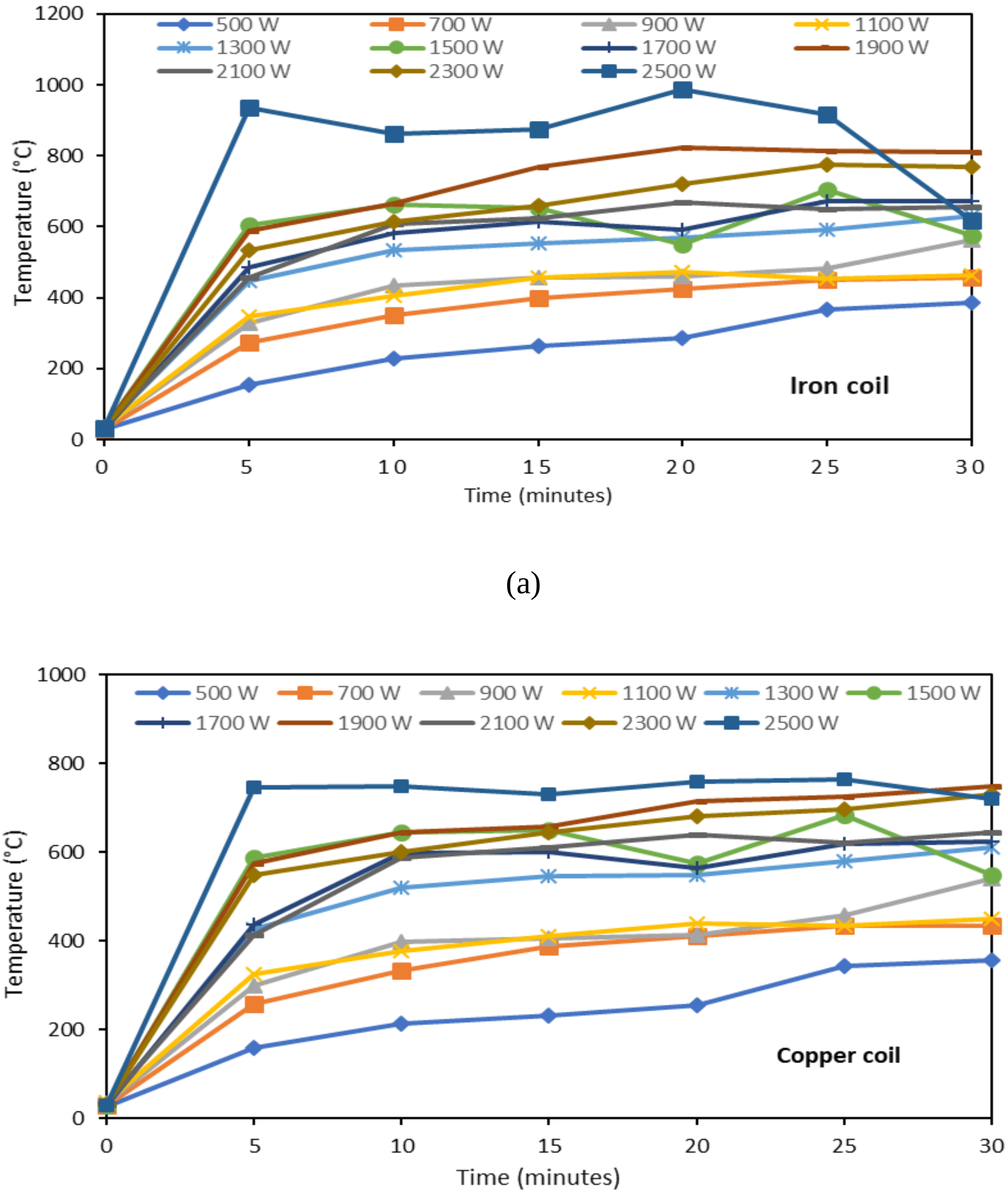


Figure 4.8: Variation in average temperature of coil with different microwave powers and observed trends

4.3 Effect of Type of Metal on Coil Temperature

The effect of type of metal on the coil temperature was investigated by comparing the temperature distributions of iron coil and copper coil of the same size. The microwave-metal interaction pyrolysis of PS was carried out using the two coils for an exposure period of 30 minutes. Fig. 4.9 shows the temperature distributions of the iron and copper coils at different microwave powers.



(a)

(b)

Figure 4.9: Comparison between temperature profiles of (a) iron coil and (b) copper coil during microwave-metal interaction pyrolysis of PS

The heating rate was found to be maximum in the initial 5 minutes of microwave exposure for both the coils. After 5 minutes, no major rise in temperature was observed except with small fluctuations. Fig. 4.10 highlights the variation of average temperature of the iron and copper coils at different microwave powers. The effect of metal on coil temperature was further analyzed by calculating and comparing the average temperature of the iron and copper coils at different microwave powers. Here, it was observed that temperatures achieved by the iron coil were consistently higher than the copper coil. The mechanism behind this variation depends upon the conductivity of the metal used for heat generation. The iron and copper coils offer equal area for microwave exposure but differ in its conductivities. It must be noted here, that, metal surface with higher conductivity weakens the skin effect (heat generated through microwave penetration) as compared to metal with lower electrical conductivity where the skin effect is stronger than the former case, and therefore, larger quantity of heat is produced [65]. Consequently, iron coil having lower conductivity than copper coil was able to reach higher temperatures than the copper coil.

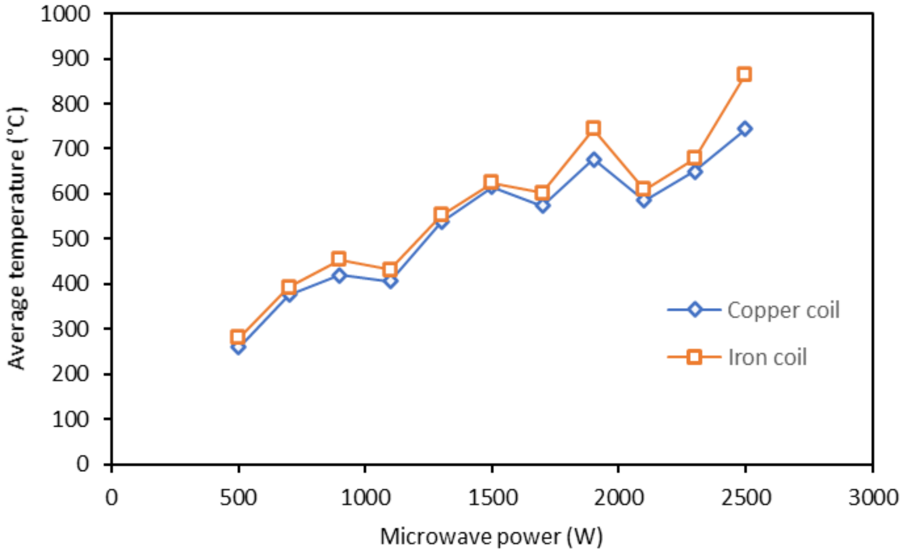


Figure 4.10**:** Variation of average coil temperature with microwave power for iron and copper coils

4.4 Effect of Microwave Power on Pyrolytic Oil Yield of PS, PP and LDPE

The effect of microwave power was investigated by analyzing the oil yield and reaction time during microwave-metal interaction pyrolysis of individual plastics comprising PS, PP and LDPE, respectively. The variation in oil yield and pyrolysis temperature with microwave power for individual plastics is presented in Fig. 4.11 and Fig. 4.12, respectively.

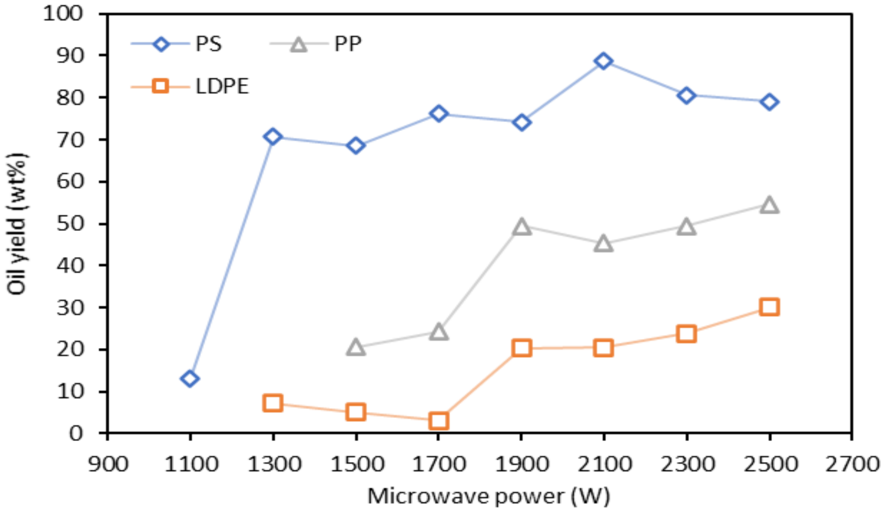


Figure 4.11: Variation of oil yield with microwave power for PS, PP and LDPE

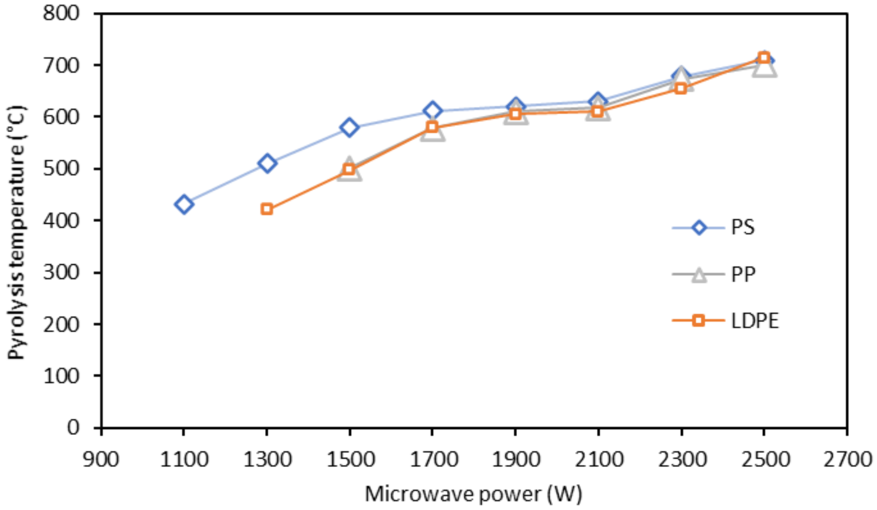


Figure 4.12: Variation of pyrolysis temperature with microwave power for PS, PP and LDPE

The trends of oil recovery showed that PS released maximum oil followed by PP and LDPE over the same range of microwave power. The pyrolysis temperatures at different microwave powers for each plastic were observed in the range of 400-720°C. It was further observed that the pyrolysis temperature increased gradually with the microwave power for each plastic. To compare the oil yield across the entire range of microwave power for each plastic, the average oil yield was calculated (Table 4.5.) The order of average oil yield for individual plastics between 1100 and 2500 W was found to be maximum for PS (68.92 wt.%) followed by PP (40.68 wt.%) and LDPE (15.74 wt.%), respectively. It must be mentioned here that no oil yield was observed below 1100 W for any plastic sample due to lack of essential heating required for pyrolysis. The conversion of the plastic into liquid oil occurred through the microwave- metal interaction mechanism which is a fast pyrolysis technique [46], [48]. The iron coil when exposed to microwaves undergo repeated reflections generating heat (skin effect or heat dissipation due to multiple penetrations of the microwaves). In addition to the skin effect, the excitation of loosely bound electrons in the metal coil (eddy currents) converts the coil into a microwave absorbent [47] which further accelerates the heating process causing rapid heating of the coil. The hot coil provides essential heating to the GI pipe for pyrolysis to occur. The iron coil can withstand high temperatures due to its high melting point (>1000°C). The range of coil temperatures observed between 500 and 2500 W in the current study was 250-800°C.

Table 4.5: Average oil yield during pyrolysis of plastic samples at different microwave powers

Sample	PS	PP	LDPE
Average oil yield (wt.%)	68.92	40.68	15.74

The first oil recovery from PS, PP and LDPE, was observed at 1100 W (432°C), 1500 W (501°C) and 1300 W (421°C), respectively. The difference in thermal degradation temperatures of each plastic was responsible for the variation in input power values. As the microwave power was increased, the oil yield also improved consistently. However, there were small fluctuations due to non-uniform heating commonly encountered in microwave heating applications. Under optimum conditions between 2100 and 2500 W, maximum oil recovery for PS, PP and LDPE, was observed to be 88.7 wt.% (2100 W, 630°C), 54.65 wt.% (2500 W, 701°C) and 30.15 wt.% (2500 W, 715°C), respectively. The oil yield at 88.7 wt.% recovered from PS was higher than 80 wt.% oil [46] and nearly equal to 88 wt.% oil [49] in the previous studies conducted on microwave-metal interaction pyrolysis of waste PS with the same feedstock size (20 g). The mass balance of pyrolysis products and conversion efficiency for different plastic samples is highlighted in Table 4.6.

Table 4.6: Mass balance and conversion (wt.%) of pyrolytic oils recovered from different plastics under optimum conditions

Sample	Microwave power (W)	Oil (wt.%)	Gas (wt.%)	Residuals		Conversion (wt.%)
				Wax (wt.%)	Char (wt.%)	
PS	2100	88.70	6.70	-	4.60	95.40
PP	2500	54.65	40.45	-	4.90	95.10
LDPE	2500	30.15	24.15	44.18	1.52	54.30

The conversion of PS and PP into oil and gas products was observed to be high in the range of 95 to 96 wt.% with char residue between 4 and 5 wt.% . The gas fraction was much higher at 40.45 wt.% in the case of PP as compared to PS with only 6 wt.%. In contrast to PS and PP, the pyrolysis of LDPE produced liquid wax residue (solid at room temperature) as a major fraction at 44.18 wt.% followed by oil (30.15 wt.%), gas (24.15 wt.%) and char residue (1.52 wt.%), respectively, and a relatively low conversion of 54.30 wt.%. The liquid wax residue from LDPE pyrolysis was a heavier fraction collected at the bottom of the GI pipe reactor while the light oil was recovered through the cold trap. The wax produced from LDPE was expected to be a paraffinic fraction; based on the study [132], the thermal cracking of polyethylene and polypropylene releases paraffins and olefins, and the ratio of paraffins to olefins decreases with the temperature and reaction time. The thermal breakdown of the polyethylene released wax into desirable yields of oil and gas may require higher temperatures in the range of 700-900°C as demonstrated in previous studies [21], [133], [134]. Further, the use of a suitable catalyst can lower down the degradation temperature as well as the required time with enhanced conversion rates giving a narrower range of products [135], [136]. The process of microwave-metal interaction pyrolysis in the current study was achieved between 400 and 700°C. A comparison between pyrolytic oils and conventional fuel oils has been highlighted in Table 4.7. It was found that density and calorific value of pyrolytic oils from PS, PP and LDPE, was quite close to that of traditional fuel oils.

Table 4.7: Comparison of pyrolytic oil samples at optimal powers with conventional fuel oils

Pyrolytic oils				Conventional fuel oils		
Sample	PS	PP	LDPE	Gasoline [137]	Kerosene [138]	Diesel [138]
Density (g/cm^3)	0.855	0.707	0.780	0.780	0.780	0.848
HHV (MJ/kg)	38.6	46.7	45.4	42.5	43.5	42.9

4.5 Effect of Microwave Power on Pyrolysis Reaction Time of PS, PP and LDPE

Figure 4.13 highlights the variation of reaction time with microwave power during the pyrolysis of PS, PP and LDPE. The curves showed an overall decline of reaction time of pyrolysis with the increasing microwave power for each plastic. At optimum microwave power range of 2100-2500 W with maximum oil recovery, the reaction times for PS, PP and LDPE, were observed to be 19, 23 and 26 minutes, respectively.

In the initial phase of the reaction, the plastic melted accompanied by the release of gases. As the reaction proceeded, the collection of first condensates into liquid oil began after a period of 9 minutes in the case of PS, 11 minutes for PP and 13 minutes for LDPE. The release of volatiles condensing into oil continued until the end of reaction, beyond which there was no further formation of oil. The collection of condensates usually took around 10-15 minutes from the appearance of first oil drop until the end of reaction. At low powers, the reaction times in case of each plastic were observed to be high up to 30 minutes for PS at 1100 W, 28 minutes for PP at 1500 W and 29 minutes for LDPE at 1300 W, respectively. The slow release of volatiles caused by a low power input increased the reaction times for each plastic observed with a marginal difference. It was observed that increase in microwave power resulted in a consistent decline of the reaction times. This was attributed to higher heating rates achieved at higher microwave powers during microwave-metal interaction pyrolysis which forced the volatiles to leave the reactor at a faster rate leading to a shorter residence time.

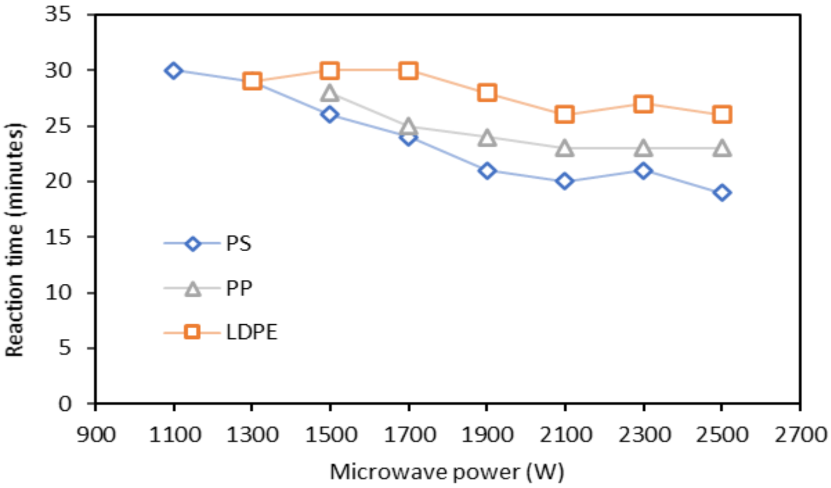


Figure 4.13: Variation of reaction time with microwave power for PS, PP and LDPE

Fig. 4.14 highlights the variation of coil temperature with respect to microwave power. The temperature of the hot coil was monitored for an exposure period of 30 minutes during pyrolysis in a separate experiment. It was inferred from the temperature profiles at different microwave powers that the heating rates were maximum in the first 5 minutes of exposure ranging between 50-130 °C/min. Similar heating rates between 50- 150 °C/min in the initial 5 minutes of microwave exposure were also observed in a study [42] on microwave assisted pyrolysis. Beyond 5 minutes, the temperatures stabilized with small fluctuations. Thus, it was confirmed that increase in microwave power produced a stronger heating effect causing the iron coil to reach high temperatures of up to 800°C within a short time interval. The GI pipe being in close contact with the hot coil was heated rapidly to give an overall improved yield with reduced reaction time.

