PYROLYSIS AND PYROLYSIS-CATALYSIS OF WASTE PLASTICS AND WASTE TIRES TO PRODUCE HIGH VALUE FUELS AND CHEMICALS

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The candidate confirms that the work submitted is her own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

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“The name of Allah, the most gracious and the most merciful”

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Author's Publications

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The candidate (Noof Alzahrani) carried out the experimental work and write the initial draft of the published paper. The co-authors, Prof. Paul Williams, and Dr. Mohamad Nahil supervised the work. Dr. Mohamad Nahil supervised the experimental part, Prof. Paul Williams made all the corrections and reviewing this published paper.

Abstract

This research focuses on the pyrolysis of waste plastic, waste tire, and 1:1 mixtures of tire and plastics using a fixed-bed reactor with the aim of determining the influence of co-pyrolysis on the yield and composition of the product oils and gases. The liquid oil produced from the pyrolysis of tires and polystyrene (PS) was mostly composed of aromatic compounds, such as BTEX, refers to benzene, toluene, ethylbenzene and xylenes; and PAHs refers to for example, naphthalene, anthracene, phenanthrene, pyrene and fluorene and their derivatives. The liquid oil formed from the pyrolysis of high density polyethylene (HDPE) and low density polyethylene (LDPE) was mostly waxes of high molecular weight consisting of aliphatic compounds, composed of a series of alkanes, alkenes, and alkadienes. Polypropylene (PP) produced more alicyclic compounds, such as methyl-cyclohexane. Polyethylene terephthalate (PET) pyrolysis oil consisted of compounds such as xylene and styrene but was mainly composed of oxygenated compounds, such as benzoic acid. Co-pyrolysis of 1:1 mixtures of tires and individual plastics involved interaction, resulting in significantly higher yields of gas than expected for all the plastic mixtures. The oil produced from the co-pyrolysis of the tire with polyalkene plastics showed interaction between the polymer pyrolysis products, resulting in higher yields of aliphatic compounds and lower yields for BTEX, PAHs, alicyclic, and aromatic compounds.

The study also investigated the pyrolysis-catalysis of waste plastic, waste tire, and a 1:1 mixture of the two materials using a two-stage fixed-bed reactor. ZSM-5 is used as a catalyst to investigate the influence on product distribution and composition of gases and oils. The results showed that pyrolysis-catalysis of tire over ZSM-5 reduced oil yield from 54.83 wt.% in thermal pyrolysis to 37.30 wt.% in pyrolysis-catalysis, with an increase in gas yield from 8.69 wt.% in thermal pyrolysis to 24.65 wt.% in pyrolysis-catalysis. Pyrolysis-catalysis of HDPE, LDPE, PP, and PS, also showed increased gas yields, mainly consisting of hydrocarbons (C_1-C_4), while decreasing oil production. PS produced the lowest gas yield, while PET produced the highest, with CO and CO_2 being the main gases generated. The pyrolysis of individual tire and plastic over ZSM-5 produced valuable chemicals such as benzene, toluene, ethyl benzene, xylenes, and styrene. The efficiency of ZSM-5 to minimize the heavy aliphatic fraction was high, on the other hand, the ZSM-5 with low deactivation by coke deposition and a high selectivity to produce light olefins.

The co-pyrolysis-catalysis of the tire and plastics with the ZSM-5 catalyst showed interaction between the tire and plastics which changed the composition of the product oils and gases over what would be expected from mere addition. Plastics co-pyrolysed with tire and the presence of ZSM-5 catalyst promoted the high production of the aromatic content, particularly BTEX compounds at the expense of aliphatic content. Tire/HDPE, Tire/LDPE, and Tire/PP mixtures showed a reduction in aliphatic and heavy molecular weight compounds when co-pyrolysed with tires, and the presence of a ZSM-5 catalyst increased the production of aromatic content, particularly BTEX compounds. Tire/PS mixture produced aromatic compounds, and the addition of the ZSM-5 catalyst increased aromatics at the expense of styrene. Tire/PET mixture produced BTEX and aromatic (refers to benzene derivatives, biphenyls, limonene, terphenyl, and indene compounds) due to the selectively of ZSM-5 that promotes the decarboxylation of the oxygenated compounds, and it gave high gas yields of mainly CO and hydrocarbons.

The pyrolysis-catalysis of waste plastic, waste tire, and 1:1 mixtures of tire and plastics was conducted over the MCM-41/ZSM-5 catalyst layer to determine the influence of two catalysts in series on oil and gas composition. The MCM-41 with a higher pore size was followed by ZSM-5 with a smaller pore size. The pyrolysis-catalysis process optimizes the conversion of plastic pyrolysis products to low molecular weight hydrocarbon fuels and chemicals. The production of gases during catalytic pyrolysis increases at the expense of oil yields, with oil yields of 39.50, 57.25, 53.50, 58.50, 77.00, and 36.75 wt.% for Tire, HDPE, LDPE, PP, PS, and PET, respectively. The highest hydrocarbon gases were produced from the tire and plastics while PET produced the highest gas yield with more CO and CO_2. Applying the two stages MCM-41/ZSM-5 has the advantage in the cracking of HDPE, LDPE, and PP. The primary products can pass through the large pores of MCM-41, then followed by ZSM-5 with (strong acidic sites and small pores) that promote the formation of light aromatic hydrocarbons and increased the production of BTEX.

The co-pyrolysis of tire/plastic mixtures over MCM-41/ZSM-5 catalyst in series showed an increase in gas yields compared to the individual tire and plastics results. The major influence of the co-pyrolysis was the reduction of paraffin and olefin compounds. According to literature, the high cracking of long chain polyolefins and the interaction between hydrocarbon radicals produced from tire rubber and the radicals produced from the thermal decomposition of PE and PP caused the reduction of both aliphatic and alicyclic contents in the mixtures of Tire/HDPE, Tire/LDPE, and Tire/PP. Tire/PET showed negative values of interaction for the oxygenated compounds.

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Abbreviations

BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
BR	Butyl Rubber
CAGR	Compounded Annual Growth Rate
CHNS	Carbon, hydrogen, Nitrogen and Sulphur Analysis
DCM	Dichloromethane
ELT	End-of-Life Tyre
ETRMA	European Tire & Rubber Manufacturers Association
FCC	Fluid Catalytic Cracking
FID	Flame Ionization Detector
GC	Gas Chromatography
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
MCM-41	Mobil Composition of Matter No. 41
MS	Mass Spectrometry
NIST	National Institute of Standards and Technology
NR	Natural Rubber
PAH	Polyaromatic Hydrocarbons
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
RF	Response Factor
SBR	Styrene Butadiene Rubber
TCD	Thermal Conductivity Detector
TGA	Thermogravimetric Analyser
ZSM-5	Zeolite Socony Mobile

Chapter 1: Introduction

1.1 Waste hydrocarbons

1.2 Plastic waste management

Plastics are a specific type of solid waste made from synthetic polymers derived from petroleum-based hydrocarbons [1], and they are also made from a variety of soft synthetic or semi-synthetic organic materials that are moulded into solid objects of various shapes[2]. Tires are made from natural and synthetic rubber, fabric, wire carbon black, and chemical compounds [3, 4].
Plastics play a significant role in human daily lives, and their increasing reliance is justified by their versatility, light weight, and low production cost in comparison to other traditional substances such as wood, concrete, and metal[5]. Thus, plastics are widely used in a variety of industries, including construction, engineering applications, automotive, electronics, medical, packaging, food, and other applications[5,6].

Waste plastic has negative issues due to incorrect disposal that can cause environmental pollution[2]. For example, 6.3 billion tons of plastic waste was generated in the last six decades, and 60% has been accumulated in waste landfills[7,8]. The environmental impacts of plastic wastes have been associated with water pollution and air pollution through landfill and incineration[9,10] as well as increasing the risk of fire and human health hazard [11]. Moreover, microplastics derived from waste plastic disposal in the marine environment are transferred to the food chain and can enter the human body through the ingestion of fish or marine organisms[9,12]. The management of plastic waste needs more attention as it becomes a serious global issue that requires control, as well as effective waste management[2]. In 2020, the European Union (EU27+3) collected more than 29 million tonnes of plastic post-consumer waste. It was also reported that one-third was delivered to recycling facilities around the EU27+3, while more than a quarter was disposed of in landfills, and more than 40% was diverted to energy recovery operations[13]. Furthermore, Figure 1.1 shows the annual growth rate over the period of 2006-2020 for the management of end life plastics, which shows a reduction in the disposal of these wastes in landfill which is about 46.4%. Moreover, recycling and energy recovery increased during the period of 2006-2020 by around 117.7% and 77.1% respectively[13].

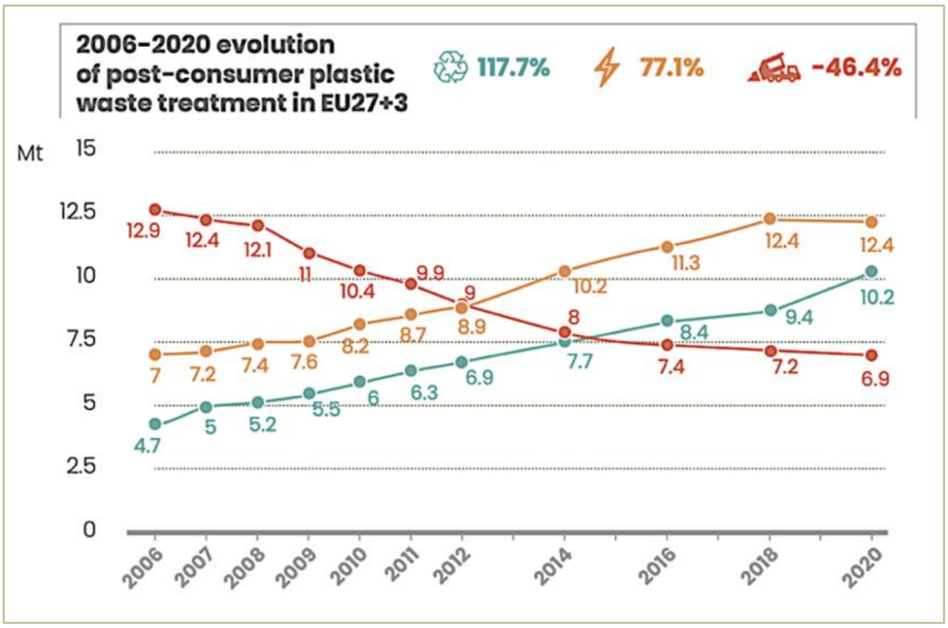


Figure 1.1 Plastic post-consumer waste and the annual growth rate over the period of 2006-2020 for the management of end life plastics [13].