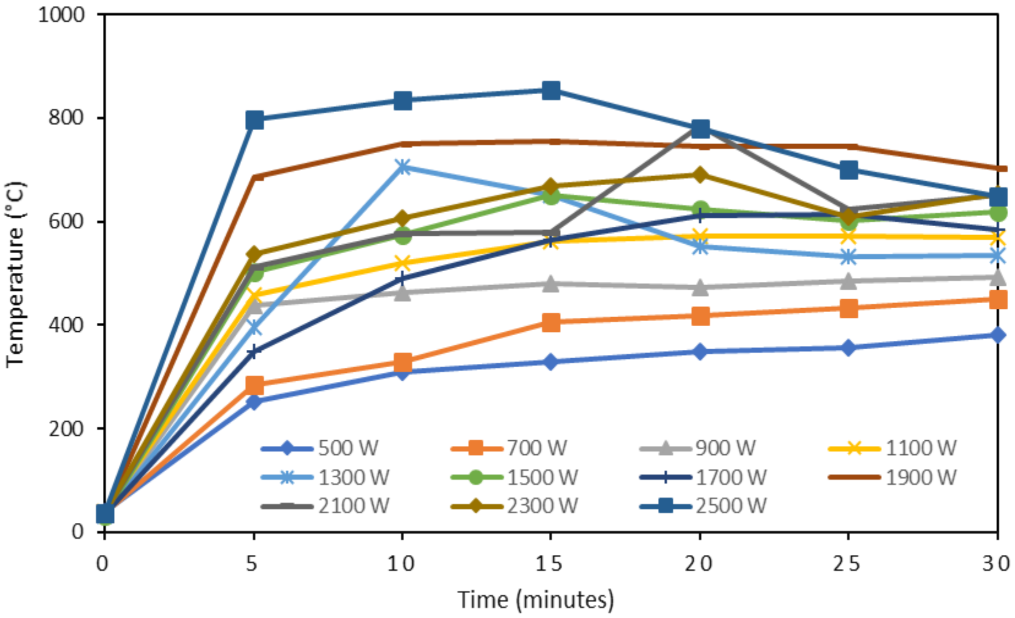


Figure 4.14: Variation of coil temperature with time at different microwave powers

4.6 Effect of Microwave Power on Pyrolytic Oil Density of PS, PP and LDPE

The effect of increase in microwave power on oil densities of different plastics is shown in Fig. 4.15. It can be clearly seen that the densities remain consistently closer with insignificant deviations except in the case of LDPE at some points. The deviation in density at 1500 and 1700 W in case of LDPE was observed due to release of extremely light oil with a very low yield between 0-5 wt.% (refer Fig. 4.11). From the plots, it can be inferred that PS gave heavier oils whereas PP and LDPE generated comparably lighter oils. Further, a comparison of densities and calorific values of pyrolytic oils with conventional fuel oils was also shown earlier (refer Table 4.7). It was inferred that the density of pyrolytic oil released from PS was close to diesel whereas the densities of oils obtained from PP and LDPE were close to gasoline and kerosene. Similarity observed in the above properties of pyrolytic oils recovered from plastics and commercial fuels, indicate the potential application of plastic derived pyrolytic oils to be used as a transportation fuel directly or after conversion in a petrochemical refinery.

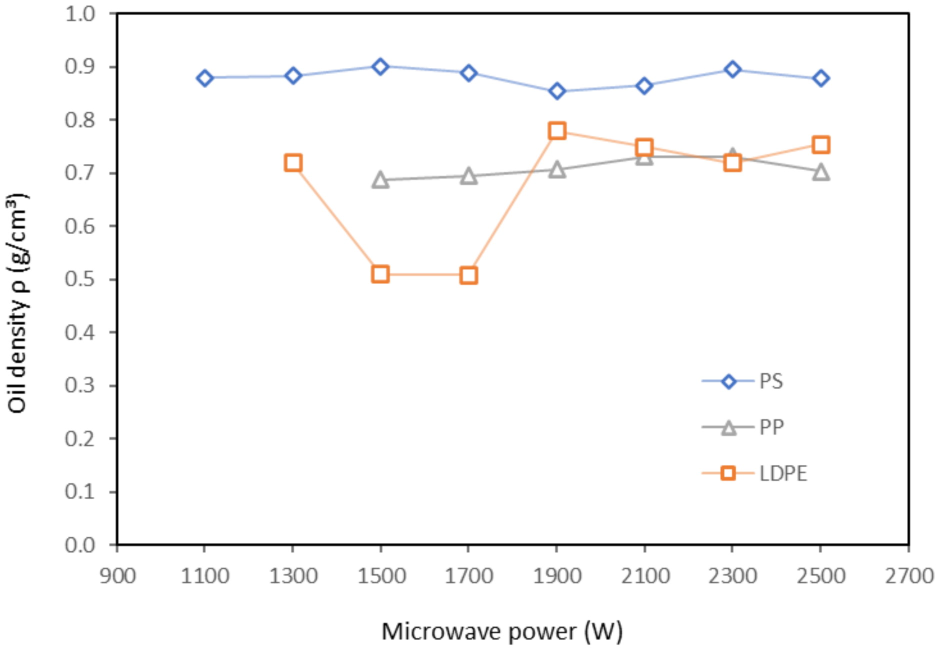


Figure 4.15: Variation of oil density with microwave power for PS, PP and LDPE

4.7 Chemical Composition Analysis of Pyrolytic Oils recovered from PS, PP and LDPE

The results of GCMS analysis of pyrolytic oils recovered from PS, PP and LDPE are shown in Tables 4.8 to 4.10, respectively. The composition of the oil samples was analyzed at a power of 2100 W considered suitable towards efficient oil recovery for each plastic. Fig. 4.16 represents the total ion chromatograms used for identification through the spectral library NIST 14. The most abundant compounds were analyzed based on the peak area (relative concentration %) and retention time. In the case of PS oil, the most abundant compound was C8 (styrene) monomer which dominated the aromatic fraction of the oil. Other species present were triazoles and benzonitrile but in minor concentrations. The presence of nitrogen in PS resin in minor concentration was observed during the elemental analysis. The additives used in plastics contained nitrogen as PS structure has no bound nitrogen. As a result, presence of compounds like triazoles and benzonitrile was detected in the pyrolytic oil produced by PS. The presence of such compounds was also reported in a study [139] on characterization of semi- volatile organic compounds released during the heating of plastics. The presence of aromatic hydrocarbons consisting of styrene monomer as the representative compound was also reported in the previous study [46], where waste PS was converted to useful hydrocarbons through microwave- metal interaction pyrolysis. Contrarily, in the case of PP and LDPE oils, aliphatic class of hydrocarbons were observed as the most abundant species. The major fraction of hydrocarbons present in PP oil were cycloalkanes and alkenes whereas LDPE oil was mainly composed of alkenes and alkanes.

Table 4.8: GCMS analysis of PS oil

Peak No.	Retention time (min)	Relative conc. (%)	Name of compound	Formula
4	9.643	65.99	Styrene,	C_8H_8
15	27.092	7.68	1-benzyl-1,2,3-triazole	$C_9H_9N_3$
34	36.763	13.92	Benzonitrile, m-phenethyl-	$C_{15}H_{13}N$

Table 4.9: GCMS analysis of PP oil

Peak No.	Retention time (min)	Relative conc. (%)	Name of compound	Formula
3	2.099	1.75	1-Hexene	C_6H_{12}
35	12.56	5.33	1-Decene	$C_{10}H_{20}$
44	15.097	6.09	1-Undecene	$C_{11}H_{22}$
46	15.301	3.56	Undecane	$C_{11}H_{24}$
53	17.369	5.19	1-Dodecene	$C_{12}H_{24}$
61	19.628	3.27	Tridecane	$C_{13}H_{28}$

Table 4.10: GCMS analysis of LDPE oil

Peak No.	Retention time (min)	Relative conc. (%)	Name of compound	Formula
6	7.949	11.27	2,4-Dimethyl-1-Heptene	C_9H_{18}
30	14.719	5.77	Cyclopentane, propyl-	C_8H_{16}
55	19.644	11.96	2-Decene, 7-methyl-	$C_{11}H_{22}$
57	19.976	8.30	6-Tridecene, 7-methyl-	$C_{14}H_{28}$

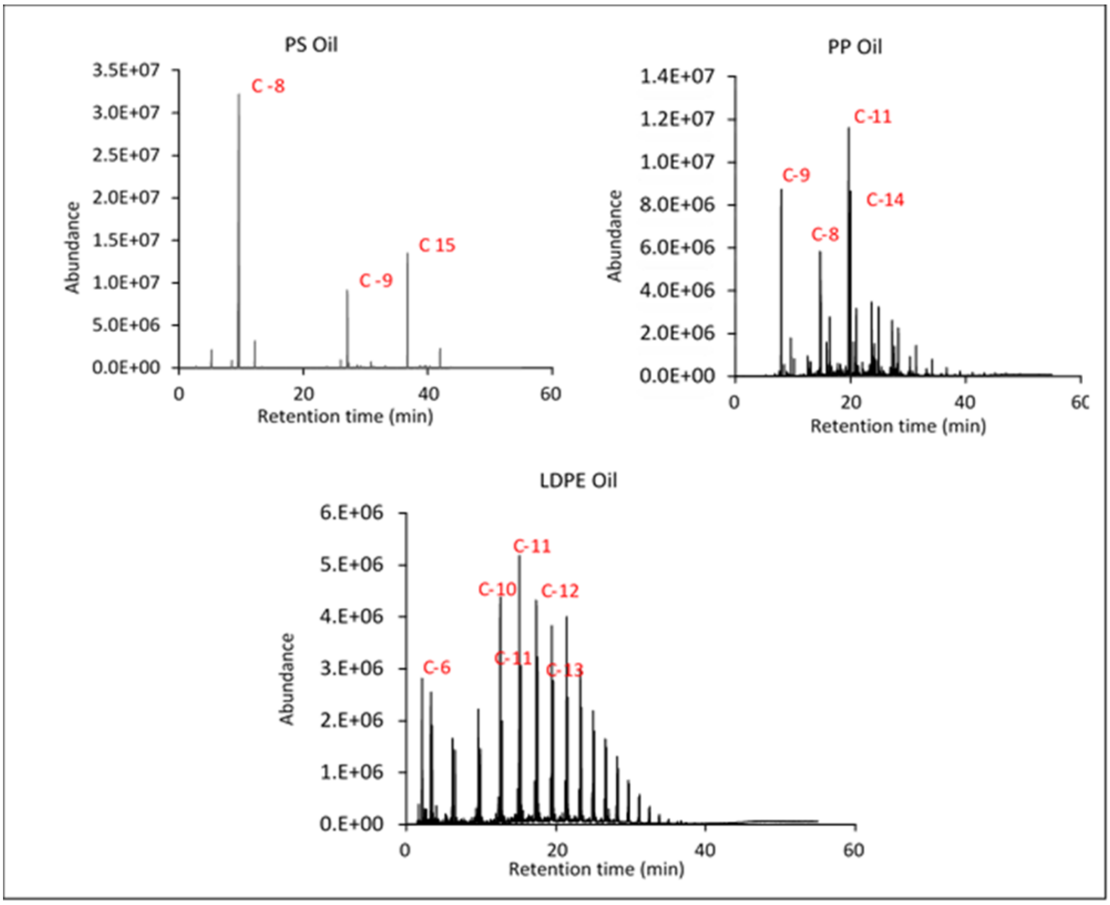


Figure 4.16: Comparison between total ion chromatograms of PS, PP and LDPE oils at 2100 W

Figure 4.17 highlights the total ion chromatograms for petroleum refined fuels comprising gasoline, kerosene and diesel [140]. A comparison between the total ion chromatograms of Figures 4.16 and 4.17, was used to identify the similarity between the pyrolytic oils and conventional fuels. From the distribution of chromatogram peaks of each pyrolytic oil and conventional fuels, it was evident that the pyrolytic oils recovered from each plastic showed a close resemblance with kerosene oil in contrast to gasoline and diesel. Most of the hydrocarbons present in the pyrolytic oils were in the kerosene range of C8-C16. Kerosene range oils are considered to be an intermediate between lighter and heavier fractions of gasoline and diesel range hydrocarbons. Based on the study [8], the pyrolytic oils are suitable to be used as diesel fuel and petroleum diesel blends, due to the absence of oxygenated species and high heating value of up to 46.16 MJ/kg. As a result, the kerosene range oils recovered from the microwave-metal interaction pyrolysis of plastics can be used as feedstock chemicals or as transportation fuels after treatment in the petrochemical refinery.

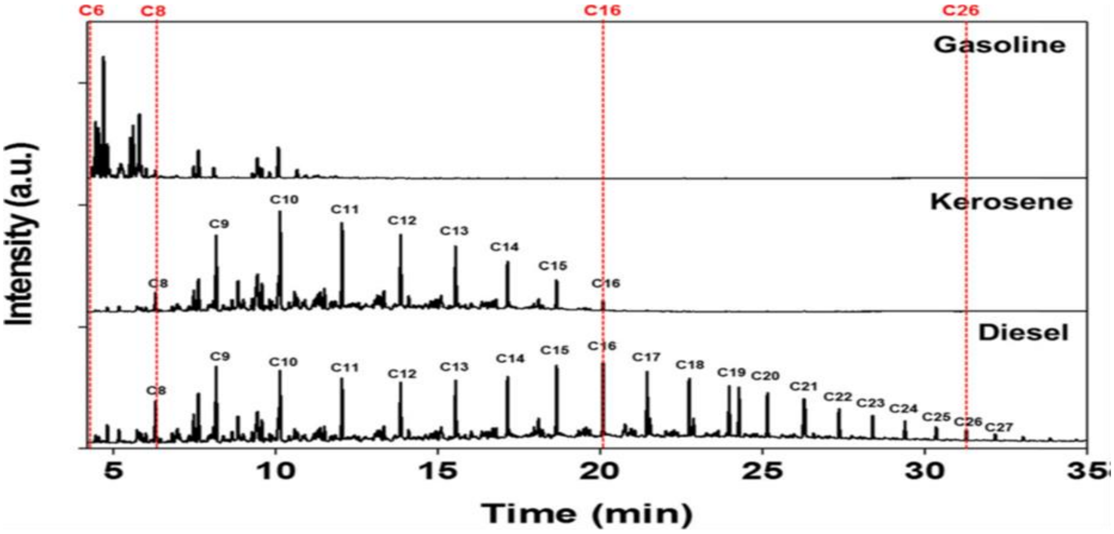


Figure 4.17: GCMS total ion chromatograms of refined petroleum products reproduced from Kwon et al. [140]

4.8 Effect of Microwave Power on Pyrolytic Oil Composition of PS, PP and LDPE

Results of GCMS analysis of pyrolytic oils recovered from PS, PP and LDPE are presented in Tables 4.11 to 4.13, respectively. For comparative study based on the effect of microwave power, oil samples recovered at 1900 W and 2500 W from PS, PP and LDPE respectively, were analyzed. The most abundant components of interest were identified using the total ion chromatograms presented in Fig. 4.18 matched to spectral library NIST 14.

Table 4.11: GCMS analysis of PS oil at different microwave powers

Microwave power (W)	Peak no.	Retention time (min)	Relative conc. (%)	Name of compound	Formula
1900 W	4	9.643	65.99	Styrene,	C_8H_8
	15	27.092	7.68	1-benzyl-1,2,3-triazole	$C_9H_9N_3$
	34	36.763	13.92	Benzonitrile, m-phenethyl-	$C_{15}H_{13}N$
2500 W	13	9.659	67.84	Styrene	C_8H_8
	63	27.091	8.28	3-Benzyl-5-chloro-1,2,3-triazole 1-oxide	$C_9H_8ClN_3O$
	89	36.749	5.06	Benzonitrile, m-phenethyl-	$C_{15}H_{13}N$

Table 4.12: GCMS analysis of PP oil at different microwave powers

Microwave power (W)	Peak no.	Retention time (min)	Relative conc. (%)	Name of compound	Formula
1900 W	6	7.949	11.27	2,4-Dimethyl-1-Heptene	C_9H_{18}
	30	14.719	5.77	Cyclopentane, propyl-	C_8H_{16}
	55	19.644	11.96	2-Decene, 7-methyl-	$C_{11}H_{22}$
	57	19.976	8.30	6-Tridecene, 7-methyl-	$C_{14}H_{28}$
2500 W	8	2.089	2.37	1-Pentene, 2-methyl-	C_6H_{12}
	26	8.002	20.64	2,4-Dimethyl-1-heptene	C_9H_{18}
	32	9.567	14.51	1,3,5,7 Cyclooctatetraene	C_8H_8
	76	19.630	4.36	2-Decene, 7-methyl-, (Z)-	$C_{11}H_{22}$

Based on the peak area and retention time, most common fractions found at microwave power of 1900 W and 2500 W were analyzed. In case of PS-oil, the most abundant compound was C8 (styrene) at both 1900 W and 2500 W. This implied that the increase in microwave power did not influence the product distribution in PS. In contrast to PS, PP and LDPE exhibited a change in the distribution of most abundant compound with the increase in microwave power. The highest oil fraction observed at 1900 W and 2500 W for PP-oil and LDPE oil was the same as: C11 and C9, respectively. It can be inferred here that the increase in microwave power from 1900 W to 2500 W produced a lighter fraction from C11 to C9 in case of both PP and LDPE.

Table 4.13: GCMS analysis of LDPE oil at different microwave powers

Microwave power (W)	Peak no.	Retention time (min)	Relative conc. (%)	Name of compound	Formula
1900W	3	2.099	1.75	1-Hexene	C_6H_{12}
	35	12.56	5.33	1-Decene	$C_{10}H_{20}$
	44	15.097	6.09	1-Undecene	$C_{11}H_{22}$
	46	15.301	3.56	Undecane	$C_{11}H_{24}$
	53	17.369	5.19	1-Dodecene	$C_{12}H_{24}$
	61	19.628	3.27	Tridecane	$C_{13}H_{28}$
2500 W	7	2.093	2.49	1-Pentene, 2-methyl-	C_6H_{12}
	30	7.916	5.64	2,4-Dimethyl-1-heptene	C_9H_{18}
	41	12.545	3.71	1-Decene	$C_{10}H_{20}$
	50	15.083	2.98	3-Undecene, (E)-	$C_{11}H_{22}$
	67	19.628	5.57	2,3-Dimethyl-3-heptene, (Z)-	C_9H_{18}
	69	19.963	3.15	2-Decene, 7-methyl-,	$C_{11}H_{22}$

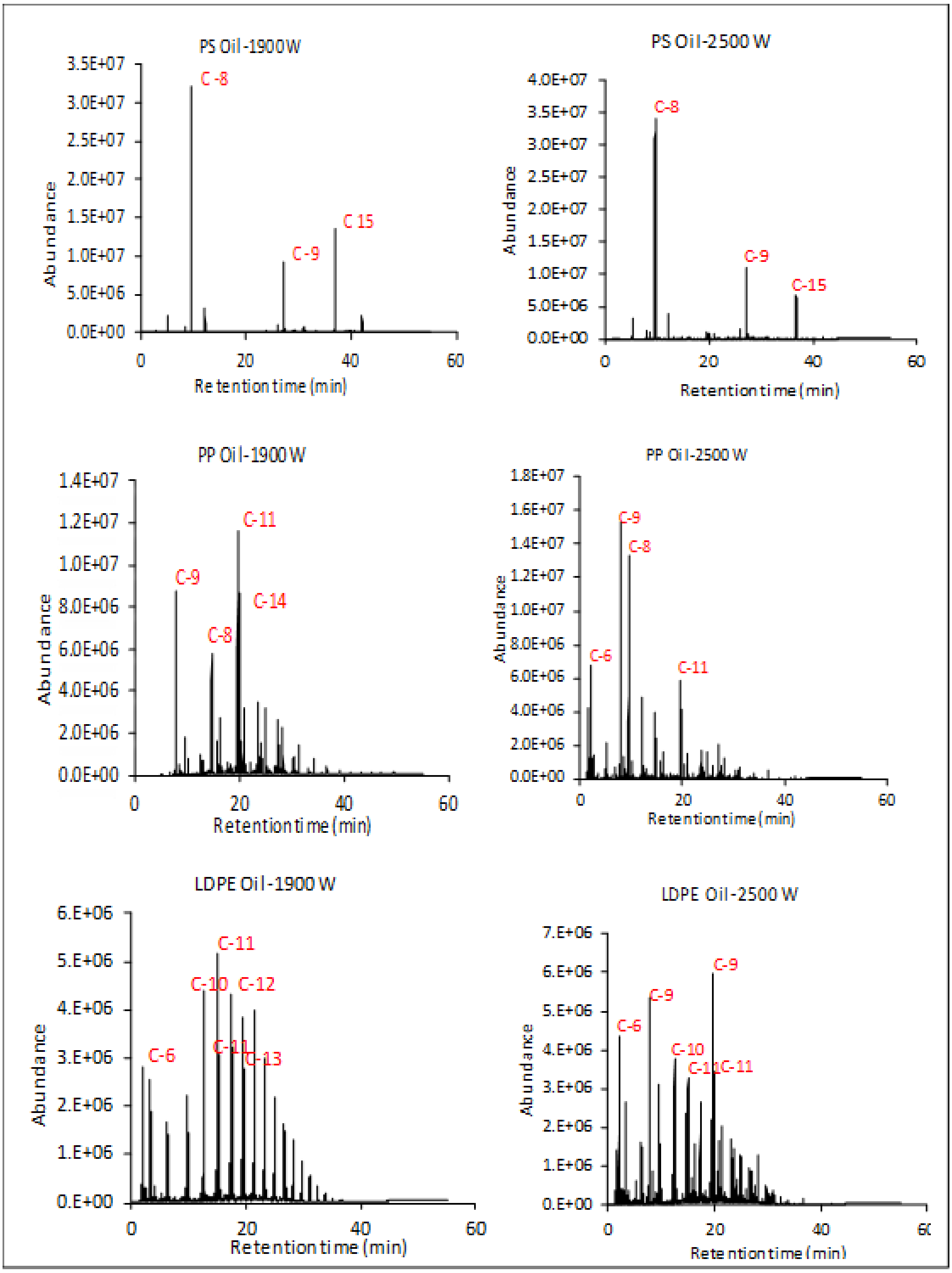


Figure 4.18: Comparison between total ion chromatograms of PS, PP and LDPE oils at 1900 W and 2500 W

4.9 Effect of Microwave Power on Pyrolytic Oil Yield of Plastic Blends

The effect of microwave power during microwave-metal interaction pyrolysis was evaluated based on the analysis of liquid oil yield and the reaction time using different plastic blends. The blends were prepared with equal proportion of each plastic. Fig. 4.19 shows the trends of oil yield versus microwave power for different plastic blends.

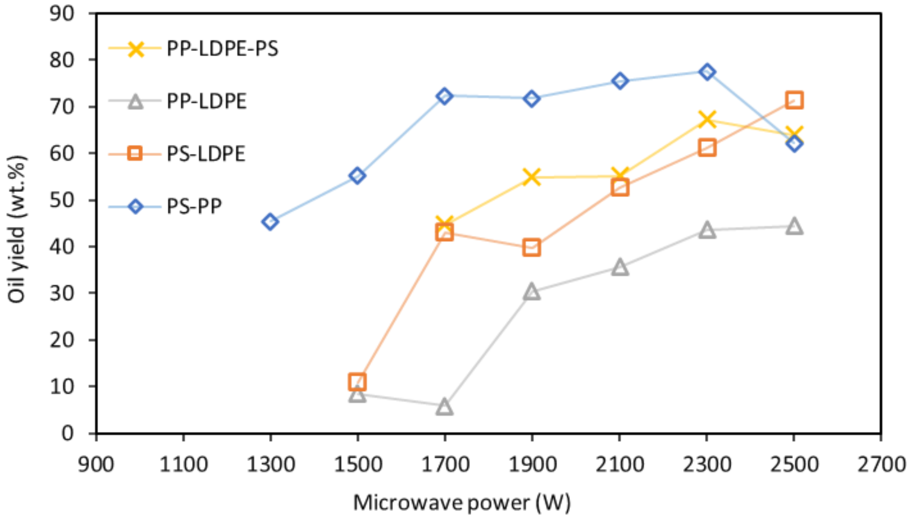


Figure 4.19: Variation of oil yield with microwave power for different plastic blends

The first oil was recovered at a microwave power of 1300 W for PS-PP, 1500 W for both PS-LDPE and PP- LDPE, and 1700 W for PS-PP-LDPE, respectively. As the microwave power increased, an overall rise in the liquid oil yield was observed for each blend. The average oil yield (wt.%) for plastic blends at different microwave powers between 1300 and 2500 W (Table 4.14) was found to be maximum for PS-PP (65.67 wt.%) followed by PS-PP-LDPE (57.23 wt.%), PS- LDPE (46.52 wt.%) and PP-LDPE (28.08 wt.%). Based on mass balance and conversion wt.% (Table 4.15), a maximum conversion of up to 96.25 wt.% was observed for PS-PP blend and a minimum of 74.99 wt.% in PP-LDPE, while rest of the blends showed intermediate capacity. The maximum oil yield obtained under optimum conditions was found to be PS- PP (77.5 wt.%, 2300 W), PS-LDPE (71.3 wt.%, 2500 W), PS- PP- LDPE (67.3 wt.%, 2300 W) and PP-LDPE (44.45 wt.%, 2500 W), respectively. The second largest fraction recovered in all the blends was gaseous with maximum yield for PP-LDPE (30.54 wt.%) followed by PS-PP-LDPE (28.43 wt.%), PS-PP (18.75 wt.%) and PS- LDPE (17.10 wt.%). The gas fraction was maximum for the PP- LDPE blend with least quantity of recovered oil amongst all the blends. The production of char residue in PS-PP and PS-PP-LDPE was in the range of (3-5 wt.%). Unlike other blends, PS-LDPE and PP-LDPE also produced waxy residue of (10.12 wt.%) and (23.21 wt.%), respectively, and char in minor quantities in the range of (1-2 wt.%).

Table 4.14: Average oil yield during pyrolysis of plastic samples at different microwave powers

Sample	PS-PP	PS-PP-LDPE	PS-LDPE	PP-LDPE
Average yield (wt.%)	65.67	57.23	46.52	28.08

The production of wax in LDPE pyrolysis unlike PS and PP was discussed earlier; based on that, a similar behavior was reflected in the blends made of LDPE. The relatively larger proportion of LDPE in the blend tends to release the waxes which is also responsible for lower conversion efficiencies. In a study [141] on mixed plastics pyrolysis carried out at 650°C, a yield of 48 wt.% oil was reported which contained 52 wt.% of heavy oil, wax and carbon black. As the temperature was increased to 730°C , the light oil fraction of 44 wt.% rose to 70 wt.%. It was implied here, that higher pyrolysis temperatures are required to convert the residual wax into light oil and gas fractions. Contrarily, in the case of PS-PP-LDPE blend, there was no wax formation. It must be pointed out here, that blends comprising PS were more efficient towards higher oil yields. It was observed that PS in combination with PP or LDPE resulted in an improved oil yield. It was evident from the mass balance (Table 4.15), that oil yield of PS-PP (77.5 wt.%) was higher than PP (54.65 wt.%) alone, PS- LDPE (71.3 wt.%) higher than LDPE (30.15 wt.%), and PS- PP- LDPE (67.3 wt.%) higher than PP- LDPE (44.45 wt.%). The same order was observed for conversion (wt.%) into oil and gas fractions as well. The studies [142]–[144] on pyrolysis of plastic mixtures have confirmed that addition of PS to polyolefins like PP or LDPE , can accelerate the decomposition process during pyrolysis giving higher conversions. The mechanism responsible for this effect is the radical formation during pyrolysis of PS, that enhances the conversion of PP and LDPE. Further, the resulting species from the breakdown of PS are immune to the presence of other polyolefins which makes it a suitable catalyzing agent.

Table 4.15: Mass balance and conversion (wt.%) of pyrolytic oils recovered from plastic samples under optimum conditions

Sample	Microwave power (W)	Oil (wt.%)	Gas (wt.%)	Residuals		Conversion (wt.%)
				Wax (wt.%)	Char (wt.%)	
PS-PP	2300	77.50	18.75	-	3.75	96.25
PS-LDPE	2500	71.30	17.10	10.12	1.48	88.40
PP-LDPE	2500	44.45	30.54	23.21	1.80	74.99
PS-PP-LDPE	2300	67.30	28.43	-	4.27	95.73
PS	2100	88.70	6.70	-	4.60	95.40
PP	2500	54.65	40.45	-	4.90	95.10
LDPE	2500	30.15	24.15	44.18	1.52	54.30

4.10 Effect of Microwave Power on Pyrolysis Reaction Time of Plastic Blends

The plots of reaction time versus microwave power for different plastic blends are shown in Fig. 4.20. The increase in microwave power resulted in a consistent decline of reaction times with the increasing microwave powers. Under optimum conditions between 2100 and 2500 W, the reaction times were found to be minimum for PS- PP- LDPE (20 minutes) followed by PS-PP (21 minutes), PS-LDPE (23 minutes) and PP-LDPE (26 minutes), respectively. The pyrolysis reaction times of different blends were compared, and it was found that PP-LDPE took more time for thermal breakdown. This was attributed to the presence of complex branched hydrocarbon chains in PP-LDPE blend which offered higher activation energy requiring higher temperature and residence time for the release of volatiles. According to Garforth et al. [145], the use of catalyst can reduce the activation energy required for the thermal cracking of polyolefins which is accomplished through different catalytic cracking mechanisms involving the effects of ionic and free radical formation. However, in the case of PS blends, the reaction times were reduced due to the catalytic action of PS released radicals which accelerated the thermal cracking process of PP and LDPE polymers, thereby reducing the reaction time.

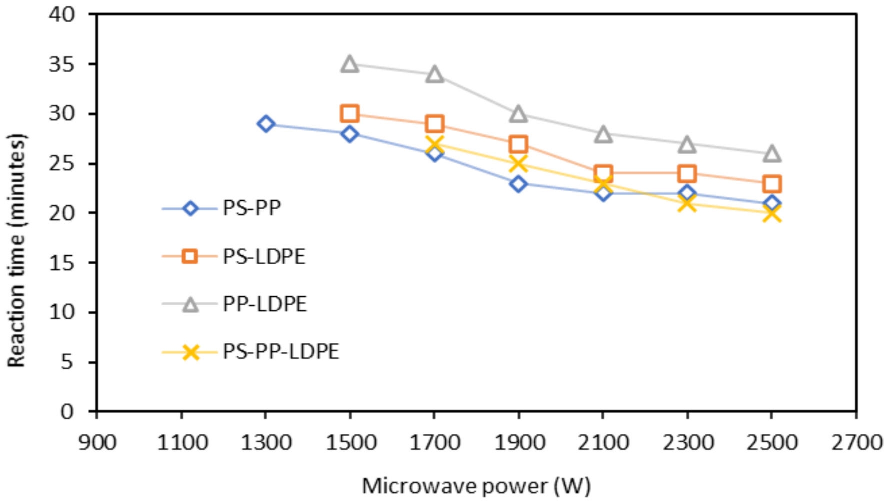


Figure 4.20: Variation of reaction time with microwave power for different plastic blends

4.11 Chemical Composition Analysis of Pyrolytic Oils recovered from Plastic Blends

The GCMS analysis of pyrolytic oils recovered from plastic blends at 2100 W is presented in Tables 4.16 to 4.19, while total ion chromatograms are shown in Fig. 4.21.

The blends of plastics prepared from PS consisting of PS-PP, PS-LDPE and PS- PP- LDPE, released oils with aromatic content composed of styrene, benzene along with aliphatic species like (2,4- Dimethyl-1-heptene, 4-methyl-2-Undecene,). The dominant aromatic character in the oil was produced by PS whereas aliphatic content was mainly due to the presence of PP and LDPE, which was also observed in the past studies on polymer pyrolysis [45], [142]. The most abundant compounds showed the presence of aromatic species only in the oils recovered from blends made of PS. Other blends devoid of PS, produced major fraction of cycloalkanes or alkenes. Most of the hydrocarbons present in the oils recovered from individual plastics and its blends were mostly in the range of kerosene oil C8-C16 [132]. It can be inferred that pyrolytic oils recovered from microwave-metal interaction pyrolysis of plastics has a great potential as an alternative source of useful hydrocarbons.

Table 4.16: GCMS analysis of PS-PP oil

Peak No.	Retention time (min)	Relative conc. (%)	Name of compound	Formula
18	7.971	7.98	2,4-Dimethyl-1-heptene	C_9H_{18}
23	9.636	51.92	Styrene	C_8H_8
84	27.085	5.43	Benzene, (3-nitropropyl)-	$C_9H_{11}NO_2$

Table 4.17: GCMS analysis of PP-LDPE oil

Peak No.	Retention time (min)	Relative conc. (%)	Name of compound	Formula
3	2.084	1.79	1-Pentene, 2-methyl-	C_5H_{10}
28	7.979	29.12	2,4-Dimethyl-1-heptene	C_9H_{18}
52	14.712	3.48	2-Undecene, 4-methyl-	$C_{12}H_{24}$
78	19.634	6.01	2,3-Dimethyl-3-heptene, (Z)-	C_9H_{18}

Table 4.18: GCMS analysis of PS-LDPE oil

Peak No.	Retention time (min)	Relative conc. (%)	Name of compound	Formula
12	5.279	4.23	Toluene	C_7H_8
17	9.642	66.06	1,3,5,7-Cyclooctatetraene	C_8H_8
22	12.225	3.77	alpha-Methyl styrene	C_9H_{10}
84	27.078	3.52	Benzenebutanenitrile	$C_{10}H_{11}N$

Table 4.19: GCMS analysis of PS-PP-LDPE oil

Peak No.	Retention time (min)	Relative conc. (%)	Name of compound	Formula
14	7.107	12.65	2,4-Dimethyl-1-heptene	C_9H_{18}
17	8.818	58.89	Styrene	C_8H_8

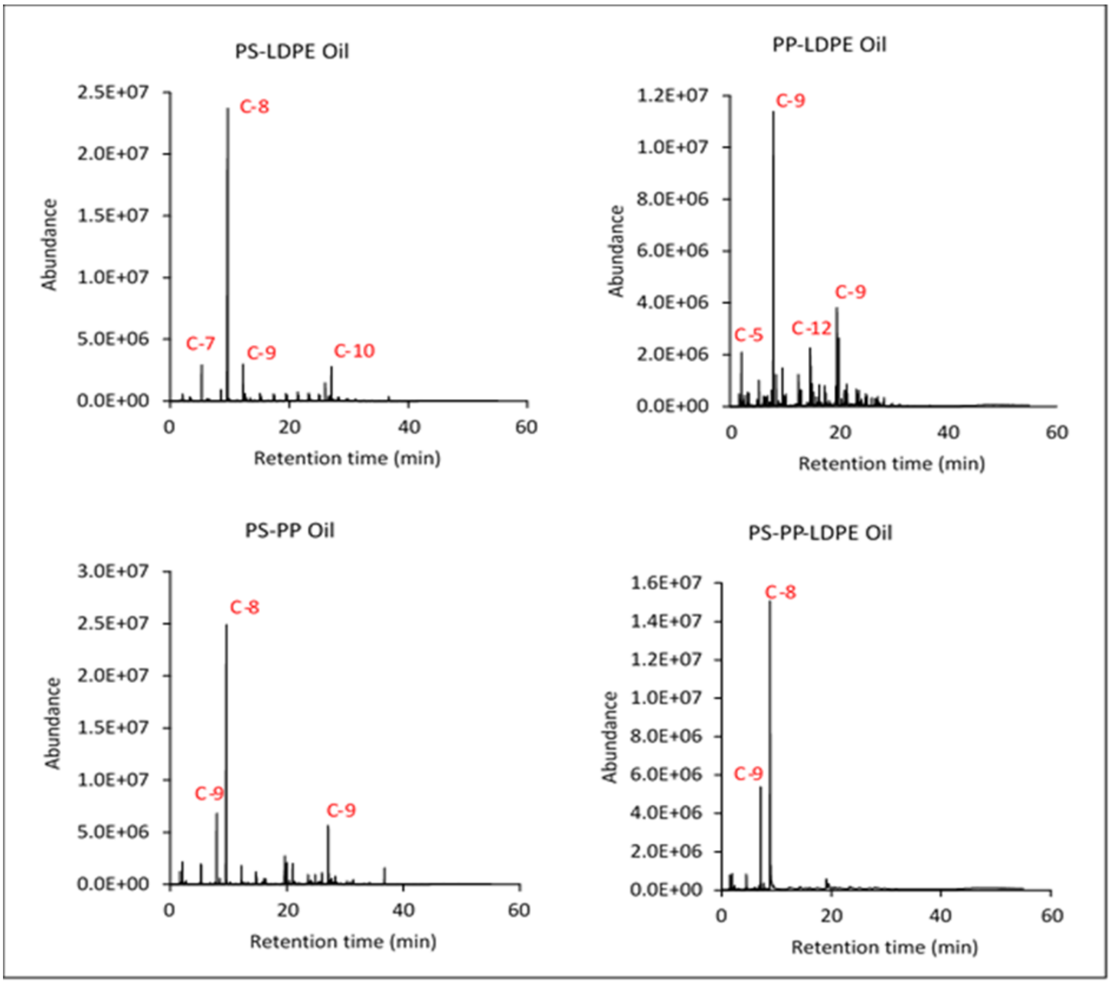


Figure 4.21: Comparison between total ion chromatograms of oils recovered from different plastic blends at 2100 W

4.12 Effect of Microwave power on Pyrolytic Oil Yield of Waste PS compared to PS

The effect of microwave power on oil yield of waste PS (PSW) was investigated and compared to the oil yield of virgin PS for the same feedstock size of 10 g of plastic sample. The variation of oil yield and pyrolysis temperature with microwave power for waste PS (PSW) and PS is presented in Fig. 4.22 and Fig. 4.23, respectively. It was observed that increase in microwave power resulted in an overall rise of oil yield. The pyrolysis temperatures for PSW and PS were observed in the range of 500-720°C. Here, it was observed that pyrolysis temperatures for PSW and PS at different microwave powers were nearly the same. It was, therefore, implied that PSW and virgin PS exhibited similar nature of thermal degradation. The trend of oil recovery showed that PSW produced lesser oil than virgin PS over the entire microwave power range of 1500- 2500 W. The waste PS contains plastic additives unlike pure form of PS which is expected to reduce its oil yielding capacity. The maximum oil yield observed at 2500 W (699°C) for PSW was 58.9 wt.% significantly lower than PS which produced 74.5 wt.% oil at 2500 W (710°C). A minimum oil yield of 31.1 wt.% was observed at 1500 W (545°C) for PSW and 45.2 wt.% at 1500 W (580°C) for PS, respectively.