1.2.1 Plastic production and demand

The economy and the population has grown over the years, which results in an increase in the need for plastics[5] . For example, the worldwide plastic market was valued at USD 568.9 billion in 2019 and is predicted to increase at a compounded annual growth rate (CAGR) of 3.2 % from 2020 to 2027 [14] when the pandemic of Coronavirus (COVID-19) started which has had a significant effect on the issue of plastic waste [14,15]. It was reported that worldwide plastic packaging industry would expand at an annual growth rate of 5.5 %[14]. According to Plastics -the Facts 2021[13], the total plastics demand reached 49.1 million tonnes in 2020. According to Plastics-the Facts 2024[16] , the European plastic production reached 54 million tonnes in 2023 with 79.4% from fossil based sources, as shown in Figure 1.2(a). Polypropylene was the most produced plastic at 15.7%. Figure 1.2 (b) shows the total global plastics production in 2023 which was 413.8 million tonnes.

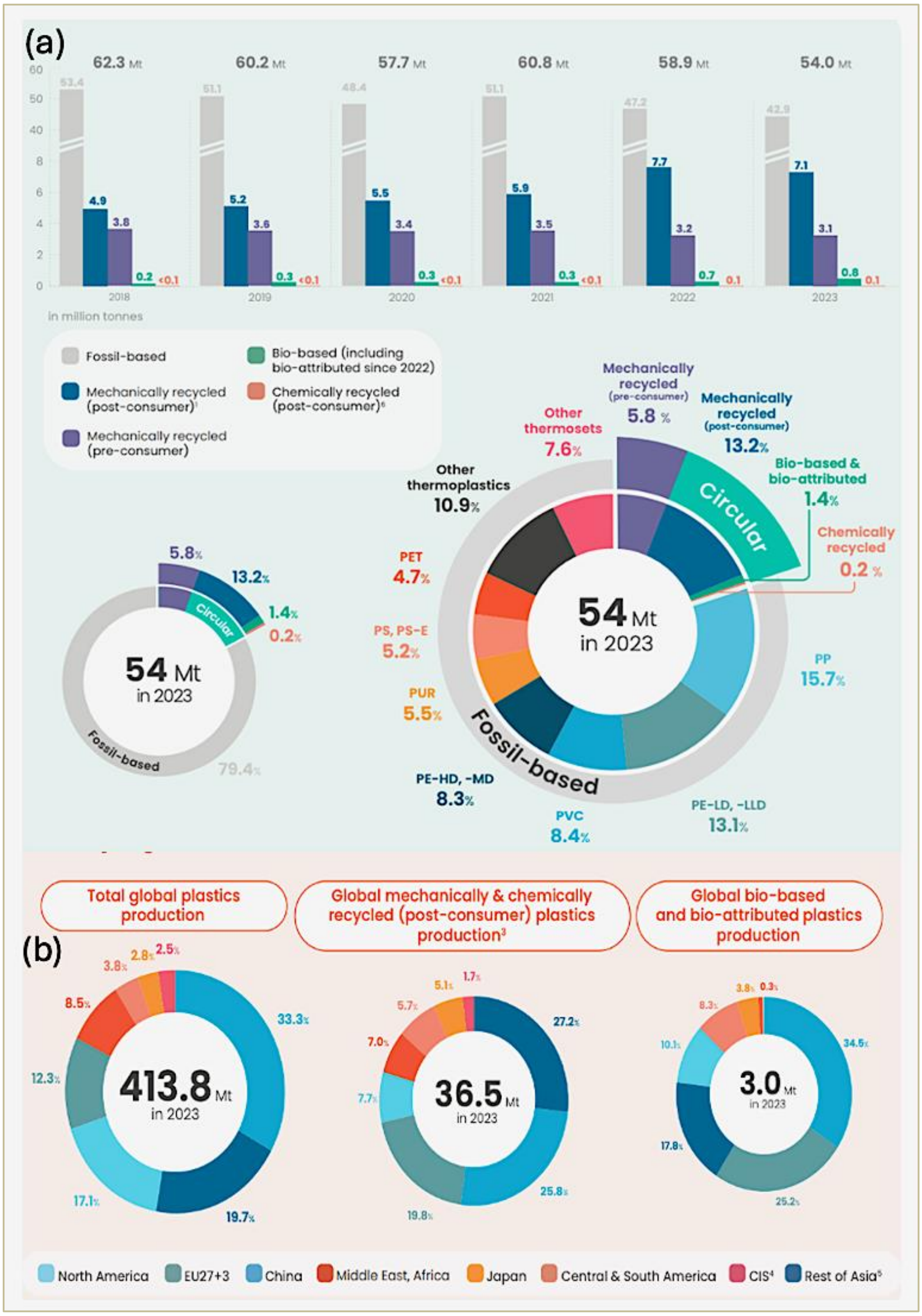


Figure 1.2 Plastics production in 2023, (a)European plastic production, (b) global plastics production and the production source [16].

1.3 Tire waste management

As the global economy has grown and the development of the transport industry, the production of tires is increasing each year[17]. European Tyre & Rubber Manufacturers

Association (ETRMA) has reported that about 289 million tires in the European Union were sold every year, which was around 20% of the world market[18] . ETRMA has compiled statistics on End-of-Life Tyre (ELT) management for 2020 and 2021, that includes 32 countries (EU28, Norway, Serbia, Switzerland, and Turkey)[19] as shown in Figure 1.3.

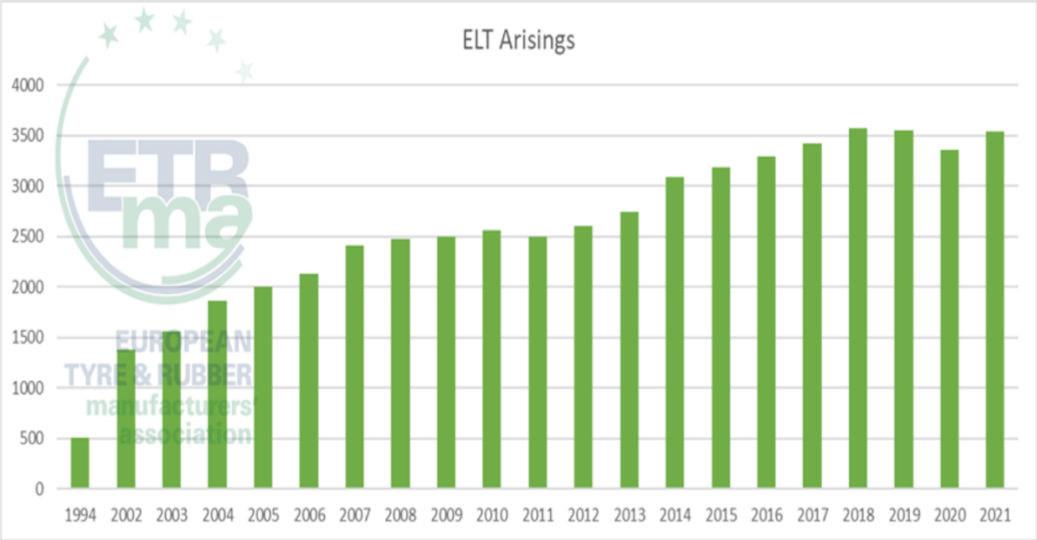


Figure 1.3 The End-of-Life Tire (ELT) management (recent data recorded 2020 and 2021)[19].

About 75% of the end life tires were disposed globally in landfill, resulting in significant concern on the environment and the high risk of fires and pollution. Recently, several countries have paid more attention to the management and recycling approaches for waste tires [17,20]. For example, the rate of recycling waste tires in countries such as USA, Canada, Australia, UK, Germany, Japan, China, and India has increased in the recent years. The practice of recycling increased in Germany, China, Australia, Japan, and Canada which reported at 100%, 94%, 85%, 84%, 81%, respectively[3]. The tire's end of life depends on the recycling application in the manufacturing industry. For example in the concrete industry, the crumb rubber is commonly used to replace aggregates, that will increase using tires in construction, and reduce environmental impacts of landfill[3].

1.4 Challenges and prospects

Plastic waste is a major concern, and authorities are attempting to limit single-use plastic usage[21]. End-of-life tires can be treated and the into rubber particles e.g., rubber chips, crumbs, and powder recovered, as well as the steel and nylon reinforcement wires[3]. The demand of these martials has increased with crumb rubber commonly utilized as an aggregate replacement in concrete. Plastic and tire waste are a major issue that require an efficient recycling procedure. Improvements in recycling infrastructure, technology, and consumer education can result in improved recycling rates, and decreasing the amount of waste transported to landfills and incineration facilities[21]. Mechanical recycling is the physical conversion of plastic and tire waste into new product without affecting their chemical structure. Thermochemical conversion procedures include the chemical transformation of plastic and tire waste into useful products using heat and chemical reactions. Gasification refers to heating plastic waste to high temperatures, resulting in syngas that may be utilized as fuel or feedstock. Pyrolysis, on the other hand, degrades plastic into smaller molecules, resulting in pyrolysis oil, gas, and char[21] .

1.5 Waste plastics and tires as an alternative source of value-added chemicals and energy

Many researchers considered waste plastics as an essential resource to create new raw chemical materials through the chemical recycling to extract value from waste[14]. Plastic waste can be converted to a secondary raw material such as monomers or pyrolysis oil. On the other hand, recycled waste material can produce new plastics, and the pyrolytic oil can be chemically treated through a steam cracker that can replace fossil-based feedstocks [14]. Recently, the research focus has been more on fuels such as hydrogen[22,23] gasoline[24,25], and ultra-low sulphur diesel [25] that are produced from plastic wastes and recycled plastics. Furthermore, producing cleaner fuels with a high molar ratio of hydrogen to carbon is one of principal goals of waste conversion processes to fuels, with the aim of reducing fossil fuel consumption[25]. Pyrolysis is an effective process for waste reduction and energy densification of the conversion products[26].