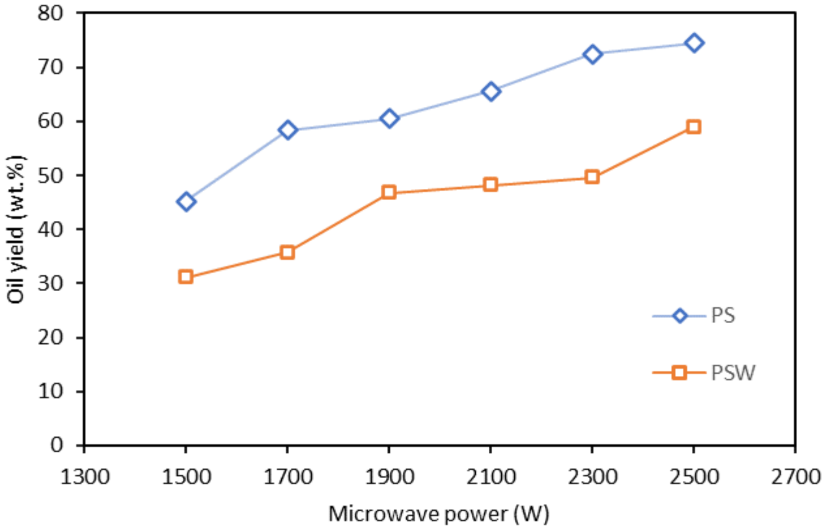


Figure 4.22: Variation of oil yield with microwave power for PSW and PS

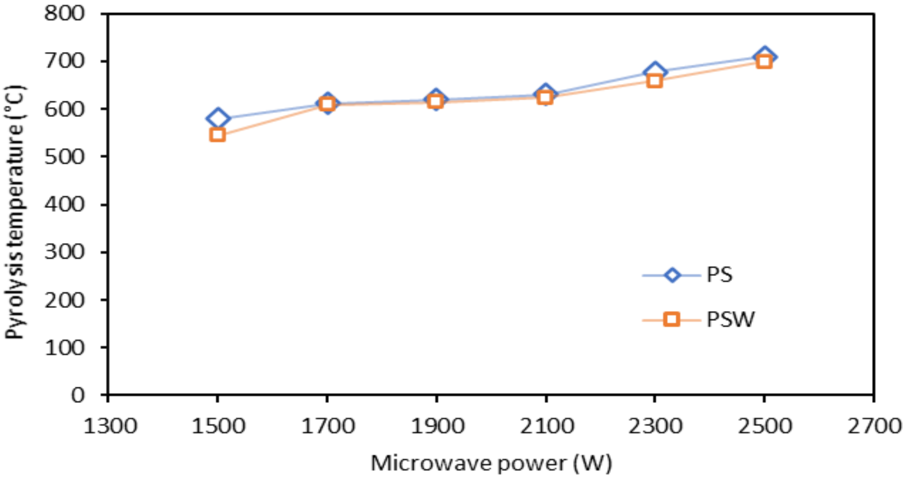


Figure 4.23: Variation of pyrolysis temperature with microwave power for PSW and PS

Table 4.20 shows the mass balance and conversion (wt.%) of products of pyrolysis for PSW and PS at 1500 W, 1900 W and 2300 W, respectively. The pyrolysis fractions were observed in the form of oil, gas, and char, respectively. The conversion of plastic into oil and gas was found between 93-94 wt.% for PSW and 94-96 wt.% for PS. The formation of char residue was slightly higher between 6-7 wt.% in the case of PSW as compared to PS in the range 4-6 wt.%. It must be pointed out that production of oil during pyrolysis of PSW was found to be consistently lower than PS (Table 4.20) for the selected values of the microwave power. Contrarily, production of gas was found to be on the higher side for PSW as compared to PS. It can be inferred here that waste PS showed lower oil yield capacity than pure form of PS.

Table 4.20: Mass balance and conversion (wt.%) of pyrolytic oils recovered from PSW and PS at 1500 W, 1900 W and 2300 W, respectively

Sample	Microwave power (W)	Oil (wt.%)	Gas (wt.%)	Char (residue) (wt.%)	Conversion (wt.%)
PSW	1500	31.10	62.29	6.61	93.39
	1900	46.70	46.87	6.43	93.57
	2300	49.56	44.40	6.04	93.96
PS	1500	45.20	48.96	5.84	94.16
	1900	60.50	34.40	5.10	94.90
	2300	72.50	22.68	4.82	95.18

4.13 Effect of Microwave Power on Pyrolysis Reaction Time of PSW compared to PS

Figure 4.24 highlights the variation of reaction time with microwave power for PSW and PS. As the microwave power was varied from 1500 W to 2500 W, the reaction time of pyrolysis reduced consistently for both PSW and PS plastic samples. The reaction time of pyrolysis of PSW decreased from 29 minutes at 1500 W to 13 minutes at 2500 W. Similar trend was also observed for PS where maximum duration was found to be 27 minutes at 1500 W which reduced to 10 minutes at 2500 W with increase in microwave power. As compared to PS, PSW exhibited slower oil recovery with longer reaction times.

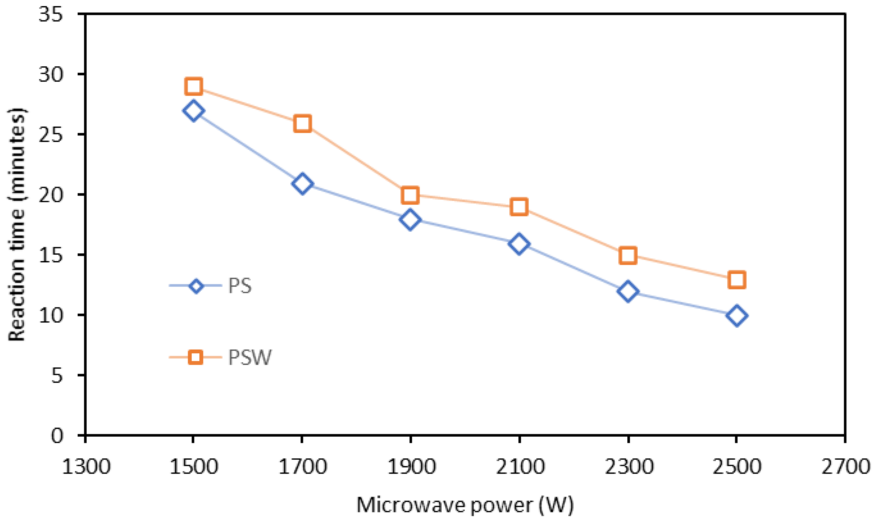


Figure 4.24: Variation of reaction time with microwave power for PS and PSW

The marginal difference observed in the trends of oil recovery time with respect to microwave power for PSW and PS can be attributed to the easier release of volatiles in case of PS unlike PSW which reflected a slower recovery. The nature of plastic being pyrolyzed was observed to be a critical factor which influenced the reaction kinetics.

4.14 Comparison between Pyrolytic Oil Densities of PSW and PS

Figure 4.25 shows the variation of oil density with microwave power during microwave-metal interaction pyrolysis of PSW and PS. The increase in microwave power was found to produce oils with higher densities with fluctuation at some points. The range of variation of oil density with microwave power varied from 1500 to 2500 W for PSW was 0.777-0.841 g/cm³ whereas in the case of PS, this range was observed to be 0.840-0.879 g/cm³. It was evident from the density plots, that PS produced heavier oils than the waste PS (PSW).

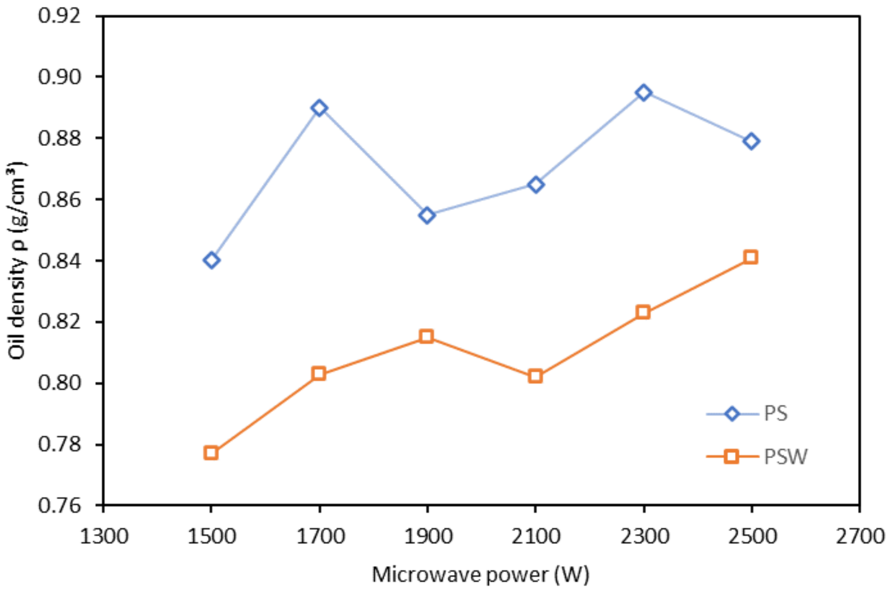


Figure 4.25: Variation of oil density with microwave power for PS and PSW

4.15 Comparison between Chemical Composition of Pyrolytic Oils recovered from PSW and PS

The GCMS analysis of pyrolytic oils recovered from PSW and PS at 2100 W is presented in Table 4.21. The most abundant chemical compounds identified in oil recovered from PS at 2100 W was earlier discussed in Section 4.7 where the total ion chromatogram showed three distinct peaks representing styrene as the most abundant compound present in the oil followed by m-phenethyl-benzonitrile and 1- benzyl- 1,2,3- triazole in minor quantities. The total ion chromatograms of oils recovered from PSW and PS is shown in Fig. 4.26. However, the total ion chromatogram of the oil recovered from PSW showed only one distinct peak highlighting styrene monomer as the dominant species with negligible concentration of other possible compounds. It was, therefore, evident from the GCMS analysis that PSW produced comparably higher quantities of styrene monomer as compared to PS which also released other compounds in minor concentrations in addition to styrene.

Table 4.21: GCMS analysis of oils recovered from PSW and PS at 2100 W

Oil sample	Peak No.	Retention time (min)	Relative conc. (%)	Name of compound	Formula
PSW	4	8.897	89.48	Styrene	C_8H_8
PS	4	9.643	65.99	Styrene	C_8H_8
	15	27.092	7.68	1-benzyl-1,2,3-triazole	$C_9H_9N_3$
	34	36.763	13.92	Benzonitrile, m-phenethyl-	$C_{15}H_{13}N$

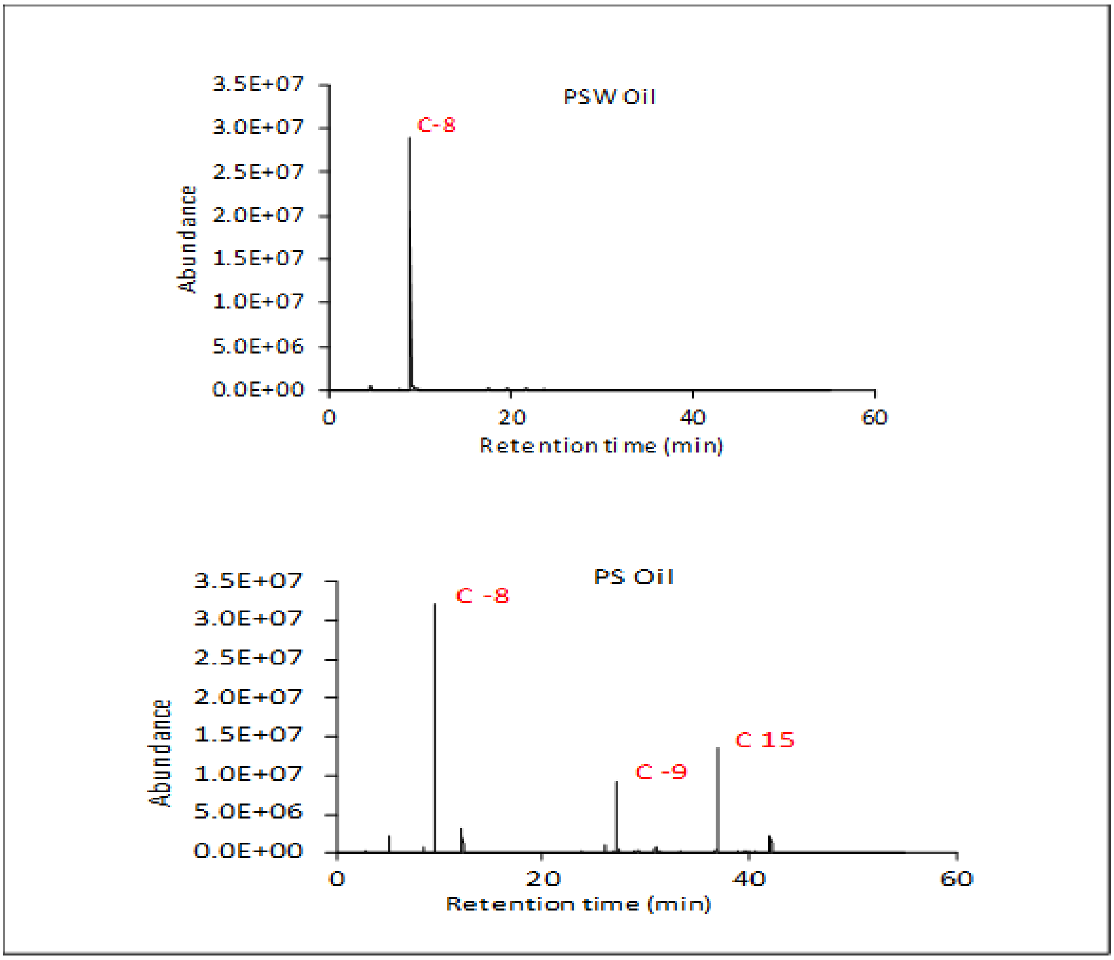


Figure 4.26: Total ion chromatograms of pyrolytic oils recovered from PSW and PS at 2100 W

4.16 Effect of Wire Gauge Size on Performance of Microwave-metal Interaction Pyrolysis of PS

The effect of wire gauge on the performance of microwave-metal interaction pyrolysis of PS was investigated by using iron coils of gauge size 1 mm, 1.5 mm, and 2 mm, respectively. The effect of gauge on oil yield and reaction time was evaluated for the microwave power range of 1500-2500 W. The variation in oil yield and pyrolysis temperature with microwave power for different gauge sizes is presented in Fig. 4.27 and Fig. 4.28, respectively.

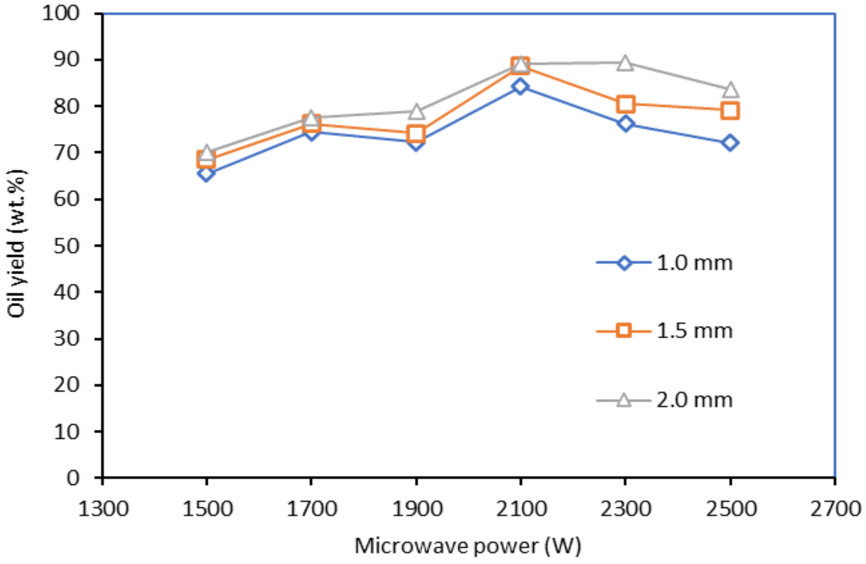


Figure 4.27: Variation of oil yield with microwave power for different gauge coils

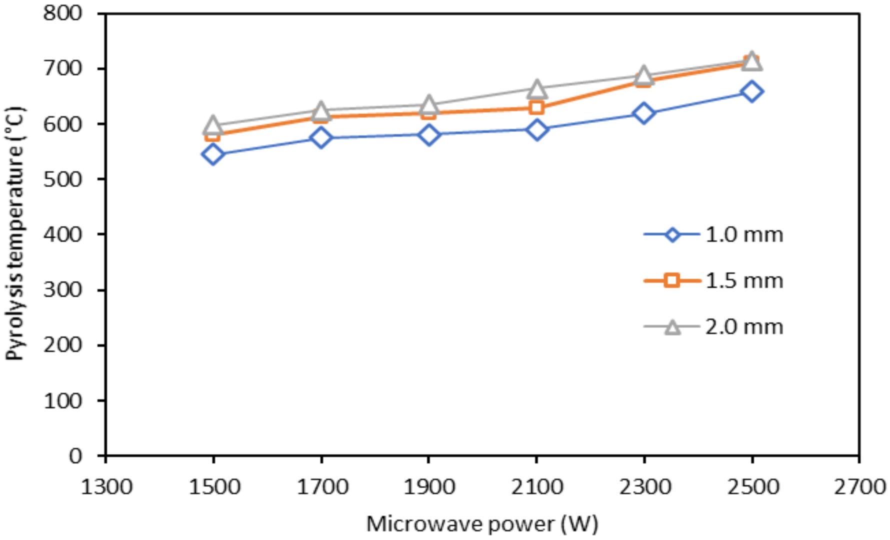


Figure 4.28: Variation of pyrolysis temperature with microwave power varied from 1500 W to 2500 W for different gauge coils

It was evident from the temperature plots that coil of higher gauge produced stronger heating as compared to a lower gauge size coil. The range of temperatures observed for each gauge size was 545-659°C for 1 mm, 580-710°C for 1.5 mm and 598-715°C for 2 mm, respectively. The increase in gauge from 1.5 to 2 mm caused a marginal increase in the oil yield over the entire microwave power range. The mechanism responsible for this improvement in oil yield is based on the wire thickness.