Utilizing waste tires as energy sources, is advantageous [27]. For example, waste tires can be used as an alternative fuel in cement kilns to generate energy [27]. This source of energy in the cement industry, makes it a cost-effective way to meet their high-temperature requirements. In the United States, it has been predicted that 53% of used tires can meet the fuel demand [28], and that has been applied in the cement and paper industries that use scrap tires for 68 % of their energy demands [27].

1.6 Pyrolysis

Plastic and tire wastes are converted into gases, oil, and char through pyrolysis at temperatures of around 500–650 °C for plastics, while at 300–900 °C for tire in an oxygen-free environment with or without catalyst[6,27]. Researchers are currently focused on pyrolysis of plastic waste and tires to produce liquid fuels in order to address the depletion of liquid fossil fuels [29]. The oil produced by the pyrolysis process contains more contaminants and residues[30,31]. As a result, the catalytic technique is preferred to upgrade the quality of the pyrolysis oil [6,29]. Pyrolysis and catalytic pyrolysis will be investigated in this project as well as the influence of parameters such as, temperature, type of feedstock, and the type of catalyst on the product yield. Figure 1.4 shows the pyrolysis process (thermal and catalytic)[6].

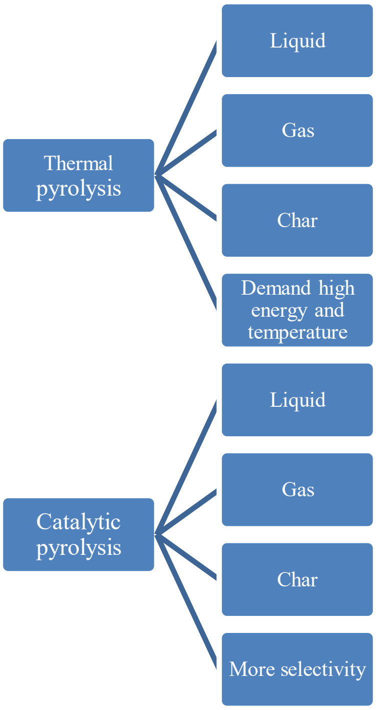


Figure 1.4 Classification of pyrolysis processes[6].

1.7 Research aim

Plastics and tire are the two major solid wastes which can be efficiently co-pyrolyzed to produce liquid fuels with valuable compounds such as, benzene, toluene, and xylene. The co-pyrolysis also enhances energy recovery and reduce the economic process of the individual pyrolysis of waste plastic and tire.

The aim of this research is to investigate the interaction of waste tires and waste plastics during pyrolysis and pyrolysis-catalysis to produce high value fuels and chemicals.

1.8 Research objectives

[1] Pyrolysis of polymeric plastics and tire waste for the production of higher value liquid fuels and chemicals, investigating the pyrolysis process. To understand the changes in composition due to interaction of waste plastics and waste tires during pyrolysis.

- Using tires, plastics, and mixtures (tire and plastic).
- Investigate the influence of process parameters on the yield and composition of the product oils, such as using different type of plastics with tire
- Analysing the products particularly oil and its quality in terms of chemical composition (e.g., benzene, xylene, toluene)
- Investigate the synergetic value (tire-plastic co-pyrolysis interaction effects).

[2] Pyrolysis with catalytic upgrading of polymeric waste for the production of higher value liquid fuels and chemicals, investigating the pyrolysis-catalysis process. To understand the changes in composition due to interaction of waste plastics and waste tires.

- Investigate the influence of process on the yield and composition of the product oils, such as the type of catalyst that was used to enhance the pyrolysis-catalysis process.
- Investigate the influence of catalysts on the yield and composition of the product oils.
- Investigate the synergetic value (tire-plastic co-pyrolysis interaction effects), to understand the impact of mixing waste tire with different plastics in relation to the yield and composition of the product oils and gases.

Chapter 2: Literature Review

2.1 Introduction

The utilisation of waste plastic for energy production by pyrolysis, which turns low-grade and non-biodegradable plastic wastes into liquid oils, syngas, and char is of growing research interest [32]. This method, which alleviates the global energy problem and lowers the environmental impact of waste[33,34], is gaining traction in research[35]. In this chapter, the literature related to the pyrolysis and pyrolysis-catalysis of waste plastics and waste tires is reviewed, in relation to the production and composition of liquid oils and gases.

2.2 Properties of plastics

The two main types of plastic are thermoplastics which soften when heated and harden again when cooled and thermosets which harden by curing and cannot be re-moulded. Thermoplastics are by far the most common types of plastic comprising almost 80% of the plastics used in Europe, they are also the most easily recyclable. Thermoplastic polymers can be recycled through various methods to produce fuel or valuable products [36]. As plastics are polymeric chains, they are categorized as linear, branched, or cross-linked, depending on the structural form[37,38]. The most common plastics found in municipal solid waste are high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) [36], which will be discussed in detail in this review.

The ultimate and proximate analysis have been reported for different types of plastics which are presented in Table 2.1 and 2.2[5,39,40]. These plastics are the main solid wastes that are going to be investigated in this research. Plastics contain high volatile matter content which is above 90 wt.% as well as high carbon and hydrogen that make plastic waste an ideal for pyrolysis in terms of producing large amounts of liquid oil and gas [39].

Table 2.1 Ultimate analysis of different plastic wastes [40].

Plastic Types	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur
HDPE	78	13	4	0.06	0.08
PP	84	14	1	0.02	0.08
PS	90	9	1	0.07	0.08
PET	77	13	5	0.20	NA

Table 2.2 Proximate analysis of various plastic types[5].

Plastic Types	Moisture Content	Fixed Carbon	Volatile Matter	Ash Content
HDPE	0.0	0.3	99.8	1.4
LDPE	0.3	0.0	99.7	0.4
PP	0.2	1.2	97.8	1.9
PS	0.3	0.2	99.6	0.0
PET	0.5	7.8	91.8	0.1

2.2.1 Polyethylene

Around 100 million tons per year of polyethylene $(C_2H_4)_n$ is produced worldwide, it is the cheapest and most produced type of plastics and is mostly comprised of HDPE and LDPE [41]. HDPE is one of the most versatile of plastics and used in detergent containers and bags [37]. HDPE is higher in density, which ranges from 0.93 to 0.97 g/cm^3. It also has strength and tolerance to several solvents, while LDPE's chemical structure consists of many branches, resulting in relatively lower density (0.91-0.94 g/cm^3) [13,37] as shown in Figure 2.1. LDPE is used in food packaging, and grocery bags, and is considered stable to acids, bases, alcohols, and esters while it has less stability to active oxidants, aromatic, and aliphatic hydrocarbons [42].

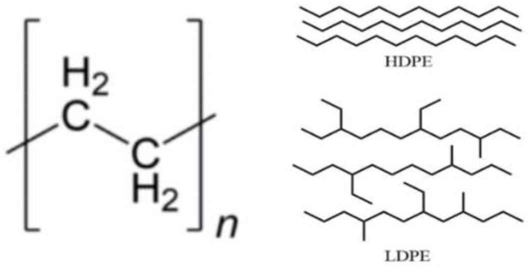


Figure 2.1 Structure of polyethylene (a) HDPE and (b) LDPE.

2.2.2 Polypropylene

Polypropylene (pp) $(C_3H_6)_n$ is a polymer in a linear hydrocarbon chain, it has a lower density (between 0.90 and 0.92 g/cm³)[13] than HDPE, higher softening, rigidity, and toughness [37]. It has weaker chemical resistance to active oxidants and non-polar solvents[37]. However, PP is resistant to the non-oxidising acids and bases, fats, and organic solvents. It is used in packing products, storage boxes, plastic mouldings, plastic tubs, stationary folders, non-absorbable sutures, diapers, car bumpers, pails, carpets, and furniture[2,43]. Figure 2.2 shows the structure of PP.

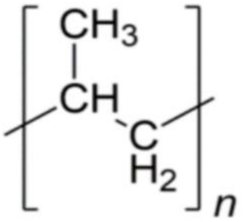


Figure 2.2 Structure of polypropylene.

2.2.3 Polystyrene

Polystyrene (PS), $(C_8H_8)_n$, is also known as (polyvinyl benzene) [37]. Its heat resistance, as well as its reasonable durability, strength, and lightweight, make this polymer ideal for usage in a wide range of industries, including food packaging, electronics, construction, medical, appliances, and toys [38]. Figure 2.3 shows the structure of PS with the monomer styrene (C_8H_8) as repeating unit.

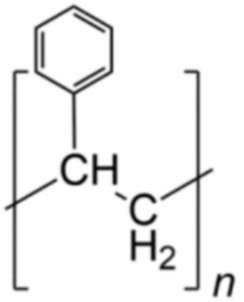


Figure 2.3 Structure of polystyrene.

2.2.4 Polyethylene terephthalate

Polyethylene terephthalate (PET), $(C_{10}H_8O_4)_n$ is a semi-crystalline polymer and is considered one of the world's largest manufactured thermoplastics[37,38]. PET has great mechanical properties and low manufacturing costs, thus is used for bottle applications, electrical insulation, printing sheets, magnetic tapes, X- ray and other photographic films [44]. Figure 2.4 shows the PET structure.

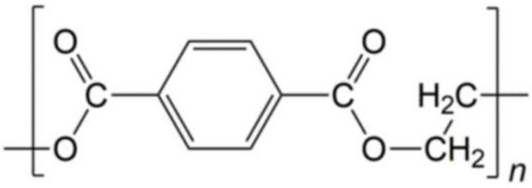


Figure 2.4 Structure of polyethylene terephthalate.

2.3 Pyrolysis of waste plastics

Pyrolysis is a technique for plastic waste treatment to produce liquid oil as the source of energy as well as the gases and char [45]. These products can be used directly to produce clean energy[46]. The pyrolysis process depends on thermal cracking in an inert atmosphere with or without a catalyst at temperatures above 400 °C resulting in breakdown of the long chain polymer into smaller hydrocarbon molecules [37,39,45,47]. Pyrolysis can be classified into slow, fast, and flash which is depended on the performed heating rate and temperature [33]. In slow pyrolysis process, temperatures between 350 and 550 °C are applied to produce liquid oil, gas, and char, the production may be varied according to the feedstock and the working conditions [33]. Fast pyrolysis is operated at temperature ranges between 500 and 700 °C, and the main product of fast pyrolysis is liquid[33]. Flash pyrolysis takes place at temperature above 700°C, and that can meet high production of gases[33].