Coil fabricated from thicker wire has more capacity for storing the heat generated through repeated skins or penetration of microwaves undergoing multiple reflections within the cylindrical space. Even though, the coil with smaller gauge size has greater surface area available for microwave exposure, the lower thickness of the coil wire reduces the heat carrying capacity of the coil, thereby, causing the effect of wire thickness to dominate the effect of available surface area for repeated skins. The resulting high temperature achieved by the coil enhanced the release of volatiles from PS sample giving higher oil yield. However, when the thickness of wire was reduced from 1.5 to 1 mm, a marginal decline of the oil yield was observed. Here, the capacity of the coil to store the induced heat was reduced unlike the coil with higher gauge size of 2 mm. During the entire analysis, the oil yield variation was observed in the range of 65-90 wt.% comprising all three coils.

The other effect observed due to change in gauge size was the variation in reaction time of pyrolysis. The variation in reaction time with respect to microwave power for different gauges is presented in Fig. 4.29.

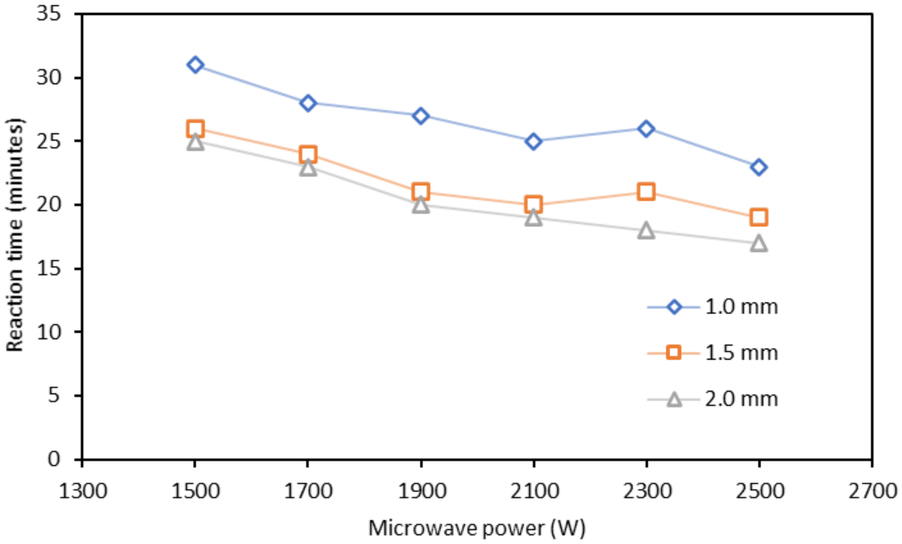


Figure 4.29: Variation of reaction time with microwave power for different gauge coils

The increase in microwave power caused a consistent reduction in the reaction time of pyrolysis for each gauge size. When the coil gauge was increased from 1.5 to 2 mm, the reaction was faster, and the oil recovery was completed in lesser time. A minimum reaction time of 17 minutes was observed with 2 mm coil. Here, the factor responsible for reduction in reaction time is the better heat storing capacity of the coil with larger gauge size which was also observed in the case of oil yield. The increase in gauge size was found to reduce the reaction time of pyrolysis while increasing the oil yield. Similarly, coil with lower gauge size reduced from 1.5 to 1 mm, retarded the pyrolysis reaction due to lower heating rate achieved causing an increase in the reaction time. A maximum reaction time of 31 minutes was observed with 1.0 mm coil. The performance of 1.5 mm coil in terms of oil yield and reaction time was found to be intermediate of between 1 mm and 2 mm coils. It must be pointed out, that gauge of the coil significantly influenced both the oil yield and reaction time of pyrolysis as the heat carrying capacity of the coil influences the heating rates thereby affecting the reaction kinetics involved in the thermal breakdown of the plastic.

4.17 Effect of Type of Metal Coil on the Performance of Microwave-metal Interaction Pyrolysis

The effect of type of metal coil used to conduct microwave-metal interaction pyrolysis was evaluated by comparing the performance of iron and copper coil in terms of the oil yield and reaction time plotted against the microwave power varied from 1500 to 2500 W. The individual plastics comprising PS, PP and LDPE, respectively, were pyrolyzed to release liquid oil by utilizing the heat generated through the microwave-metal interaction. The repeated reflections inside the coil space causes multiple skin penetrations of the microwaves into wire surface. Initially, small amount of heat is produced from skin effect which is later augmented as a result of continuous reflections from available surface area for microwave exposure [50]. The microwave discharge during microwave-metal interaction also contributes to the heat. The effectiveness of skin effect is largely dependent on the available surface area and conductivity of the metal. In the present study, both the iron and copper coils have same size except the difference in nature of the metal used for coil fabrication. The iron and copper coils offer equal area for microwave exposure but differ in its conductivities. It must be noted here, that, metal surface with higher conductivity weakens the skin effect (heat generated through microwave penetration) as compared to metal with lower electrical conductivity where the skin effect is stronger than the former case, and therefore, larger quantity of heat is produced [65]. As a consequence, iron coil having lower conductivity than copper coil was able to reach higher temperatures than the copper coil. Thus, higher oil yields with lower reaction times were observed in the case of iron coil than the copper coil. The proceeding discussion compares the variation of oil yield and reaction time with microwave power for the iron and copper coils used to carry out microwave-metal interaction pyrolysis of PS, PP and LDPE, respectively.

The PS sample was converted to oil at different microwave powers using iron and copper coils in separate experiments. The variation in oil yield and pyrolysis temperature with microwave power for different metal coils is presented in Fig. 4.30 and Fig. 4.31, respectively.

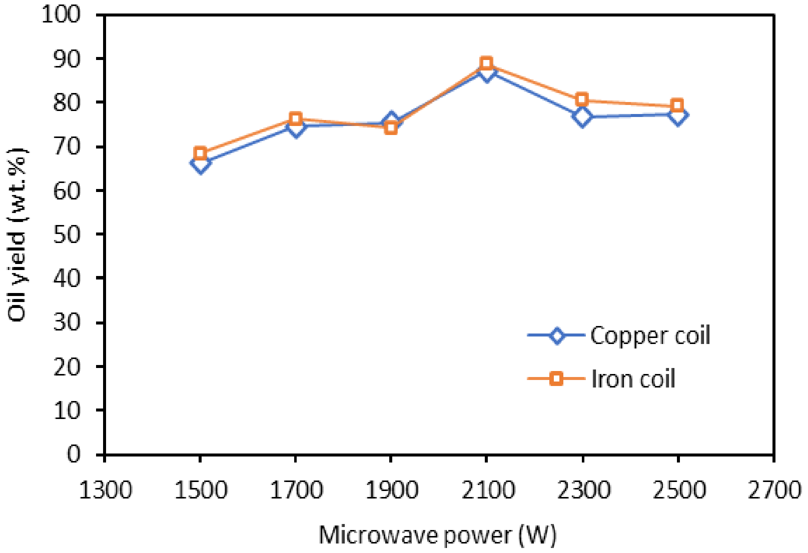


Figure 4.30: Variation of oil yield with microwave power for PS using iron and copper coils

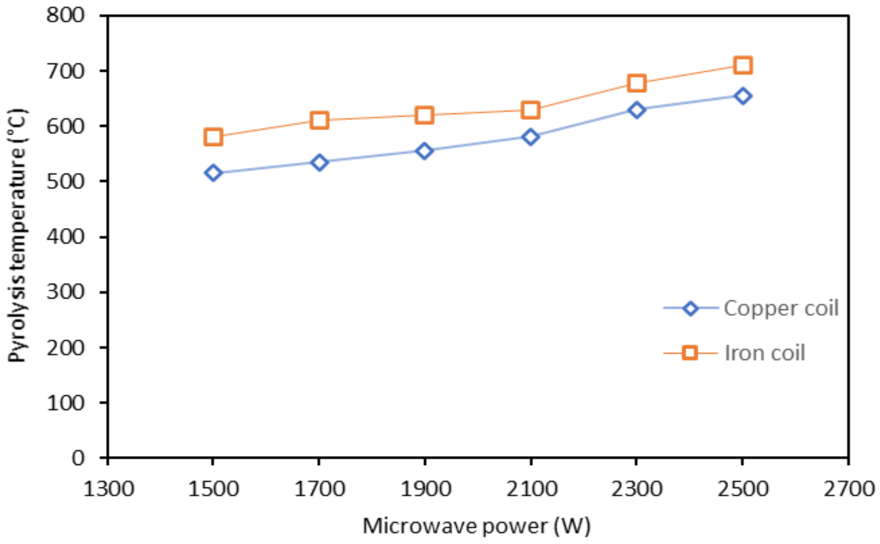


Figure 4.31: Variation of pyrolysis temperature with microwave power for PS using iron and copper coils

It was evident from the trends of oil recovery that iron coil produced higher oil yield than the copper coil consistently over the entire microwave power range between 1500 and 2500 W. The iron coil produced oil in the range of (68.5-88.7)wt.% while for copper coil the range was (66.23-87.26)wt.%. As discussed earlier, the higher conductance of copper coil was responsible for producing lower skin penetration into wire surface which reduces the amount of heat generated in the process, thereby, achieving lower temperatures as compared to iron coil. The range of pyrolysis temperatures of PS between 1500 and 2500 W was found to be 580-710°C for iron coil and 515- 656°C for copper coil, respectively.

The other significant effect was observed on the reaction time of pyrolysis. Fig. 4.32 highlights the plots of reaction time with microwave power for the iron and copper coils. The recovery of oil was found to be faster in case of iron coil due to higher temperatures and heating rates which accelerated the release of volatiles completing the reaction in shorter duration. The reaction period observed for the iron coil varied from a minimum of 19 minutes to a maximum of 26 minutes, while in the case of copper coil, the reaction time varied from a minimum of 21 minutes to a maximum of 28 minutes, respectively.

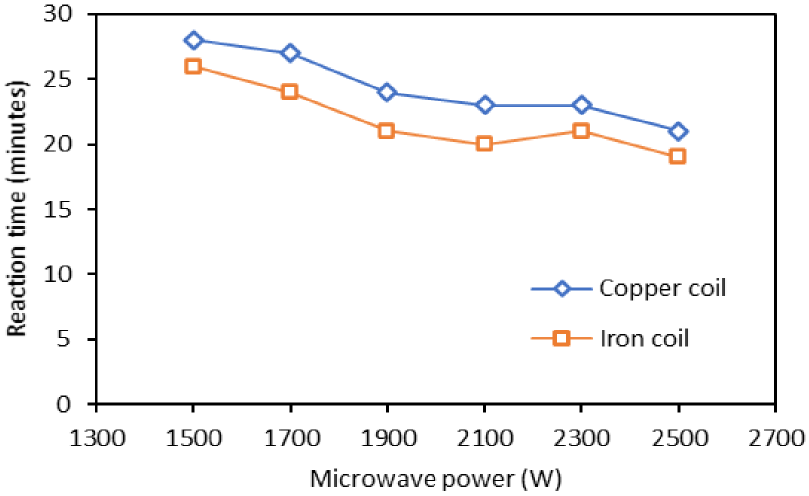


Figure 4.32: Variation of reaction time with microwave power for PS using iron and copper coils

The effect of type of metal used in microwave-metal interaction pyrolysis was also investigated for the PP and LDPE samples using iron and copper coils. Figures 4.33 and 4.34, presents the variation of oil yield with microwave power for PP and LDPE samples, respectively.

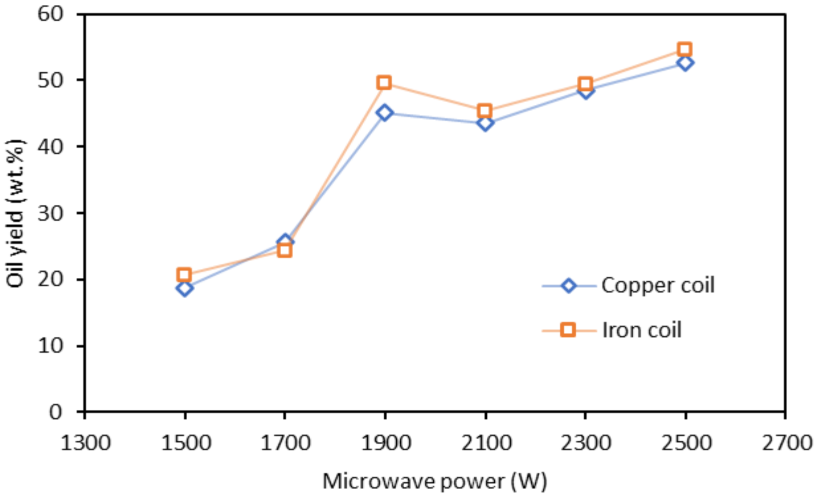


Figure 4.33: Variation of oil yield with microwave power for PP using iron and copper coils

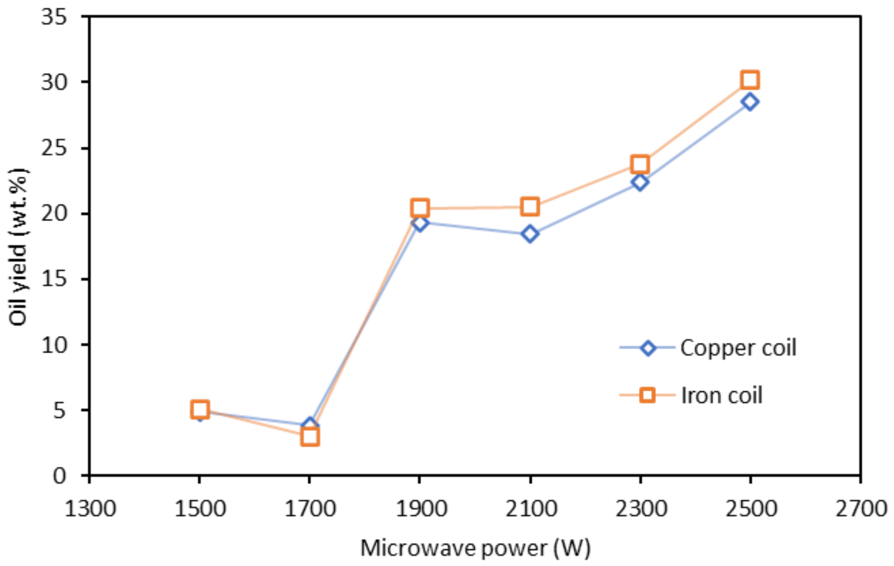


Figure 4.34: Variation of oil yield with microwave power for LDPE using iron and copper coils

The oil yield produced using iron coil was found to be higher than the copper coil for both PP and LDPE samples. The oil produced from PP varied in the range of (20.65- 54.65)wt.% for iron coil and (18.78-52.65)wt.% for copper coil. For the LDPE sample, the oil yield varied between (3.05-30.15)wt.% for iron coil and (3.86- 28.50)wt.% for copper coil. Though the oil yield observed in case of PS was much higher as compared to PP and LDPE but the effect of type of metal exhibited a similar trend in all the three samples comprising PS, PP and LDPE, respectively, showing improvement in oil yield achieved with iron coil over that of copper coil. The effect of type of metal used for pyrolysis was observed to be marginal for a gauge size of 1.5 mm, that is, the effect was reflected with a small difference in oil yields for the two coils. However, with higher gauge size of iron and copper coils, this effect is expected to become pronounced with larger difference in oil yields for the two coils.

The variation of pyrolysis temperature with microwave power for PP and LDPE samples is presented in Fig. 4.35 and Fig. 4.36, respectively. The pyrolysis temperatures of PP varied from 501°C to 701°C for iron coil and 450°C to 656°C for copper coil. Similarly, pyrolysis temperature in the case of LDPE showed variation from 498°C to 715°C for iron coil and 465°C to 654°C for copper coil, respectively. It was inferred that iron coil produced a stronger heating effect with higher pyrolysis temperature and improved oil yield in contrast to copper coil.

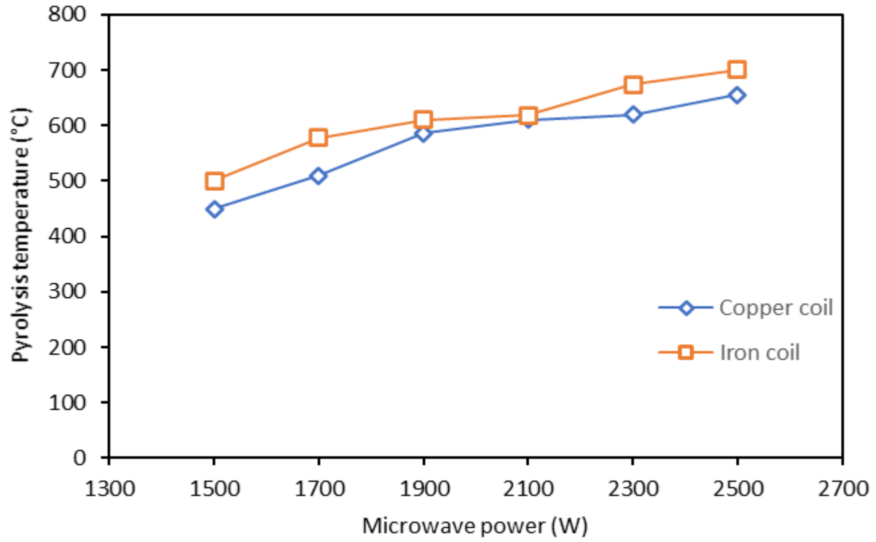


Figure 4.35: Variation of pyrolysis temperature with microwave power for PP using iron and copper coils

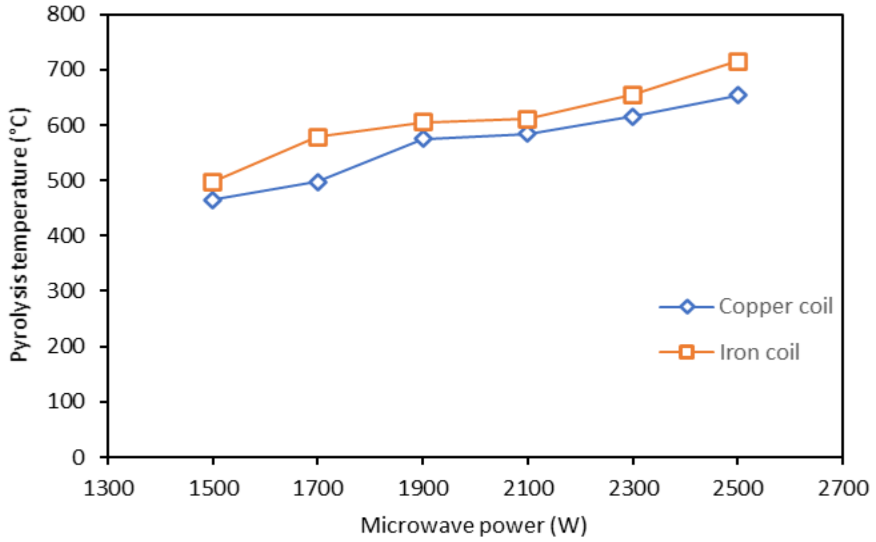


Figure 4.36: Variation of pyrolysis temperature with microwave power for LDPE using iron and copper coils

The influence of type of metal coil on the reaction time was also analyzed for PP and LDPE samples using the iron and copper coils. The trends of reaction time versus microwave power for PP and LDPE samples using the two coils is presented in Figures 4.37 and 4.38, respectively.

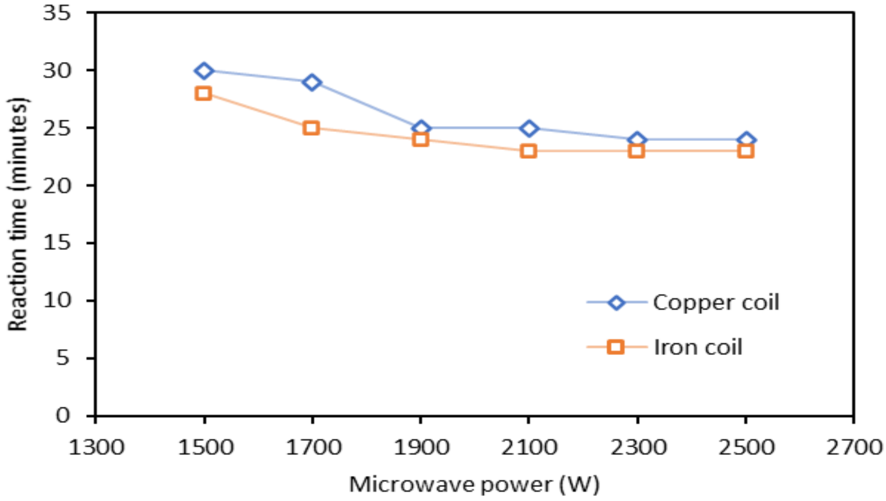


Figure 4.37: Variation of reaction time with microwave power for PP using iron and copper coils

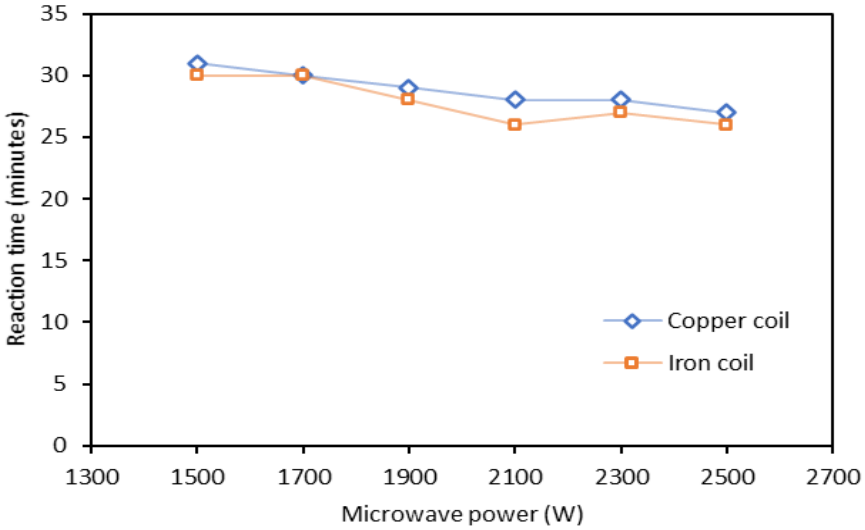


Figure 4.38: Variation of reaction time with microwave power for LDPE using iron and copper coils

The analysis of the plots showed that reaction time was consistently higher for copper coil over that of iron coil for both PP and LDPE samples. Further, the plots of reaction time for the two coils are quite close to each other for both PP and LDPE unlike PS where a greater difference was observed between the reaction times for the two coils. The reaction time for PP varied from a minimum of 23 minutes to a maximum of 28 minutes for iron coil whereas for copper coil, it varied from a minimum of 24 minutes to a maximum of 30 minutes. In the case of LDPE sample, the reaction time varied from a minimum of 26 minutes to a maximum of 30 minutes for iron coil whereas for copper coil, it varied from a minimum of 27 min to a maximum of 31 min.

4.18 Energy Efficiency of Microwave-metal Interaction Pyrolysis Process

The energy efficiency of the microwave-metal interaction pyrolysis process was determined by comparing the energy recovered in the form of pyrolytic oil with the electrical energy consumed during the reaction period. Table 4.22 highlights the estimate of energy efficiency (%) and energy recovered in oil (%) for PS, PP and LDPE, respectively. The maximum oil recovery for each plastic at optimal microwave power and corresponding reaction time was used to determine the percentage of energy recovered in oil and the energy efficiency of the process. The energy recovery in oil for each plastic was found to be maximum for PS at 83.71% followed by PP and LDPE at 54.65% and 29.5%, respectively. The higher energy recovered in oil for PS was due to its higher oil yield capacity as compared to PP and LDPE which produced significantly lower quantity of oil.

The energy efficiency of the microwave-metal interaction pyrolysis process was found to be maximum for PS at 26.75% followed by PP and LDPE at 14.78% and 7.01%, respectively. The energy efficiency of the process was directly proportional to the energy recovered in oil and inversely proportional to the microwave power and reaction time. The PS sample produced higher quantity of oil at lower microwave power of 2100 W with shorter reaction time of 20 minutes as compared to PP and LDPE which gave lower amount of oil at a higher microwave power of 2500 W each with longer duration of 23 and 26 minutes, respectively. It can be inferred, here, that overall PS showed better performance during microwave-metal interaction pyrolysis unlike PP and LDPE. The highest energy efficiency of 26.75% was achieved by PS which implied that 26.75% of the electrical energy consumed during the process was recovered as pyrolytic oil. However, the energy efficiency for PP and LDPE was quite low as compared to PS due to its higher cracking temperatures and longer reaction times. It must be pointed out here, that, improving the energy efficiency of the process would require scale-up of the process converting higher quantity of plastic into oil.

Table 4.22: Estimate of energy recovered in oil and energy efficiency of the process for each plastic

Plastic sample pyrolyzed	PS	PP	LDPE
Applied microwave power (W)	2100	2500	2500
HHV of plastic sample (MJ/kg)	40.9	46.7	46.4
Maximum oil yield (wt.%)	88.7	54.65	30.15
HHV of recovered oil (MJ/kg)	38.6	46.7	45.4
Reaction time (minutes)	20	23	26
Energy recovered in oil (%)	83.71	54.65	29.50
Energy efficiency of the process (%)	26.75	14.78	7.01

4.19 Process Optimization for Maximum Oil Recovery

The optimization of microwave-metal interaction pyrolysis process for maximum oil yield was performed for each plastic (PS, PP, LDPE) using the response surface methodology. The results and discussion of the study are presented in the following sub-sections.

4.19.1 Response Surface Analysis for PS

The investigation on microwave-metal interaction pyrolysis of PS was conducted using the central composite design model of experiments. It was known from the preliminary study that the liquid oil yield during microwave-metal interaction pyrolysis is significantly influenced by the effects of microwave power and the reaction time. Based on this knowledge of the process, microwave power (P, W) and reaction time (t, min) were selected as the two independent continuous variables to predict the response taken as oil yield (Y).

The detailed experimental design based on different operating conditions and the corresponding observed and predicted response is shown in Table 4.23 . The linear regression equation was developed for predicting the response (Y, wt.%) as:

$$\mathrm{Y_{oil}} = -805.3 + 0.5254\mathrm{P} + 29.22\mathrm{t} - 0.000085\mathrm{P}^2 - 0.2885\mathrm{t}^2 - 0.007378\mathrm{Pt} \tag{4.1}$$

The statistical significance of the model was proved from the ANOVA analysis (Tables 4.24) based on the p-values (<0.05). It was observed that the effects of microwave power and reaction time including the terms P, t, P^2, t^2 and Pt, respectively, were all significant with p-values less than 0.05. Further, it was evident from the high value of coefficient of determination (R^2) equal to 99.5% (Table 4.25) that the model finely represented the relationship between the independent variables. The R^2 value showed that the 99.5% of the variability in the response data can be explained by the fitted model. Further, the lack of fit for the model was found to be insignificant with p- value greater than 0.05 which showed that the model adequately predicted the response within the experimental range of study and that, no systematic variation in the response was unaccounted for by the hypothesized model.

Table 4.23: Experimental design values with observed and predicted oil yield

Run	Microwave power (W)	Reaction time (minutes)	Observed oil yield (wt.%)	Predicted oil yield (wt.%)
1	1900	27	85.35	86.47
2	1900	20	74.1	74.95
3	1900	20	75.6	74.95
4	1900	20	73.45	74.95
5	1900	20	74.82	74.95
6	2466	20	78.92	78.92
7	1334	20	15.12	16.56
8	1900	13	34.8	35.16
9	2300	25	80.24	79.76
10	1500	15	0	-0.97
11	1500	25	66.7	65.20
12	2300	15	72.56	72.61
13	1900	20	76.81	74.95

Table 4.24: ANOVA regression model of oil yield

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model (Y)	5	8911.30	1782.26	905.73	0.000
P	1	3886.44	3886.44	1975.07	0.000
t	1	2660.17	2660.17	1351.88	0.000
P^2	1	1288.25	1288.25	654.68	0.000
t^2	1	351.09	351.09	178.42	0.000
Pt	1	870.84	870.84	442.56	0.000
Lack-of-Fit	3	6.90	2.30	1.34	0.380
Pure Error	4	6.87	1.72	-	-

Table 4.25: Model summary

S	R^2	R^2(adj)	R^2(pred)
1.40277	99.85%	99.74%	99.33%

The model assumptions were verified based on the residual plots as shown in Fig. 4.39. The normal residual plot showed that the residuals were normally distributed close to the straight line. The random nature of residual distribution across the center line with no fixed pattern observed confirmed the principle of equal variance. Further, the random pattern observed for the residuals against the run order showed that the residuals were independent of each other.

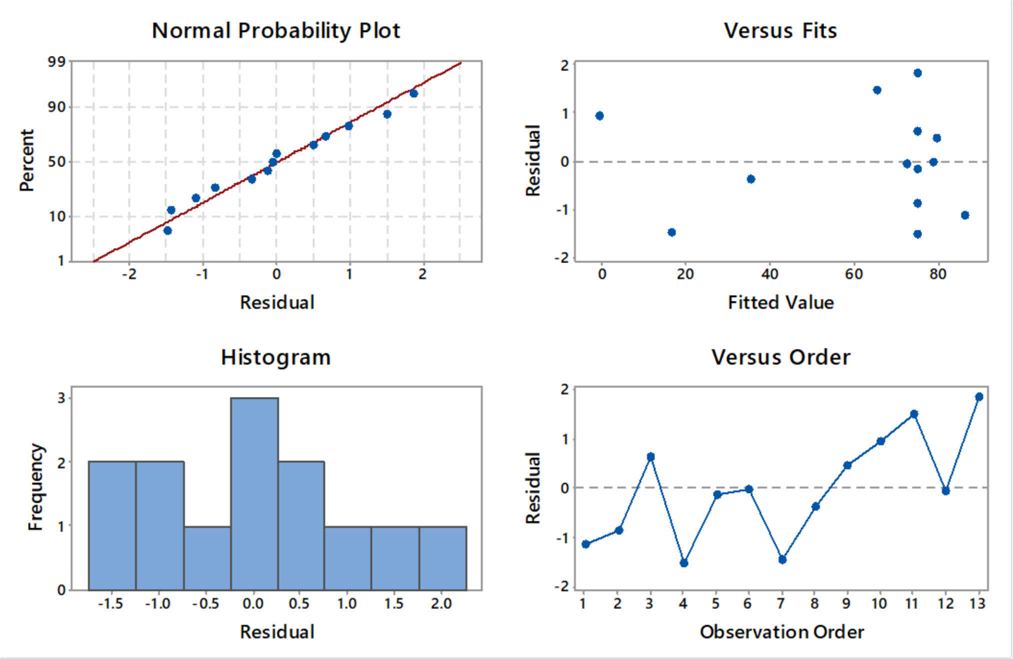
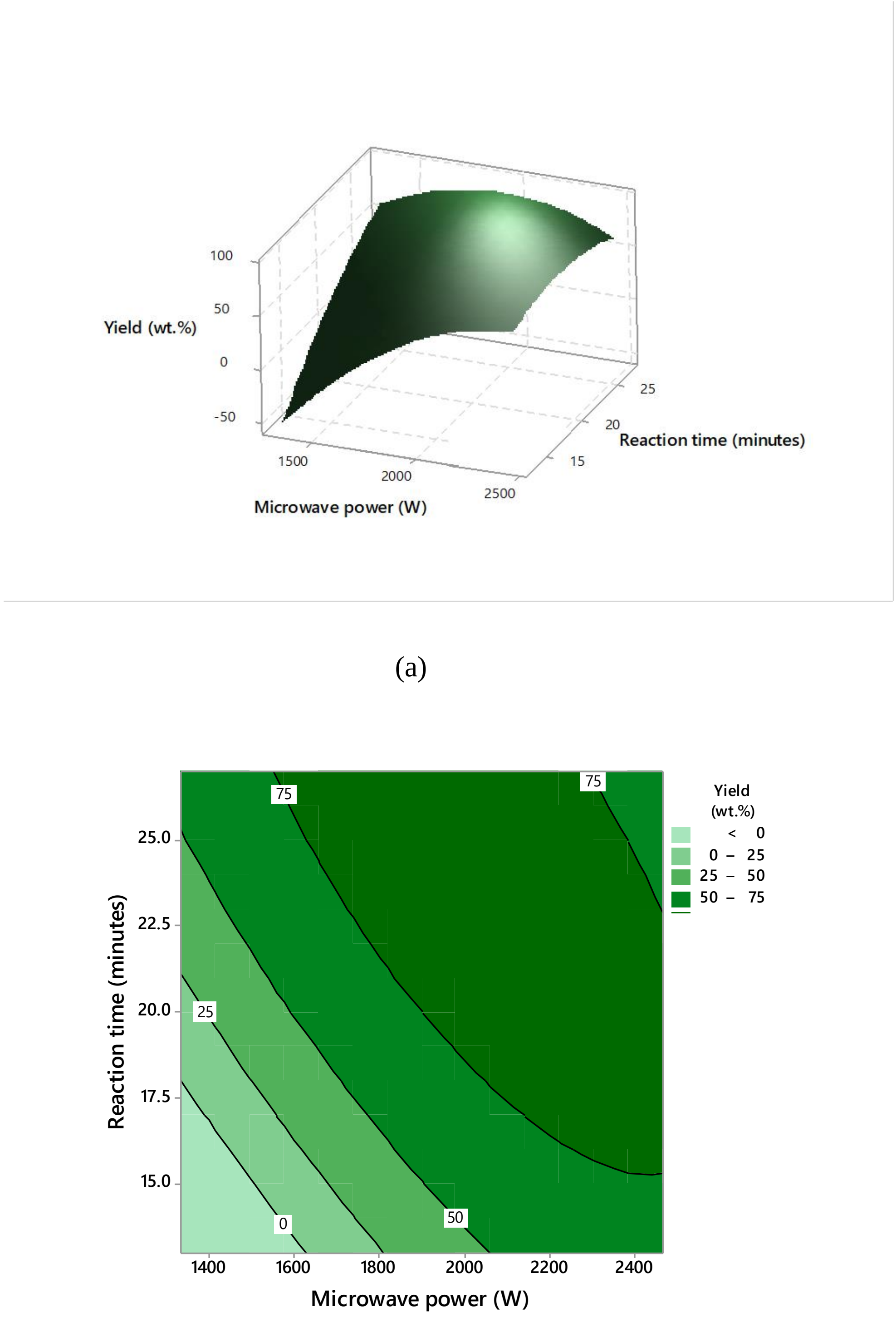


Figure 4.39: Residual plots for the oil yield

Figure 4.40 shows the response surface and contour plots of oil yield distribution. A high oil yield greater than 75% was observed in the range of 1548-2466 W and 15- 27 minutes. The optimal value of the oil yield was estimated by using the response optimizer function of the Minitab Software as shown in Fig. 4.41. The highest oil yield of 87 wt.% was predicted at an optimal value of 2008 W and 25 minutes. The optimal response was further validated through additional experiment under the optimal conditions. The experimental value of the oil yield was found to be 85.28 wt.% which was closer to the predicted value of 87 wt.%. Thus, the model was confirmed to be adequate within the experimental range of study.



(a)

(b)

Figure 4.40: (a) Response surface and (b) contour plot showing the effects of microwave power and reaction time on oil yield of PS

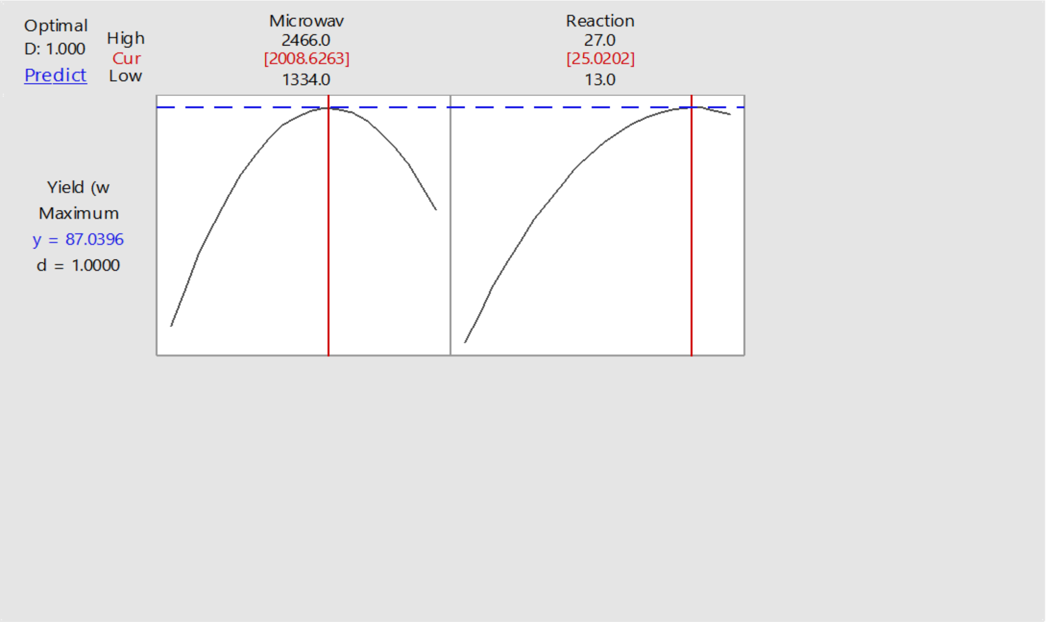


Figure 4.41: Optimization plot of maximum oil yield for PS

4.19.2 Response surface analysis for PP

The response surface analysis of microwave-metal interaction pyrolysis of PP was based on the central composite design of experiments. The detailed experimental design with observed and predicted response is presented in Table 4.26. The linear regression equation was developed for the response Y (wt.%) as:

$$Y_{oil} = -317.0 + 0.2468P + 6.05t - 0.000054P^2 - 0.0942t^2$$

$$-0.000086Pt \qquad (4.2)$$

The ANOVA for the regression model is presented in Table 4.27. The model showed insignificant lack of fit with p-value equal to 0.076 higher than 0.05 which highlighted the adequacy of the model in predicting the response within the experimental range of values. Further, the high value of R^2 equal to 99.17% (Table 4.28), reflected the capability of the model in explaining the variability of the response data. It was observed that the p-value for the interaction term (Pt) was greater than 0.05 making it insignificant while rest of the terms comprising P, t, P^2 and t^2, were all significant ($p<0.05$). As such, the insignificant term was removed using the backward reduction of the regression model presented in Equation (4.2). The new

ANOVA analysis for the reduced model along with model summary is presented in Tables 4.29 and 4.30).