2.3.1 Pyrolysis mechanism of the waste plastics

The degradation mechanism plays a significant role in the pyrolysis of plastic waste. Pyrolysis of the plastic produces free radicals[2,47,48]. Then several reactions take place via scission reaction at the beta position of the polymer chain which produces small chain hydrocarbons with a higher amount of H^+ as free radical[47]. At low pyrolysis temperature, the degradation is usually followed by end-chain beta scission compared to the random chain as it requires less energy to breakdown, resulting in producing more non-condensable hydrocarbon gases [47]. Random and end chain beta scission reaction produces a pyrolytic oil (C_6-C_{34}). Radical recombination (depolymerization) followed by intramolecular hydrogen shift results in the formation of olefins[47]. At higher temperatures, polymer degradation is mediated by side chain elimination followed by alpha scission process creating heavier hydrocarbon fractions in the pyrolytic oil, which can be validated by the presence of wax components [47]. The breaking of the sigma bond (sp^2 bond) generally occurs due to alpha scission which utilizes a high amount of dissociation energy compared to beta scission [47]. For example, the thermal degradation of the polyethylene polymer is complicated, but the initiation reactions that occur in the reactor can be explained in the following equations [37].

- End-chain scission or unzipping (depolymerisation)

$$M^*_n \rightarrow M^*_{n-1} + M \tag{2.1}$$

$$M^*_{n-1} \rightarrow M^*_{n-2} + M \tag{2.2}$$

- Random-chain scission or fragmentation

$$M^*_n \rightarrow M_x + M_y \tag{2.3}$$

When the thermal degradation of PE by the random chain scission mechanism occurs, then free radical fragments are produced [47,48]. The hydrogen chain transfer reactions also occur, these free radical fragments can form a wide range of hydrocarbons such as alkanes (C_1-C_{60}), alkenes and alkadienes [48]. Sakata et al. [49] and Vasile et al. [50] reported that PE produced long chain hydrocarbons and that may depend on the reaction conditions. As shown in Figure 2.5, conventional pyrolysis of HDPE involves random chain scission, which consists of three steps: initiation (the formation of a radical), propagation (via intramolecular and intermolecular hydrogen transfer), and finally termination through recombination of the free radicals to form alkanes, alkenes, and dienes. In a linear hydrocarbon chain, the fourth carbon typically has the weakest C-C bond. This means that the chain will break far from its end, resulting in larger molecules. This mechanism explains the low gas yields produced from the thermal pyrolysis of polyethylene[51].

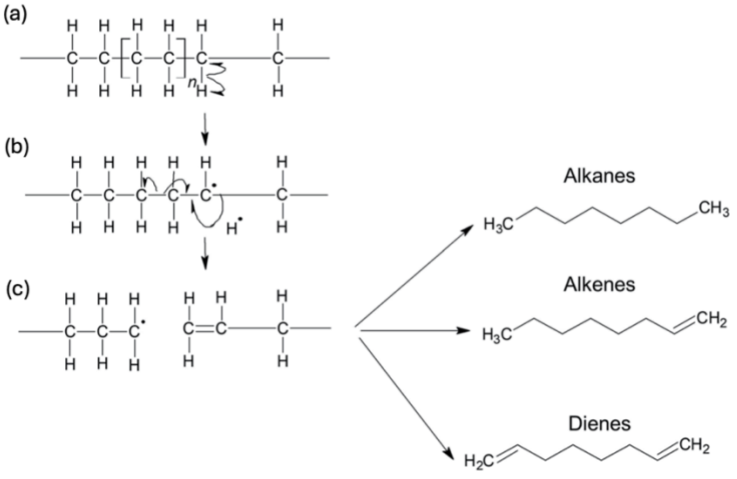


Figure 2.5 Schematic representation of the random chain scission mechanism of high density polyethylene, (a) initiation, (b) propagation, and (c) termination. Adaptation of[51,52].

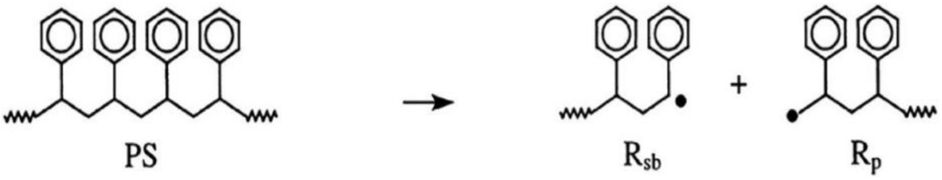
Similarly, PP also follows the random chain scission degradation that produces the free radicals which beta scission to produce monomers stabilized by intramolecular or intermolecular hydrogen transfer [35,47]. However, it is suggested that end chain scission to be the possible mechanism, when the carbon alpha end groups are large, such as the methyl group in polypropylene or the phenyl group in polystyrene, as the intermolecular hydrogen transfer (which is required for the random scission) and this step becomes difficult (steric hindrance), which leads to depolymerisation or unzipping (end chain scission) and increased monomer yield[51,52].

In the case of PS, the thermal degradation is started by end chain scission, and beta scission occurs as PS degrades at a lower temperature compared to PE [47]. The side elimination and the aromatic polymer structure of PS lead to produce high concentrations of the aromatic products particularly styrene[53]. Two mechanisms such as end chain scission and random scission that occur as the initial step during PS degradation [54]. The following equations demonstrate the PS degradation mechanism [47].

End chain scission mechanism

(2.4)

Random chain scission mechanism



(2.5)

The thermal degradation of PET follows the random scission of the chain which occurs at the ester linkage, resulting in carboxyl and vinyl ester groups [55]. Martin-Gullon et al. [56] and Holland and Hay [57] reported that the thermal decomposition of PET undergoes two main parts and that includes intramolecular back biting, and C–H hydrogen transfer [55]. Figure 2.6 presents the degradation mechanism of PET [57].

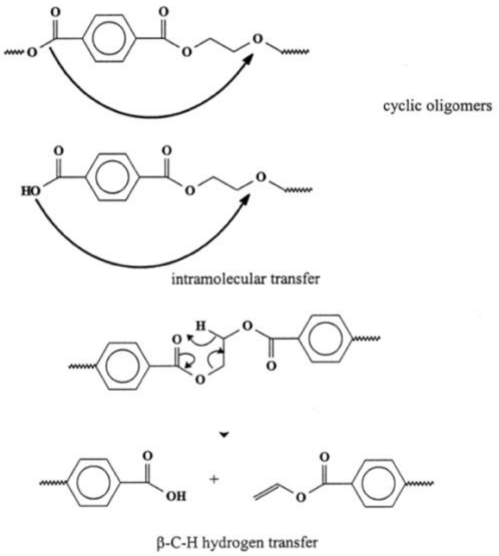


Figure 2.6 Degradation mechanism of polyethylene terephthalate. Adaptation of [44,57].

2.3.2 Thermal degradation of waste plastics

The thermal degradation of the plastics is very important for the study of waste pyrolysis and can be investigated using thermogravimetric analysis (TGA). This thermal analysis process depends on the weight loss during the increase in temperature in an inert atmosphere. The TGA produces two types of thermogram (TG): (i) the first TG curve measures the weight change of the substance with temperature and time [58]. While (ii) the second differential mass loss (DTG) curve gives information on the degradation steps. These indicators can explain the optimum temperature ranges when the substance starts the thermal degradation, the peak temperature of weight loss and the end of the degradation process [38].

The thermal degradation of polyethylene terephthalate determined by TGA showed that the thermal degradation of PET occurred over a temperature range of 350–520 °C [38]. In the case of HDPE, the study by Chin et al. [59] showed that the HDPE thermal degradation started at 378–404 °C. Marcilla et al. [60] reported the maximum degradation rate of HDPE appeared at 467 °C [38,60]. However, Ahmed et al. [61] found that the highest thermal degradation of HDPE occurred at 350 °C with high liquid yield (80.88 wt.%). Chin et al [59] investigated the conditions of HDPE thermal degradation using TGA at different heating rates in the range of 10–50 °C min^{-1}, and it was found that high heating rates can speed up the weight loss, resulting in the increases in the rate of reaction. Polypropylene has a lower thermal degradation temperature than HDPE according to Marcilla et al. [60] who reported the maximum degradation for PP at 447 °C due to the composition of PP which allows the formation of tertiary carbocation when the degradation occurred [38,62]. Jung et al. [62] investigated the influence of temperature on HDPE and PP pyrolysis in a fluidized bed reactor, they reported that the primary degradation of HDPE and PP occurred between 400 and 500 °C, based on derivative thermogravimetry analysis (DTG) curves. However, it was demonstrated that the weight loss of the PP fraction started at lower temperatures below 400 °C when compared to the HDPE fraction [38].

Polystyrene has the lowest degradation temperature of municipal solid waste plastics and was investigated by Onwudili et al. [63]. They found that the PS produced a highly viscous dark-colored oil at a temperature of 350°C and the highest liquid oil yield was achieved at 425 °C [63]. Consequently, the thermal degradation temperature of PS was in the range of 350–500 °C. TGA was performed for each type of plastic waste to identify the optimum temperature for thermal degradation. Miandad et al. [64]reported the thermal degradation profile for each type of plastic. Figure 2.7 shows the maximum degradation in the temperature range of 420–490°C, PS and PP show a single step decomposition, while PE and PET obtained a two-stage decomposition [64]. The thermal degradation of plastics from the higher to lower degradation temperatures is following this order PE>PET>PP>PS.

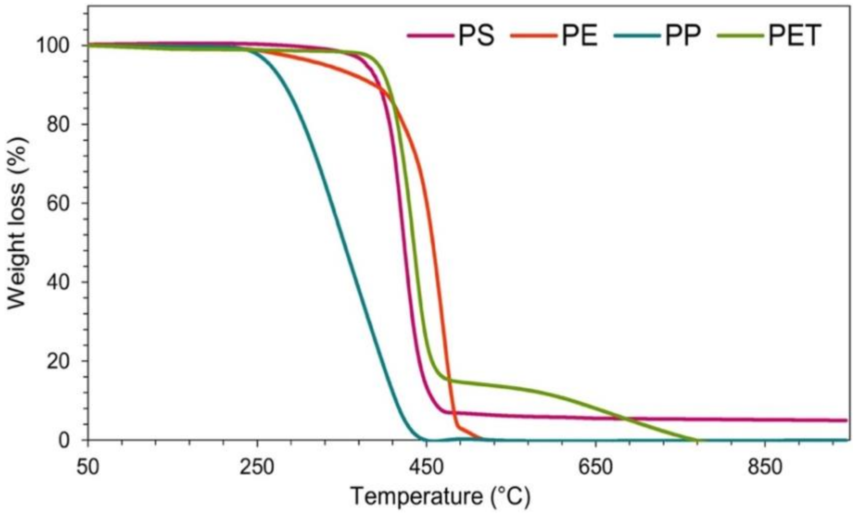


Figure 2.7 Thermogravimetric analysis (TGA) of PS, PE, PP, and PET plastic waste. Adaptation of [64].