Table 4.26: Experimental design values with observed and predicted oil yield

Run	Microwave power (W)	Reaction time (minutes)	Observed oil yield (wt.%)	Predicted oil yield (wt.%)
1	1500	20	10.9	13.02
2	1900	25	45.4	45.89
3	1900	25	47.22	45.89
4	1900	25	46.15	45.89
5	1900	25	44.25	45.89
6	2300	20	43.68	45.00
7	1334	25	7.82	6.01
8	1900	32	50.72	49.53
9	1900	18	34.86	33.01
10	1900	25	46.35	45.89
11	1500	30	23.51	24.83
12	2300	30	55.6	56.80
13	2466	25	52.42	51.26

Table 4.27: ANOVA regression model of oil yield

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model (Y)	5	2850.99	570.20	167.90	0.000
P	1	2046.19	2046.19	602.53	0.000
t	1	275.77	275.77	81.20	0.000
P^2	1	518.14	518.14	152.57	0.000
t^2	1	37.44	37.44	11.03	0.013
Pt	1	0.12	0.12	0.04	0.857
Lack-of-Fit	3	18.80	6.27	5.04	0.076
Pure Error	4	4.98	1.24	-	-

Table 4.28: Regression model summary

S	R^2	R^2(adj)	R^2(pred)
1.84282	99.17%	98.58%	95.08%

It can be observed here that all the modelled terms comprising P, t, P^2 and t^2 are now significant with p-value less than 0.05 with insignificant lack of fit ($p = 0.112$) which confirmed the significance of the model. The equation of the reduced model was established as:

$$Y_{oil} = -312.9 + 0.2446P + 5.89t - 0.000054P^2 - 0.0942t^2 \tag{4.3}$$

The high value of coefficient of determination R^2 equal to 99.17% (Table 4.30), showed that the reduced model was significant and finely represented the relationship amongst the independent variables.

Table 4.29: ANOVA reduced regression model of oil yield

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model (Y)	4	2850.87	712.72	238.66	0.000
P	1	2046.19	2046.19	685.18	0.000
t	1	275.77	275.77	92.34	0.000
P^2	1	518.14	518.14	173.50	0.000
t^2	1	37.44	37.44	12.54	0.008
Lack-of-Fit	4	18.91	4.73	3.80	0.112
Pure Error	4	4.98	1.24	-	-

Table 4.30: Reduced model summary

S	R^2	R^2(adj)	R^2(pred)
1.84282	99.17%	98.58%	95.08%

The residual plots of the regression model are presented in Fig. 4.42 . It can be inferred from the pattern of residuals in each plot that the model qualified all the necessary assumptions of equal variance, independence of the residuals and normal distribution. It was evident that the residuals were randomly distributed around the center line with respect to the fitted values and run order and were close to the straight line in the probability plot. Fig. 4.43 shows the response surface and contour plot generated by the model response function. The surface plot reflected the linear and quadratic effects leaving out the interaction effect based on the final reduced model as the interaction effect was found to be insignificant. The region of high oil yield for PP greater than 50 wt.% was observed in the range of 1909-2466 W and 23-32 minutes.

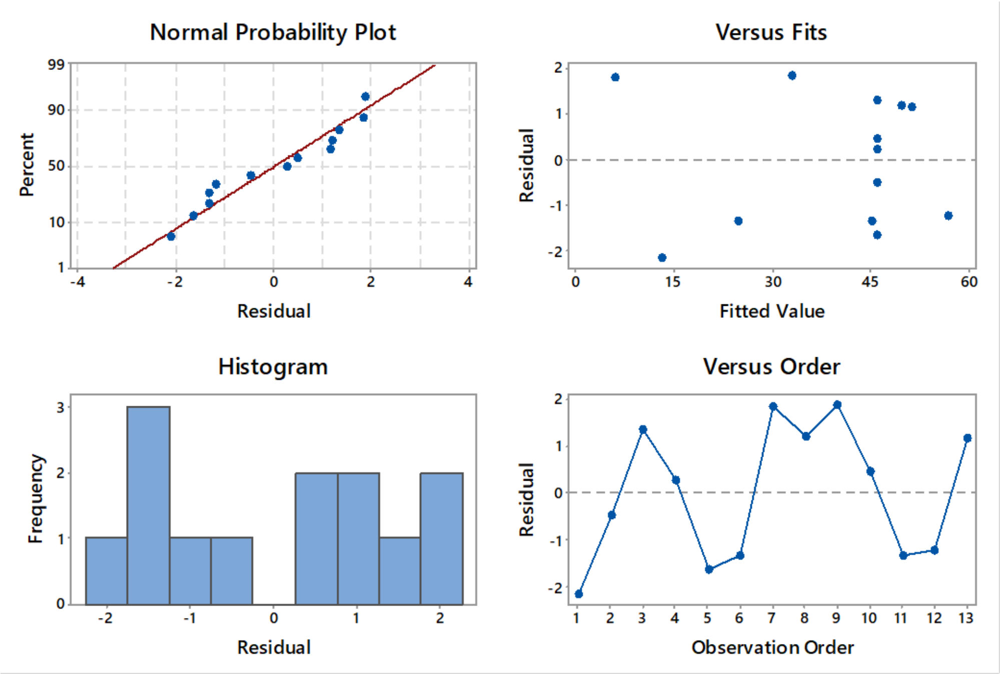
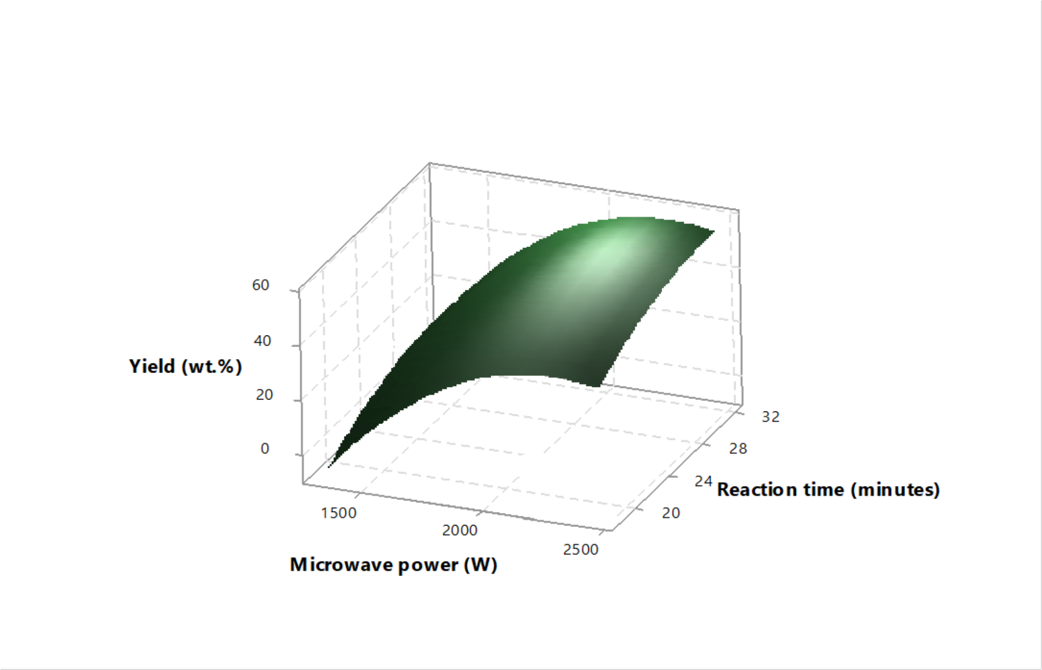
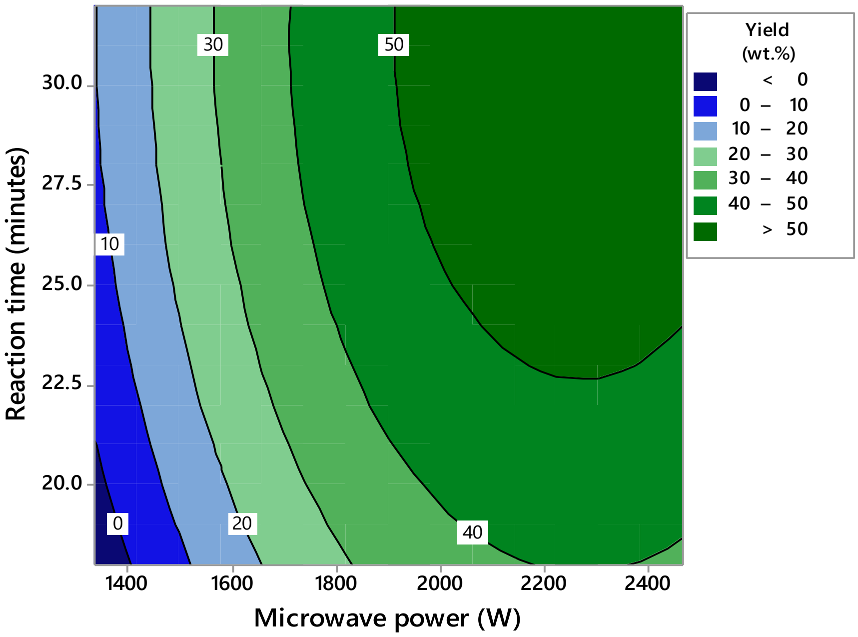


Figure 4.42: Residual plots for oil yield



(a)



(b)

Figure 4.43: (a) Response surface and (b) contour plot showing the effects of microwave power and reaction time on oil yield of PP

Figure 4.44 shows the optimization plot for maximum oil yield. The response optimizer function in Minitab was used to maximize the oil yield within the experimental range of both microwave power and reaction time. It was found that maximum oil yield of up to 57 wt.% was produced at an optimal microwave power of 2271 W and reaction time of 31 minutes. The optimal response was further validated through additional experiment under the optimal conditions. The experimental value of the oil yield was found to be 54.84 wt.% which was closer to the predicted value of 57 wt.%. Thus, the model for PP was confirmed to be adequate within the experimental range of study.

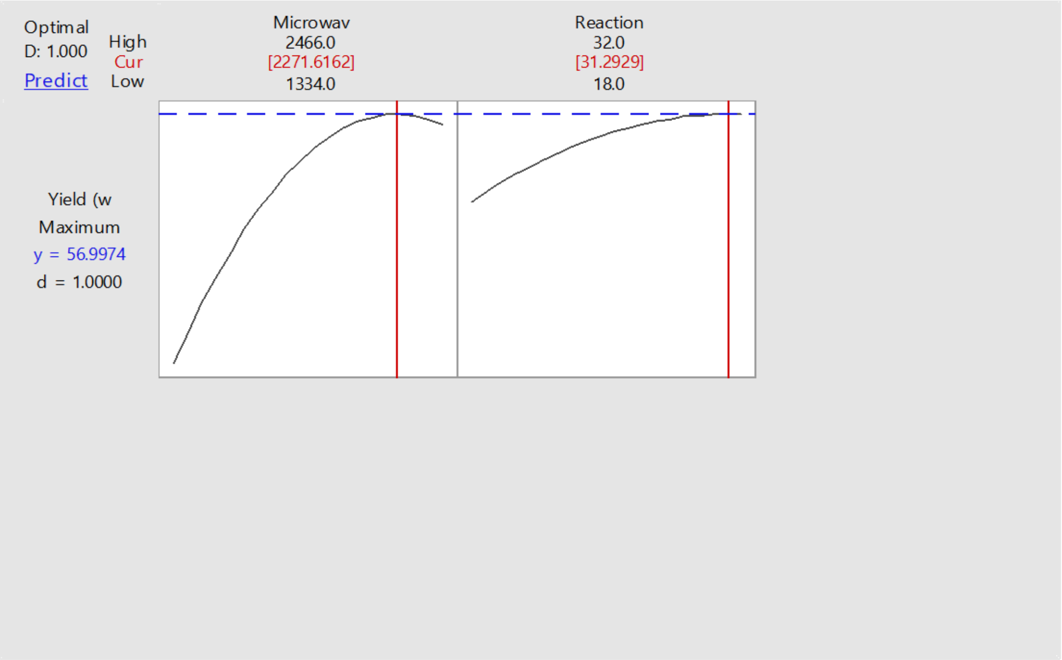


Figure 4.44: Optimization plot of maximum oil yield for PP

4.19.3 Response Surface Analysis for LDPE

The central composite design was applied to the microwave-metal interaction pyrolysis of LDPE to investigate the optimum operating conditions as was demonstrated in the case of PS and PP. The experimental design values of the independent variables with observed and predicted response is presented in Table 4.31. The model regression equation developed for the yield (Y) was:

$$\mathrm{Y_{oil}} = -27.5 - 0.0044\mathrm{P} + 0.74\mathrm{t} - 0.000002\mathrm{P}^2 - 0.0481\mathrm{t}^2$$
$$-0.001506\mathrm{Pt} \qquad (4.4)$$

The ANOVA for the regression model is shown in Table 4.32. It was observed that the p-value for the quadratic terms was higher than 0.05 which showed that the effect produced by such terms was insignificant and therefore, must be eliminated using backward regression as was done in the case of PP. Further, the high value of R^2 equal to 97.61% (Table 4.33), showed the capability of the model in explaining the variability of the response data. However, the lack of fit for the current model was significant with p-value equal to 0.046. It was therefore, expected that the removal of unnecessary terms will improve the fit of the model. The reduced model equation was developed as:

$$Y_{oil} = 9.6 - 0.0127P - 1.671t + 0.001506Pt \quad (4.5)$$

Table 4.31: Experimental design values with observed and predicted oil yield

Run	Microwave power (W)	Reaction time (minutes)	Observed oil yield (wt.%)	Predicted oil yield (wt.%)
1	1900	25	16.48	15.26
2	1900	32	23.11	23.59
3	1900	18	7.82	6.92
4	1500	30	6.85	8.21
5	1900	25	15.26	15.26
6	1500	20	0	2.33
7	2466	25	31.72	29.40
8	1334	25	2.46	1.12
9	2300	30	32.16	34.22
10	1900	25	16.75	15.26
11	1900	25	17.5	15.26
12	2300	20	13.26	16.28
13	1900	25	14.98	15.26

The reduced ANOVA model analysis (Tables 4.34 and 4.35) showed all terms to be significant with p-value greater 0.05 which included P, t and Pt. Further, the model lack of fit was improved after the reduction step from initial p-value of 0.046 to 0.054 which validated the model for precise prediction within the experimental set of values. The high R^2 value of 96.73% showed that the variation in response data can be explained by the model under study making it significant. Thus, the model adequately represented the interaction between the independent variables controlling the process.

Table 4.32: ANOVA regression model of oil yield

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model (Y)	5	1126.15	225.229	57.10	0.000
P	1	799.01	799.014	202.57	0.000
t	1	280.77	280.769	71.18	0.000
P^2	1	0.85	0.853	0.22	0.656
t^2	1	9.78	9.778	2.48	0.159
Pt	1	36.30	36.301	9.20	0.019
Lack-of-Fit	3	23.17	7.723	6.95	0.046
Pure Error	4	4.44	1.111	-	-

Table 4.33: Model summary

S	R^2	R^2(adj)	R^2(pred)
1.98605	97.61%	95.90%	85.13%

The model developed qualified the necessary assumptions of residuals based on the plots of Fig. 4.45. As in the case of PS and PP, LDPE model showed equally spread out residuals across the center line with respect to the fitted values, randomized pattern of residuals with the run order and normal distribution close to the straight line of the probability plot. The histogram represented the frequency of the residual values.

The response surface and contour plot in Fig. 4.46 shows the distribution of response values with respect to the operating conditions. It was evident from the surface plot that LDPE model generated a flat surface unlike PS and PP, where curvature in the response surface could be observed. The model of LDPE exhibited only the linear and interaction effects. It was observed from the contour plot that oil recovery increased with increase in microwave power and reaction time. The region with maximum oil recovery higher than 40 wt.% was very small as compared to PS and LDPE and was located in the range of 2358-2466 W and 30- 32 min.