2.3.3 Product yield distribution of pyrolysis of waste plastics

The product yield distribution is mainly dependent on the operating conditions through the pyrolysis process that is required to produce significant yields of the target product. The pyrolysis of each type of plastic produces oil, gas, and char yields that may have a variation in quantity and quality, which is reported in various studies [45,65,66]. Liquid oil is considered the essential product of the pyrolysis of different types of plastics, as it can be produced in high yield of up to 95 wt.% [66]. The thermal degradation of plastics produces an oil/wax product which depends on the pyrolysis temperature and the temperature of condensation. For example, it has been reported that pyrolysis of PE produced wax instead of liquid oil and that was attributed to long carbon chain that is present in the PE structure [45,66]. PS showed the maximum yield of liquid oil (80.8 wt.%); less yields were reported for gases (13 wt.%) and char (6.2 wt.%) in comparison to other types of plastic waste [65]. Onwudili et al. [63] report a very high liquid oil yield of about 97 wt.% at an optimum temperature of 425 °C, while the gas yield was very low at around 2.5 wt.%. Thermal pyrolysis of PP produced relatively less amounts of liquid oil (42 wt.%) and char (3.5 wt.%) along with high yield of gases (54.6 wt.%) [45,67]. Generally, the pyrolysis of HDPE, LDPE, PP, PS, and PET was shown to produce gas compounds which include hydrogen, methane, ethane, ethene, propene, propane, butane and butene. PET produced more CO_2 and CO due to the presence of oxygen in the polymer structure[67]. Generally, the oil produced from the plastic waste consists of aliphatic, mono-aromatic and poly-aromatic compounds which are produced through the degradation of the carbon bonds, which includes radical reactions, hydrogen transfers, cyclization, and aromatization reactions [62,67].

2.3.3.1 Influence of plastic types on product distribution and composition

It is important to investigate the impact of several plastic waste types, including PS, PE, PP, and PET, on the yield and quality of generated products, particularly liquid oil[45]. Each type of plastics will be discussed in more detail.

Polyethylene:

Kumar and Singh [58] investigated the thermal pyrolysis of HDPE using a semi-batch reactor at higher temperature range of 400–550 °C and reported that the highest liquid yield was obtained at 79.08 wt.%, and gas yield at 24.75 wt.% at a temperature of 550 °C. Wax was obtained along with oil consisting of gasoline, kerosene, and diesel type fractions. Marcilla et al. [68] have conducted the pyrolysis of HDPE at 550 °C, and they reported the production of the oil yield was 84.7 wt.% and gas yield at 16.3 wt.%. Mastral et al. [69] have examined the pyrolysis of HDPE in a fluidized bed reactor at 650 °C, they reported the oil and gas yields at 68.5 wt.% and 31.5 wt.%, respectively. The characteristics of the oil indicated by Sharma et al. [24] using a batch reactor for pyrolysis of HDPE, showed the liquid yield was 74 wt.% which was characterized by the presence of aliphatic, olefin, and aromatic hydrocarbons were 96.8 wt.%, 2.6 wt.%, and 0.6 wt.% respectively. The HDPE liquid oil has a high aliphatic concentration which is approximately 90 wt.% due to the HDPE structure [62].

Pyrolysis of LDPE has been investigated in different studies in terms of producing high oil yield, as the structure of LDPE has more branching as compared to HDPE that leads to weaker intermolecular force [26]. Bagri and Williams [70] investigated the pyrolysis of LDPE in a fixed-bed reactor at 500 °C [70], and a high liquid yield of 95 wt.% was reported with low gas yield and low char yield. Marcilla et al. [68] carried out for the pyrolysis of LDPE, also using a batch reactor at 550 °C, the liquid yield was shown to be 93.1 wt.%. Another study at a temperature of less than 500 °C was conducted by Onwudili et al. [63] , where they investigated the product yield in a pressurized autoclave batch reactor (0.8–4.3 MPa) for LDPE pyrolysis at 425 °C, the product yields were observed for liquid, gas, and char and were reported as 89.5, 10, and 0.5 wt.% respectively. It has been shown that the oil produced from the pyrolysis of LDPE was mainly aliphatic compound composed of alkanes, alkenes, and alkadienes [71]. The concentration of aliphatic chemicals decreased as the temperature was increased. However, aromatic compounds had the reverse impact when the temperature was raised as compared to aliphatic compounds. The concentration of aromatic compounds (benzene and toluene) increased dramatically as the pyrolysis temperature was increased. At temperatures ranging from 500 to 550°C, the liquid oil contained no aromatic or polyaromatic hydrocarbons. However, increasing the temperature to 700 °C resulted in a considerable rise in single ring aromatic compounds and polycyclic aromatic compounds which were approximately 25 wt.% of the liquid oil composition. Jaafar et al.[72] reported the oil composition of HDPE, and they found that linear aliphatic hydrocarbon from C_8-C_{26} were produced with triple peaks comprising alkanes, alkenes and alkadienes as shown in Figure 2.8.

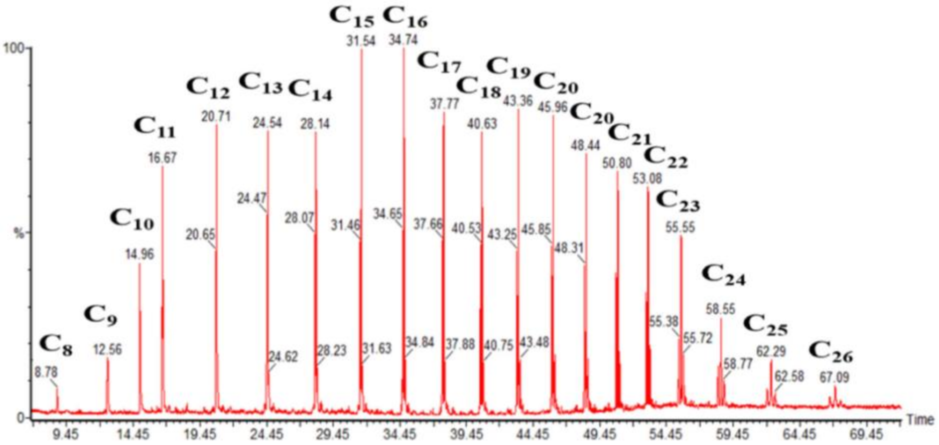


Figure 2.8 GC/MS chromatogram of HDPE pyrolytic oil at 450 °C. Adaptation of [72].

Polypropylene:

Several studies have investigated the pyrolysis of polypropylene (PP) to optimize its products particularly the oil yield. Ahmad et al. [61] reported the pyrolysis of PP at temperatures of 250 – 400 °C in a steel micro reactor. The results showed that 69.82 wt.% of liquid oil was produced at a temperature of 300°C. Sakata et al. [73] have investigated PP pyrolysis at 380°C and showed a higher liquid yield of 80.1 wt.%, 6.6 wt.% of gas yield and 13.3 wt.% solid residue. Another pyrolysis study of PP pyrolysis has been conducted by Fakhrhoseini and Dastanian [74], they reported a higher liquid yield of 82.12 wt.% when the pyrolysis temperature applied was 500 °C, but at higher temperature > 500 °C they observed a reduction in the liquid yield. Demirbas [75]pointed out the PP pyrolysis at high temperature of 740°C in a batch reactor which resulted in 48.8 wt.% liquid, 49.6 wt.% gas, and 1.6 wt.% char.

Polypropylene has low density and is easily degraded by following the chain scission mechanism of C-C bonds. Furthermore, the high branching in PP as well as the presence of tertiary carbons in the polypropylene structure is substantially higher than in polyethylene, thus PP has lower thermal resistance and is degraded at lower temperatures[61,76]. Moreover, heavy liquid hydrocarbons were the main product of polypropylene pyrolysis at degradation temperatures of less than 500°C.

Polystyrene:

As previously mentioned, PS has the lowest degradation temperature at 350 °C compared to other plastics, thus it requires lower temperature of pyrolysis compared to the other plastics. For example, Onwudili et al. [63] used the batch pressurized autoclave reactor to investigate the pyrolysis of PS at 300–500 °C for one hour duration. They found that PS pyrolysis generated a very high liquid oil yield about 97wt.% at optimum temperature of 425°C, while the gas yield was very low at around 2.5 wt.%. The production of the high yield of liquid oil was also shown by Liu et al. [77] investigating the pyrolysis of PS using a fluidized bed reactor at temperatures of 450–700°C, and they reported the high liquid oil yield at 98.7 wt.% at 600°C. However, the study by Demirbas [75] reported a lower liquid oil yield at 89.5 wt.% when the pyrolysis temperature was at 581°C in a batch reactor. The highest liquid oil yield was produced by the pyrolysis of PS at higher temperatures due to the formation of styrene. Because of the structure of polystyrene and the presence of a phenyl group in the structure, aromatic compounds account for more than 90% of the pyrolysis products[78,79].

Liu et al. [77] reported the composition of the pyrolysis oil from PS as mainly styrene and monoaromatics which were the main components in the liquid oil which comprised around 80 wt.% in the liquid fraction. According to Onwudili et al. [63] the major components in the PS oil product that increased with temperature were benzene, toluene, and ethyl benzene. Furthermore, styrene monomer decreased with temperature, implying that the styrene radical produced during the PS degradation process was highly reactive, decreasing in concentration at higher temperatures.

Styrene was reported as the main product by Scott et al.[80] with other aromatic compounds which included toluene, ethylbenzene, propenyl benzene, propynyl benzene, and naphthalene.

Polyethylene terephthalate:

Cepeliogullar and Putun [44] have investigated the pyrolysis of PET to produce liquid oil using a fixed-bed reactor at 500°C. The gas yield was 76.9 wt.%, while the liquid oil yield was 23.1 wt.%. A higher amount of liquid oil was reported by Fakhrhoseini and Dastanian [74] where the reported yields for liquid, gas, and char were 39.89 wt.%, 52.13 wt.%, and 8.98 wt.% respectively. The thermal degradation mechanism principally decomposes and separates terephthalic acid and benzoic acid, with the benzoic acid entering the decarboxylation step to produce acetophenone. Artetxe et al. [81] found that benzoic acid and acetylbenzoic acid were the most prevalent products in thermal degradation products at a pyrolysis temperature of 600 °C, and that higher temperatures boosted acetophenone yields. The polymer structure of PET with the C-O bonds along polymer chains, are weaker and most likely affected by thermal cleavage, followed by degradation to phthalic and benzoic acid, possibly converting to benzene with CO_2 release at higher temperature [82] as shown in Figure 2.9.

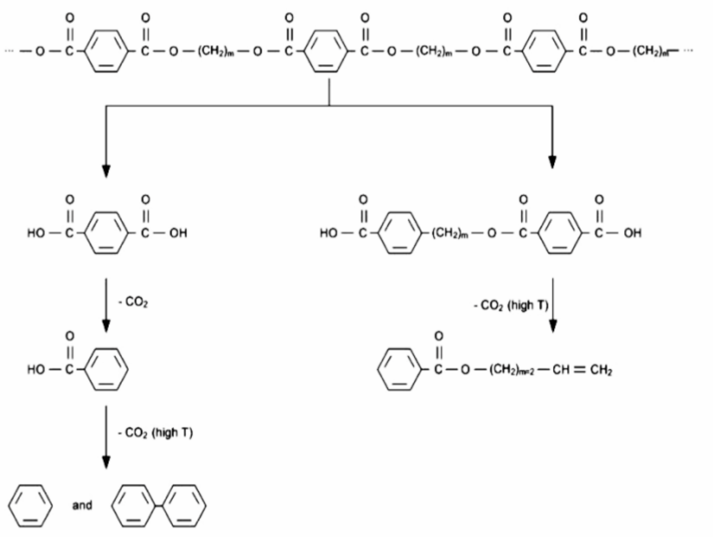


Figure 2.9 PET and its most likely thermal cleavage mechanisms to various products. Adaptation of[82].

2.3.3.2 Influence of temperature

Temperature is the essential parameter in pyrolysis which is controlling the cracking reaction of the polymer chain. The product yields of the plastic pyrolysis mainly depend on the operating temperature range during the process. Several studies investigated temperature through the plastic pyrolysis to evaluate the yields particularly the oil yield and its quality.

The pyrolysis temperature of different type of plastics ranges from 300 to 500 °C[38,46]. For example, Miandad et al.[83] reported the effect of temperature on PS conducted at different temperatures (400 °C, 450 °C, and 500 °C), at 75 minutes of reaction time in a batch pyrolysis reactor. At lower temperatures 400°C, highest char yield was obtained (16%), while the gas and liquid yields were 8% and 76% respectively. At higher temperatures 500°C, the highest gas yield was obtained of 16.8 %, while the lowest yield was reported for char 4.5%. At 450°C, gas and char yields were reported 13.1% and 6.1% respectively, while liquid oil reached the maximum yield 80.8%. Figure 2.10 shows the main compounds in the liquid oil (toluene, ethyl benzene, and styrene), particularly the styrene yield, was increased with temperature and time, but beyond a certain temperature and time, the oil yield and styrene yield decreased. This was attributed to various secondary reactions take a place after reaching optimum temperature [84,85]. Gas production increased at higher temperature which was confirmed by several studies [86,87], and that due to the strong cracking of C-C bonds that encouraged the production of lighter hydrocarbons.

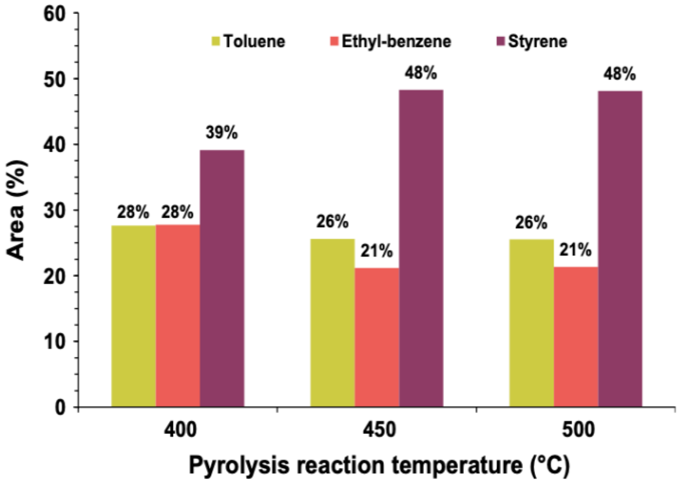


Figure 2.10 Effect of temperature on composition of polystyrene pyrolysis oil, and the main compounds were included toluene, ethyl benzene, and styrene). Adaptation of [83].

Table 2.3 shows the distribution of the product yields with operating temperature for PP and HDPE [61].

Table 2.3 Effect of temperature on product yields from pyrolysis of PP and HDPE [61].

Plastic types	Temperature °C	Total yield (wt.%)	Liquid (wt.%)	Gas (wt.%)	Char (wt.%)
PP	250	86.32	57.27	29.05	13.68
	300	98.66	69.82	28.84	1.34
	350	97.74	67.74	30.00	1.56
	400	94.3	63.23	31.07	5.7
HDPE	250	ND	ND	ND	ND
	300	66.95	30.70	36.25	33.05
	350	98.12	80.88	17.24	1.88
	400	99.46	54.17	45.29	0.54

Jaafar et al.[72] investigated the pyrolysis of polystyrene at 450 °C, 500 °C, 550 °C, and 600 °C, using a tubular semi-continuous reactor under an inert nitrogen atmosphere. When the temperature was increased from 450 °C to 600 °C, the concentration of styrene increased from 40 wt.% to 60 wt.%. Similarly with other compounds, BTX obtained at temperatures over 550 °C, reaching a concentration of 3 wt.% at 600 °C. A similar trend was observed in all other compounds, whereas di-aromatic concentration decreased dramatically from 50 wt.% to 24 wt.%, and a slight increase was noticed for mono-aromatic compounds. Figure 2.11 shows the main oil compounds obtained from the pyrolysis of polystyrene with temperature ranging from 450-600 °C.

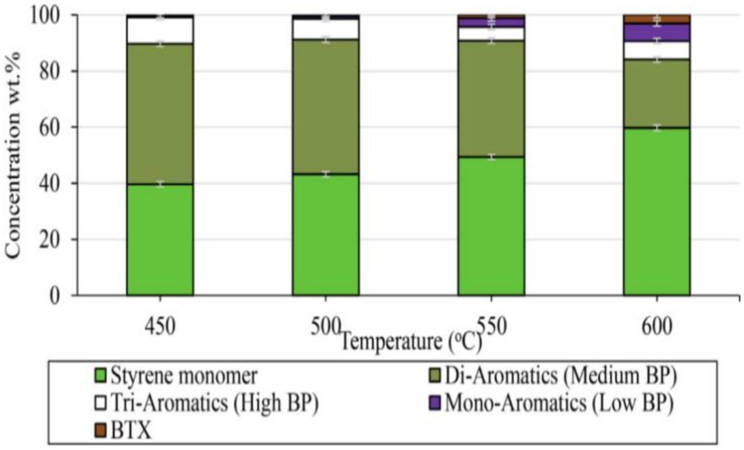


Figure 2.11 The main compounds of polystyrene pyrolysis oil as a function of temperature. Adaptation of[72].

Dhahak et al.[88] examined the thermal pyrolysis of PET in a horizontal tube reactor. They employed PET powder and varied temperatures (410, 430, 450, and 480 °C), with residence times of 120, 90, 60, and 60 min, respectively. The gas yield was analysed, and it consisted mainly of CO_2 and CO, with ethylene and benzene appearing in low concentration. The wax content contained the highest concentration of benzoic acid. The gas yield ranges between 25.8 and 30.7 wt.% and the maximum waxy product yields were 54.3 wt.% at 410 °C and 55.5 wt.% at 450 °C. Benzene was found at high temperatures >384 °C. The highest CO_2 and CO production were obtained at 431 °C and 444 °C, respectively. On the other hand, the solid residue yield decreased from 19.9 wt.% at 410 °C to 17.1 wt.% at 480 °C. This residue is the product of chain coupling, which tends to occur at low temperatures[89].

2.3.3.3 Influence of reactor types

The reactor also has a crucial role in the pyrolysis process, and the type of reactor utilised can influence the pyrolysis process, which includes the mass and heat exchange, residence time, transfer of heat, and overall reaction efficiency to achieve the desired products[38]. Several and different reactor types have been used which include batch, semi-batch, fluidized bed, fixed bed, and the influence of the reactor types on the distribution of the product yields has been investigated by many researchers. For example, fixed bed produced the maximum oil yield from the pyrolysis of LDPE (95 wt.%) at 500 °C [6]. Similarly, the maximum oil yield from the pyrolysis of PS (97 wt.%) at 425 °C when a pressurized batch reactor used. The common reactors that have been studied through the pyrolysis of waste plastics will be discussed in detail.

Batch and semi-batch reactors:

Batch reactors are closed systems that do not permit the input or outflow of reactants or products during the reaction[38]. They provide high conversion by leaving the reactant in the reactor for long periods of time, but have limitations such as product variability, high labor costs, and difficulties in large-scale manufacturing. Semi-batch reactors allow for the simultaneous input of reactants and the removal of products, providing better reaction selectivity[38]. They have comparable labor costs to batch reactors, making them appropriate for small-scale manufacturing. Some researchers favor batch reactors or semi-batch reactors for plastic pyrolysis laboratory size investigations because of their simplicity and ease of control over operating settings[38]. Thermal and catalytic pyrolysis are commonly carried out at temperatures ranging from 300 to 800 °C. Some researchers add catalysts to polymers to boost the hydrocarbon production. Some batch and semi-batch reactors had stirrers that ran at different speeds based on the intended setting[38]. Seo et al.[90] investigated the pyrolysis of HDPE in a batch reactor with a stirrer at 450 °C and the stirrer's speed was 200 RPM. A higher liquid oil content was achieved, about 84.0 wt.%. Abbas-Abadi et al.[91] in a semi-batch reactor to pyrolyze PP at 450 °C. The experiment resulted in a very high liquid yield of 92.3 wt.%. According to the literature, batch or semi-batch reactors are best suited for thermal pyrolysis since their parameters are easily controlled. However, they are not suggested for catalytic pyrolysis due to the possibility of coke production on the catalyst surface. Batch operation is not ideal for large-scale production due to the high cost of operation associated with feedstock refilling, which makes it less appropriate for laboratory work[38].