Table 4.34: ANOVA reduced regression model

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model (Y)	3	1116.08	372.028	88.87	0.000
P	1	799.01	799.014	190.87	0.000
t	1	280.77	280.769	67.07	0.000
Pt	1	36.30	36.301	8.67	0.016
Lack-of-Fit	5	33.23	6.646	5.98	0.054
Pure Error	4	4.44	1.111	-	-

Table 4.35: Reduced model summary

S	R^2	R^2(adj)	R^2(pred)
1.98605	97.61%	95.90%	85.13%

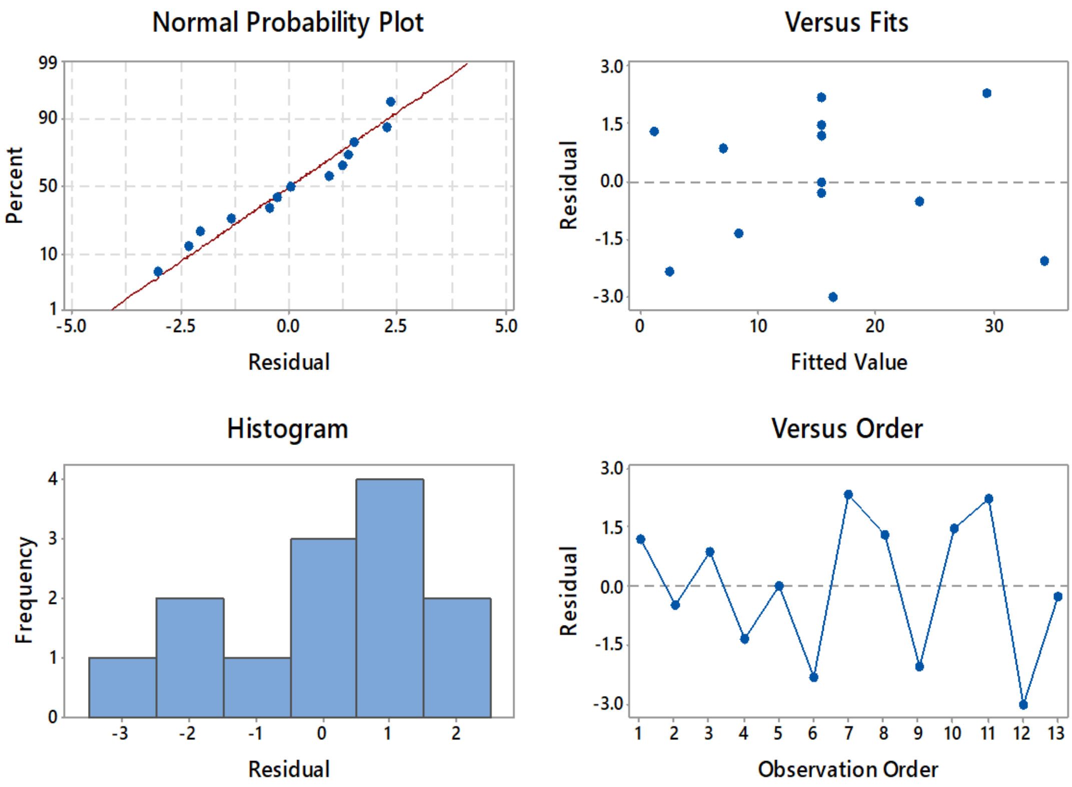
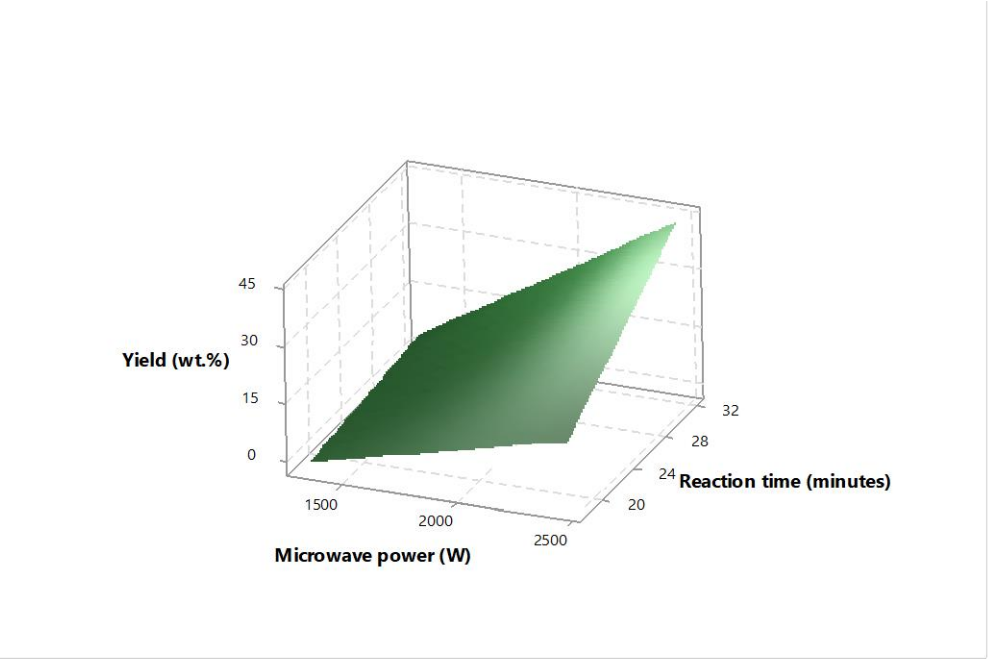
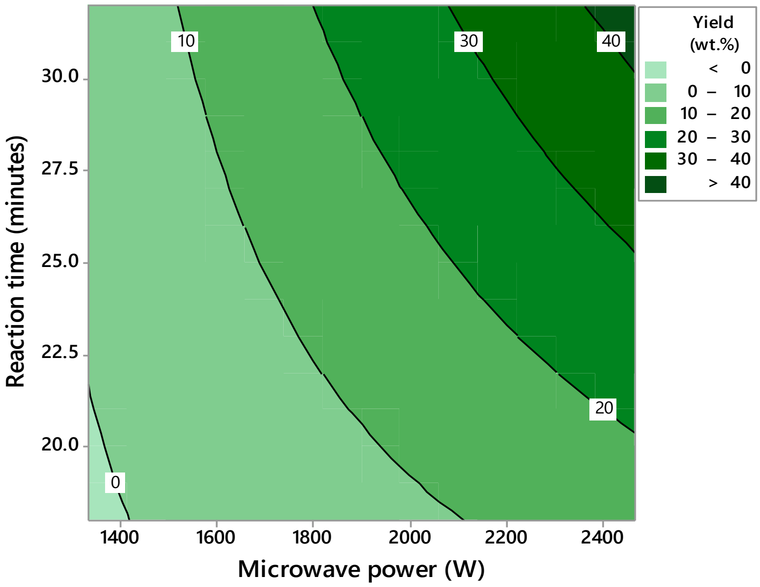


Figure 4.45: Residual plots for oil yield



(a)



(b)

Figure 4.46: (a) Response surface and (b) contour plot showing the effects of microwave power and reaction time on oil yield of LDPE

The optimization of the process model was performed using the response optimizer function of the software . The optimal value plot is presented in Fig. 4.47. It was found that the optimal operating values of the microwave power was 2466 W with a reaction time of 32 minutes that produced maximum oil yield of up to 43.69 wt.%. The model was validated by conducting the experiment at the optimal value of microwave power and reaction time which produced an oil yield of over 40.56 wt.% sufficiently close the predicted value of 4.69 wt.%. Overall, it can be inferred that the model developed was reliable for response prediction within the experimental range of the current device.

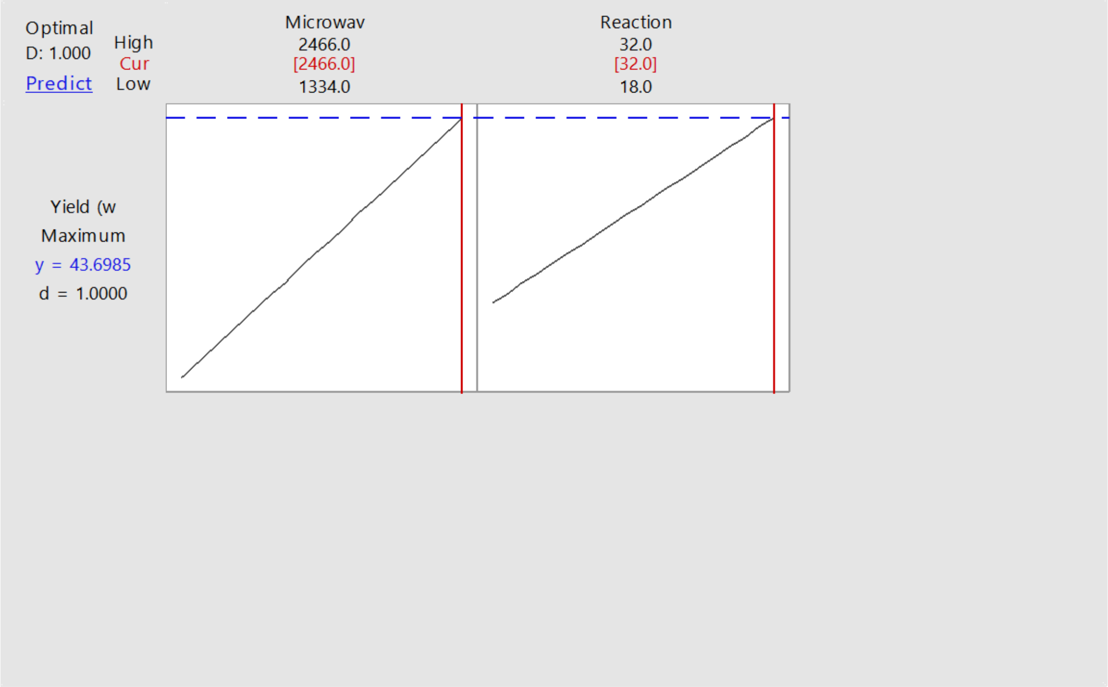


Figure 4.47: Optimization plot of maximum oil yield for LDPE

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

This chapter summarizes the key findings of the research work undertaken and comments on the research objectives that were achieved during the study. The chapter ends with recommendations for future works.

5.1 Dissertation Summary and Conclusions

The dissertation begins with preliminary characterization of model materials followed by stepwise analysis of different process parameters in line with the objectives of the study.

5.1.1 Preliminary Characterization

The initial investigation was conducted to determine the properties of the model materials which comprised measurement of calorific value, elemental analysis, proximate and TGA/DTG analysis. The plastics comprising PS, PP, LDPE, respectively, showed high calorific values in the range of 40-46 MJ/kg. The hydrocarbon content was found to be high in all the plastics with carbon and hydrogen in the range of 84-87 wt.% and 4-11 wt.%, respectively. The proximate analysis revealed a high volatile content in the plastics between 95-100 wt.%. The TGA analysis showed the thermal degradation range as: PS = (378- 439)°C, PP = (407-483)°C, LDPE = (420- 499)°C and PSW = (353-438)°C. The DTG peaks were found as: PS = 422°C, PP = 469°C, LDPE = 477°C and PSW = 425°C.

5.1.2 Temperature Profile of Heating Coil

The analysis of the iron coil temperature profiles for different plastics comprising PS, PP and LDPE, respectively, showed that the coil achieved maximum heating rate in the initial 5 minutes of microwave exposure beyond which no significant rise in temperature occurred with small fluctuations until the end of reaction period. Further, the fluctuations of temperature were observed to be the effect of trips and sparks caused by the interaction of microwaves with the thermocouple probe. The temperature profiles monitored during the study reflected the heating response of the metal coil.

5.1.3 Effect of Type of Metal on Coil Temperature

The effect of type of metal on coil temperature was also investigated by using iron coil and copper coils of the same size. The conductance of metal was observed to play an important role in achieving higher heating rates. The difference in heating profiles for the two coils was found to be significant based on the average temperature achieved by each coil at different microwave powers. The iron coil having lower conductivity than copper coil produced stronger skin effect generating higher amount of heat and consequently, higher temperatures and heating rates. Thus, it was confirmed that metal conductivity influenced the performance of the heating coil.

5.1.4 Effect of Microwave Power on Oil Yield and Reaction Time in the case of Individual Plastics

The effect of microwave power on the pyrolytic oil yield and reaction time was evaluated at different microwave powers and for each plastic comprising PS, PP and LDPE, respectively. A systematic set of experiments were conducted to achieve the stated objective. The study revealed that increase in microwave power produced an overall rise in the oil yield. The trends of oil recovery showed that PS released maximum oil followed by PP and LDPE. The oil yield observed for PS, PP and LDPE, under optimum conditions was 88.7 wt.% (2100 W), 54.65 wt.% (2500 W) and 30.15 wt.% (2500 W), respectively. The repeated skin effect caused by multiple reflections within the coil space and continuous focus of microwaves on to the GI pipe was observed to be principal mechanism for achieving fast pyrolysis. The process of microwave-metal interaction pyrolysis in the current study was achieved between 400 and 700°C under optimum conditions. Further, it was found that LDPE pyrolysis produced significant amount of waxes which adversely affected its oil yielding capacity. The conversion into oil and gas was found to be as high as 95-96 wt.% for PS and PP while LDPE achieved considerably low conversion of up to 54.3 wt.%.

The effect of microwave power on reaction time was observed to be a critical factor in evaluating the efficiency of the microwave-metal interaction pyrolysis process. It was found that PS achieved fastest oil recovery followed by PP and LDPE at optimum microwave power range of 2100-2500 W and reaction times of 20, 23 and 26 minutes, respectively. The heating rates observed in the current study were in the range of 50- 130 °C/min. The effect of microwave power on oil densities was also investigated for each plastic. It was inferred from the trends of density plots that PS released heavier oils whereas PP and LDPE generated comparably lighter oils.

5.1.5 Chemical Composition of Pyrolytic Oils recovered from PS, PP and LDPE

The chemical composition analysis of the pyrolytic oils found styrene monomer as the dominant species in PS oil whereas PP and LDPE oils were composed mostly of aliphatic class of hydrocarbons comprising cycloalkanes, alkenes, and alkanes. The pyrolytic oils were found to contain valuable hydrocarbons in the kerosene oil range C8-C16 which can be used directly as feedstock chemicals or as transportation fuels after treatment in the petrochemical refinery.

5.1.6 Effect of Microwave Power on Oil Composition

The effect of microwave power on the nature of pyrolytic oil was also investigated. It was found that rise in microwave power from 1900 to 2500 W did not alter the distribution of chemical compounds in PS oil as styrene monomer (C8) remained the dominant species. However, in the case of PP and LDPE, increase in microwave power from 1900 to 2500 W produced a lighter fraction from C11 to C9.

5.1.7 Effect of Microwave Power on Oil Yield and Reaction Time in the case of Plastic Blends

The effect of microwave power on oil yield and reaction time was also investigated for the case of plastic blends prepared with uniform proportion of mixture components. The average oil yield for the different plastic blends was found to be maximum for PS- PP (65.67 wt.%) followed by PS- PP- LDPE (57.23 wt.%), PS- LDPE (46.52 wt.%) and PP- LDPE (28.08 wt.%). It was concluded that blends comprising PS were more efficient towards higher oil yields. The mechanism responsible for this effect was the radical formation during pyrolysis of PS, that enhanced the conversion of PP and LDPE. As a result, the wax breakdown was improved giving higher oil yields.

Under optimum conditions between 2100 and 2500 W, the reaction times were found to be minimum for PS-PP-LDPE (20 minutes) followed by PS-PP (21 minutes), PS-PP (23 minutes) and PP-LDPE (26 minutes), respectively. The catalytic action of PS in the case of PS blends was found to be responsible for the reduction of pyrolysis reaction time. The blends composed of relatively higher content of LDPE was found to produce lower oil yields unlike blends made of larger proportion of PS and PP. During the chemical composition analysis, distribution of hydrocarbons present in the pyrolytic oils recovered from plastic blends were analyzed. The most abundant compounds showed the presence of aromatic species only in the oils recovered from blends made of PS. Other blends devoid of PS, produced major fraction of cycloalkanes or alkenes.

5.1.8 Effect of Microwave Power on Oil Yield and Reaction Time in the case of PSW and Chemical Composition

The effect of microwave power on oil yield, reaction time and density was also analyzed for waste PS (PSW) taken from post-consumed plantation cups and compared to pure PS. It was found that PSW produced lesser oil than virgin PS over the entire microwave power range of 1500-2500 W. Overall, PSW exhibited slower oil recovery with longer reaction times. It was further inferred that PS produced heavier oils than the waste PS (PSW). The chemical composition analysis showed that PSW produced comparably higher quantities of styrene monomer as compared to PS which also released other compounds in minor concentrations in addition to styrene.

5.1.9 Effect of Coil Gauge Size and Type of Metal on Oil Yield and Reaction Time

It was found that gauge size of the iron coil significantly influenced both the oil yield and reaction time of pyrolysis. The variation in oil yield was observed between 65 and 90 wt.% for three gauge sizes of 1 mm, 1.5 mm and 2.0 mm, respectively. It was concluded that increase in gauge size produced greater amount of heat that resulted in higher oil yield and lower reaction time of pyrolysis.

The effect of type of metal was found to play a critical role in controlling both the oil yield and reaction time in case of each plastic (PS, PP, LDPE). The copper coil showed poor performance as compared to iron coil due to its higher conductivity which produced a weaker skin effect that resulted in lower oil yield and higher reaction time.

5.1.10 Energy Efficiency of the Process

The energy efficiency of the microwave-metal interaction pyrolysis process was found to be maximum for PS at 26.75% followed by PP and LDPE at 14.78% and 7.01%, respectively. Further, the energy efficiency of the process was found to be directly proportional to the energy recovered in oil and inversely proportional to the microwave power and reaction time. Thus, PS demonstrated higher energy efficiency during microwave-metal interaction pyrolysis as compared to PP and LDPE.

5.1.11 Process Optimization for Maximum Oil Recovery

An experimental investigation based on response surface methodology was conducted on microwave-metal interaction pyrolysis process. It was important to ascertain the optimum conditions of process performance for each plastic. A central composite design model was developed for each plastic (PS, PP, LDPE) based on microwave power and reaction time as the independent variables and liquid oil yield as the response function. The conclusions were based on the ANOVA analysis, residual plots, response surface and contour plot, and the optimization plot. The model developed for oil yield for individual plastics was found to be significant and adequate in predicting the response within the experimental range of study. Further, each model qualified the assumptions of equal variance, independence, and normal distribution of the residuals. At the end, response function for each plastic was optimized for maximum oil recovery during microwave-metal interaction pyrolysis process. The model developed determined the favorable operating conditions of the experimental set-up required for maximum oil recovery in case of each plastic.

The optimal conditions established for each plastic were found as:

1. PS produced maximum oil of up to 87 wt.% at 2008 W and 25 minutes. The contour plot showed that high oil yield greater than 75 wt.% was produced in the range of 1548 to 2466 W with reaction time between 15 and 27 minutes.
2. PP produced maximum oil of up to 57 wt.% at 2271 W and 31 minutes. The contour plot showed that high oil yield greater than 50 wt.% was produced in the range of 1909 to 2466 W with reaction time between 23 and 32 minutes.
3. LDPE produced maximum oil of up to 43 wt.% at 2466 W and 32 minutes. The contour plot showed that high oil yield greater than 40 wt.% was produced in the range of 2358 to 2466 W with reaction time between 30 and 32 minutes.

5.2 Recommendations for Future Works

The recommendations were made based on the nature of the process and the design limitations:

1. The current study was conducted on a sample size of 20 g which was also the sample loading capacity of the GI pipe reactor. As a result, the useful oil produced by the microwave-metal interaction pyrolysis process only recovered around 26% of the input electrical energy, maximum for PS. Since the microwave cavity was relatively large, a significant portion of the microwave energy was wasted. Consequently, further improved designs can be developed for better utilization of the microwave energy by conducting pyrolysis of higher quantity of plastic which will not only increase the oil yield but also can improve the energy efficiency of the process.

2. It must be pointed out here, that increasing the sample size will also require large sized coil. In the current set- up, coil was fabricated from a low gauge wire of 1.5 mm subject to availability. The gauge size can be increased in future studies as higher gauge coil is known to produce significant improvement in the heating rates.

3. The process optimization performed on the current set-up, though, demonstrated the model to precisely predict the oil yield within the experimental range of study, a new input of observations beyond the experimental range can cause the model to predict differently from the real nature of response. The reason for this deviation is the spatial configuration of the microwave field which can vary for a new design as microwaves generate different field patterns due to multiple reflections from the cavity walls and specific geometry of the object being heated, especially when it is a metal as for the present study. Since, the current study undertaken involved optimization of microwave- metal interaction pyrolysis process that was done for the first time, it is suggested for extended studies on microwave- metal interaction pyrolysis to model the performance of the device for best results.

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