Yan et al.[92] observed that pyrolysis of LDPE and PP in a semi-batch reactor at 460 °C produces a significant amount of waste polymer residues, indicating that this process is effective for decomposing waste plastics without the need for additional separation. This separation, as well as the potential capacity for handling waste polymers that are difficult or cumbersome to deal with in fluidized bed reactors and closed batch reactors, suggests that thermal cracking of plastics under atmospheric pressure in a semi batch reactor might be an effective technology that required more attention.

Fixed-bed reactors:

Several research investigations have used fixed-bed reactors for plastic pyrolysis[70,93,94]. It is simple to design, but there are several limits, such as the irregular particle size and form of plastics as feedstock, which might cause problems during the feeding process. Fixed-bed reactors are often employed as secondary pyrolysis reactors, as the initial pyrolysis product may be conveniently supplied into the reactor's liquid and gas phases. A few studies have been conducted using a two-step procedure due to its high cost[38].

Fluidized bed reactors:

Fluidized bed reactors address issues similar to fixed-bed reactors. Many studies chose fluidized bed reactors for catalytic cracking of polymers over fixed bed reactors[69,71,77]. Jung et al.[62] chose a fluidized bed reactor for PP and PE pyrolysis because it manages a nearly constant temperature with high mass and heat transfer, resulting in a shorter residence time in the reactor and more consistent range of products. Plastic pyrolysis in fluidized bed reactors was carried out typically at temperatures ranging from 290 to 850 °C for both thermal and catalytic processes. A fluid state is used to carry the samples and the catalyst, which gives more surface area for the reaction to take place[95]. This minimizes the variability of the process conditions while ensuring effective heat transmission. Furthermore, it is more adaptable than the batch reactor as frequent feedstock charge may be eliminated, and the process does not require to be restarted regularly. As a result, at typical design size, fluidized bed reactors would be the optimum reactor to be used in the pilot plant due to the reduced operating cost.

The conical spouted bed reactor (CSBR):

The conical spouted bed reactor (CSBR) effectively mixes particles with varying sizes and densities[38]. Some researchers employed CSBR for catalytic cracking of plastic in studies [96–98]. Olazar et al.[99] reported that CSBR had lower attrition and bed segregation than fluidized bed. It possessed strong heat transfer between phases and experienced mild defluidization issues while handling sticky products. The reactor's operation has faced technical hurdles, including catalyst feeding, entrainment, and product collection, making it less beneficial. Furthermore, its complex construction needs the use of many pumps, leading in high operational costs[38] .

For example, Arabiourrutia et al.[98] investigated the wax production and characterisation of HDPE, LDPE, and PP pyrolysis at 450-600°C using the CSBR. According to them, CSBR was effective of controlling sticky solids that were difficult to deal with in fluidized bed reactors. The spouted bed design proved suitable for low-temperature pyrolysis to yield wax. They also reported that the wax content decreased with temperature. At higher temperatures, more waxes are converted into liquid or gases products. The wax production were quite similar for HDPE and LDPE at approximately 80 wt.%, but PP derived higher waxes at lower temperatures at 92 wt.%.

2.3.4 Summary of pyrolysis of waste plastics literature

Pyrolysis of waste plastic has been investigated in several studies, and the TGA results showed the degradation of plastics was in the range of 420–490°C [64]. Pyrolysis of different types of plastics produced liquid oil in high yield compared to gas and char yields. It was found that PS pyrolysis generated a very high liquid oil yield about 97wt.% at optimum temperature of 425 °C, while the gas yield was very low at around 2.5 wt.% [63]. The influence of the main parameters such as temperature and type of reactor was also reported by numerous researchers. The high oil yield produced from the pyrolysis of PS, LDPE, HDPE, and PP were above 80 wt.%. The results reported high yield of liquid oil at the pyrolysis temperature of 450 °C, while the maximum oil yield from the pyrolysis of LDPE was reported at 500 °C. The type of reactor used has an essential impact on the plastic products distribution such as fixed bed reactors have been conducted for the pyrolysis of waste plastics due to its simple design. However, fluidized bed reactors minimize the variability of the process conditions while ensuring effective heat transmission. Pyrolysis of HDPE, LDPE, PP, PS, and PET yielded significant gases such as hydrogen, methane, ethane, ethene, propene, propane, butane, and butene, CO_2 and CO[67]. Overall, the oil produced from the plastic waste consists of aliphatic, mono-aromatic, and poly-aromatic compounds[62,67].

2.4 Pyrolysis-catalysis of waste plastic

Pyrolysis–catalysis is a method for waste plastic treatment[48,100–102], where plastics can be converted to high-value products through the pyrolysis catalysis technique, such as syngas, and liquid chemicals [102]. Plastic pyrolysis has been developed using catalysts to produce high quality liquid fuel [103]. Catalysts play a significant role in thermochemical processing and many advantages can be obtained which include reducing reaction temperature, supporting the targeted reactions as well as improving the overall process efficiency[48,103]. The quality of products from the plastic pyrolysis-catalysis process are dependent on the right choice of catalyst. Furthermore, selecting the optimal catalyst is required to exhibit the targeted products[102]. For the pyrolysis-catalysis of waste plastic, many researchers have investigated oil production in terms of maximizing the oil yield as well as upgrading the oil quality which can be used as fuel or chemical feedstock [104]. It should be noted that temperature, and the type of catalyst are the most influential parameters on products yield.

There are two different processes of using catalysts for the pyrolysis of waste plastics. The catalyst can be mixed with waste plastic which are degraded together in one stage of catalytic pyrolysis, or the catalyst is applied downstream of the thermal pyrolysis stage, which means two-step process of pyrolysis- catalysis has taken place [48]. The advantages of the two-stage pyrolysis- catalysis process which has been recommended by several researchers[102,105,106]. These advantages[48] include:

- The interaction of the pyrolysis gases and catalyst can enhance the contact between pyrolysis products and the catalyst during the catalytic stage and that can reduce the mass and heat transfer issues.
- Catalysts are implemented to reduce the temperature, thus that can minimize sintering effects.
- Temperature may be easily and independently regulated during both the pyrolysis and catalytic process.

2.4.1 Catalysts

Catalysts for pyrolysis of plastic waste have been investigated and include for example, fluid catalytic cracking (FCC), zeolites, and silica–alumina catalysts [107]. FCC catalysts are silica–alumina catalysts with a binder composed of non-zeolite matrix and zeolite crystal [108]. Silica-alumina catalysts are amorphous catalysts which consist of Lewis acid sites as electron acceptors and Bronsted acid sites with ionizable hydrogen atoms. Zeolite catalysts are crystalline alumino-silicate sieves with a three-dimensional framework with cavities and channels where cations can reside[107]. Catalyst properties such as BET surface area, pore size, pore volume, and acidity are the essential parameters which are influencing the catalytic activity in the pyrolysis process[107].

The structures of the major zeolites utilized in pyrolysis processes are shown in Figure 2.12[109]. HZSM-5, a ten-membered ring zeolite, has a three-dimensional pore structure with pores ranging from 5.1 to 5.5 Å and 5.3 to 5.6 Å, whereas HY, a twelve-membered ring zeolite, has a three-dimensional pore structure with pore channels measuring 7.4 Å [110]. As a result, one of the distinctions between these zeolites is their shape selectivity due to their varied pore sizes, with the larger molecule diffusing into the HZSM-5 type catalyst being of the same size as a C_{10} molecule, similar to naphthalene[111]. However, the larger pores of the HY zeolite facilitate the diffusion of C_{12} compounds, such as dimethyl naphthalene[112]. Literature studies have focused on zeolites such as Hβ, HZSM-22, and SAPO. Hβ that have a three-dimensional structure with pore diameters midway between those of HZSM-5 and HY, demonstrating intermediate efficiency during pyrolysis[17,65,113–116]. HZSM-22 and SAPO-11 has intermediate pore sizes, and they produced high gas and aromatic contents due to their high acidity[109]. On the other hand, the mesoporous catalysts such as MCM-41 have been receiving more attention in the literature. This type of catalyst improves compound diffusion via the pore structure, which reduces catalytic deactivation. However, it is not shape-selective, which results in an extended product distribution[109].

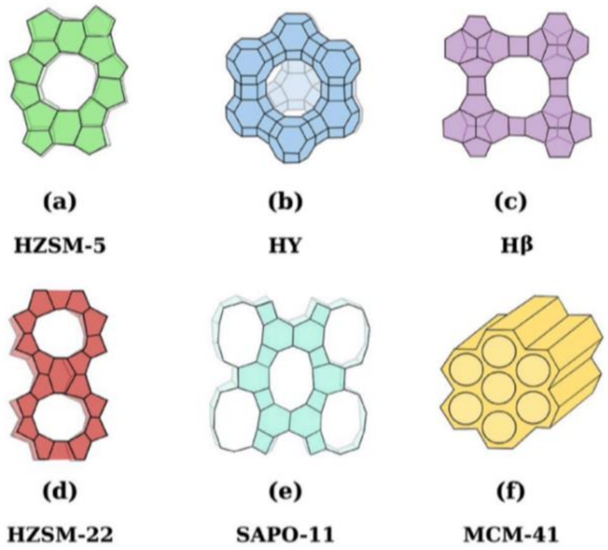


Figure 2.12 Structures of the main zeolites, (a) HZSM-5, (b) HY, (c) Hβ, (d) HZSM-22(e) SAPO-11, and (f) MCM-41. Adaptation of [109].

The acid sites of the catalyst play an essential role in the catalytic cracking mechanism via β-scission reactions. Cracking starts to occur with the formation of carbenium ions by the addition of a hydride ion to an olefin on Brønsted acid sites or the abstraction of a hydride ion to a paraffin on Lewis acid sites[117] . In C-C bond cracking, the mechanism of cracking includes isomerization, hydrogen transfer, cyclization, aromatization, and condensation reactions, all of which are prompted by zeolite acid sites [109].

For example, the pyrolysis of HDPE over HZSM-5 occurred via carbocation formation[51]. In this case, the zeolite's Lewis acid sites take a proton (H−) from the HDPE chain, forming a carbocation (positively charged carbon ion). The carbocation can either receive a proton (H+) from the Brönsted acid sites of the zeolite (termination to form another long alkane), propagate according to what occurs in the random scission mechanism, or require a β-scission reaction that the C-C bond between the beta carbon (next to the carbocation) and the following one is broken, resulting in a smaller carbocation and shorter olefin[51,118]. Figure 2.13 shows the carbocation mechanism of HDPE over HZSM-5[51] .

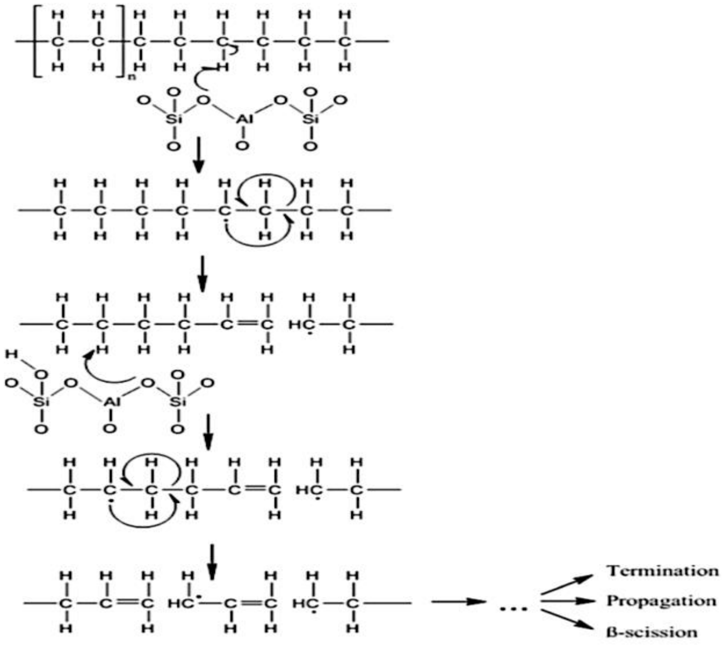


Figure 2.13 Schematic representation to illustrate carbocation mechanism of HDPE over zeolites. Adaptation of[51,118].

Base catalysts such as metal oxides, alkali carbonates, and metal complexes were mainly utilized to increase monomer recovery, which may then be reused for direct resynthesis of new polymers. The degradation of plastic over base catalysts produces more oils than solid acids, however the decomposition process requires more time[119]. The oil composition consists of mainly 1-olefins and low in aromatics/branched isomers. For example, BaO was used as a catalyst in the catalytic pyrolysis of PS, and it was found that around 90 wt.% of styrene monomers and 10 wt.% dimers were produced at 623 K, whereas benzene and indene tend to be one of the typical products with solid acids[120].

2.4.2 Product yield distribution of the pyrolysis-catalysis of waste plastics

As the catalysts can speed up the reaction between the reactants, it also improves the products yield distribution to particularly produce the maximum pyrolysis oil (gasoline and diesel properties)[46] . Catalysts such as, zeolite ZSM-5, MCM-41, MgO, CaO, and FCC, have been used by many researchers to enhance the yield and the mechanism of the catalytic pyrolysis [79,99,116,121,122]. The product yield distribution was investigated by several studies, and reported that the gas, oil, and char yields obtained from the pyrolysis-catalysis of waste plastics. For example, Batool et al.[123] reported the highest gas yield from the pyrolysis of PE over acidic ZSM-5 catalyst. Moreover, Syamsiro et al.[121] found that catalytic pyrolysis of PP and PS over natural zeolite catalyst produced high gas yield, and was mainly attributed to its high acidity. This demonstrated that high acidity catalysts promoted polymer cracking during catalytic pyrolysis, as the cracking in the presence of a high acidic catalyst increased and that improved the gas production [45,83].

2.4.2.1 Influence of the catalyst type

Different catalysts have been investigated for the pyrolysis of plastic wastes. For example, Rehan et al.[124] have examined the use of natural and synthetic zeolite catalysts with PS. The catalytic pyrolysis of PS obtained the maximum oil yield at 54% when natural zeolite was used compared to the synthetic zeolite that produced 50% oil yield. In the case of the gas yields, natural zeolite produced the gas yield at 12.8%, while the gas yield was increased to 22.6% with synthetic. The increasing amount of gas yield can be explained in terms of the BET surface area and acidity of the catalyst. Thus, due to its microporous structure and high BET surface area, synthetic zeolite has the lowest liquid oil yield and maximum gas generation in catalytic pyrolysis. According to Seo et al.[90] using a microporous catalyst with a high BET surface area can increase the gas yield while decreasing liquid oil yields. Natural zeolites have a lower BET surface area and microporous volume than synthetic zeolites. Catalysts with a higher acidity speed up the degradation process, which enhances gas yield while decreasing liquid oil yields[107]. This is demonstrated in that the synthetic catalyst utilised in their study was more acidic than natural zeolite, so it enhanced the gas production while decreasing liquid oil yields. The oil composition obtained from the pyrolysis of PS with natural zeolite, included the main compounds such as styrene (60.8%), methylstyrene (10.7%), azulene (4.8%), 1H-indane (2.5%) and ethylbenzene (1.3%). While in the catalytic pyrolysis with synthetic zeolite, the main compounds were alpha-methylstyrene (38.4%), styrene (15.8%), benzene (16.3%), ethylbenzene (9.9%), and isopropylbenzene (8.1%)[124].

The study by Ratnasari et al.[103] used MCM-41 and ZSM-5 zeolite catalysts in a staged layered system for the two-stage catalytic pyrolysis of waste plastics is highly effective to produce a high content of gasoline range hydrocarbons in the product oil from the pyrolysis- catalysis of HDPE. A high content of gases product was observed when ZSM-5 zeolite catalyst was loaded alone, whereas a high content of oil product (83.15 %) was produced over the MCM-41 catalyst at a weight ratio of 1:1 with a ratio of feedstock plastic and catalyst of 1:2. This suggests that the catalytic performance of the ZSM-5 catalyst, which has a lower number of acid sites enhances the production of gases due to the high activity for C-C bond scission, while MCM-41 acidity was appropriate to crack polyethylene into liquid hydrocarbons. The main gases produced during the catalytic pyrolysis of the plastics were mainly ethene, propene, butene and butadiene gases. The oil product for the catalytic pyrolysis of high-density polyethylene contained a high yield of gasoline range hydrocarbons (C_8 –C_{12}) reaching 97.72 wt.% of yield with aromatic contents of 95.85 wt.%.

Tian et al.[125] examined the effect of using different catalysts (HZSM-5, Hβ, HY, and MCM-41) on the thermodynamics, kinetics, and pyrolysis of LDPE. 2:1 was the ratio of LDPE/catalyst, using a quartz reactor. They found that variations in pyrolysis product distributions and kinetic characteristics were mostly due to pore structure and acid site concentrations. MCM-41 had the lowest activity for catalytic pyrolysis of LDPE, attributed to its larger pore size and lower acid site concentration. However, it demonstrated a significant aliphatic hydrocarbon selectivity compared to the other catalysts. HZSM-5 achieved the highest level of monocyclic aromatic hydrocarbons and facilitated end-chain scission, resulting in a gas production of 62.33%, while Hβ produced a gas yield of 67.00%. This is because HZSM-5 has larger pores (0.64 × 0.76 nm) than Hβ (0.53 × 0.56 nm), allowing C_3-C_5 compounds to remain longer in the pores and become involved in secondary reactions more easily. HY produced a higher liquid yield, which was primarily due to its shape that has "cages" with a diameter of 1.24 nm, which allowed larger chain molecules to pass through its large pores (0.74 x 0.74 nm)[126]. Thus, HZSM-5 has the potential to serve as a catalyst in the conversion of polyolefin plastic waste into monocyclic aromatic hydrocarbons. Figure 2.14 shows the liquid composition obtained from the pyrolysis-catalysis of LDPE over different zeolites catalysts[125].

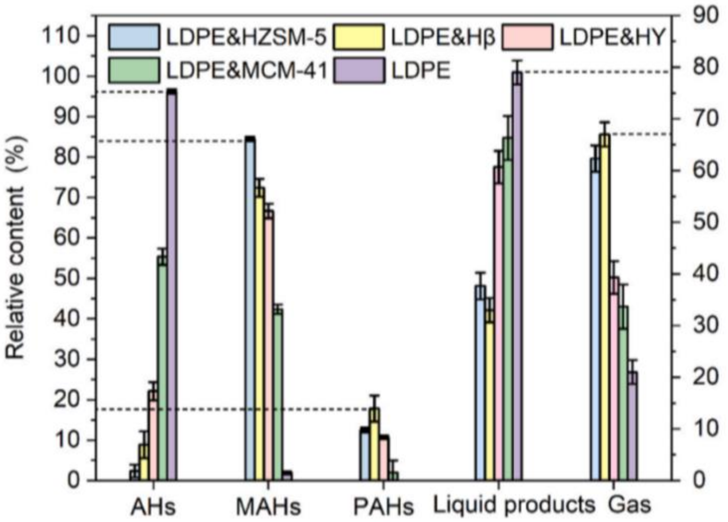


Figure 2.14 Product yields (right) and chemical compositions of liquid products (left). AHs: aliphatic hydrocarbons; MAHs: monocyclic aromatic hydrocarbons; PAHs: polycyclic aromatic hydrocarbons. Adaptation of [125] .

The selectivity of the ZSM-5 catalyst has been confirmed to improve deoxygenation reactions in synthetic polymer pyrolysis, reducing the amount of acids in the products[127], which leads to a lower oil content and more gas yield. For example, calcium oxide (CaO) catalysts were used to enhance the quality of PET pyrolysis oil. As shown in Figure 2.15, the degradation mechanism in the presence of CaO can typically convert aromatic acids into aromatic hydrocarbons due to its selectivity in releasing OH from polyaromatic compounds[127].

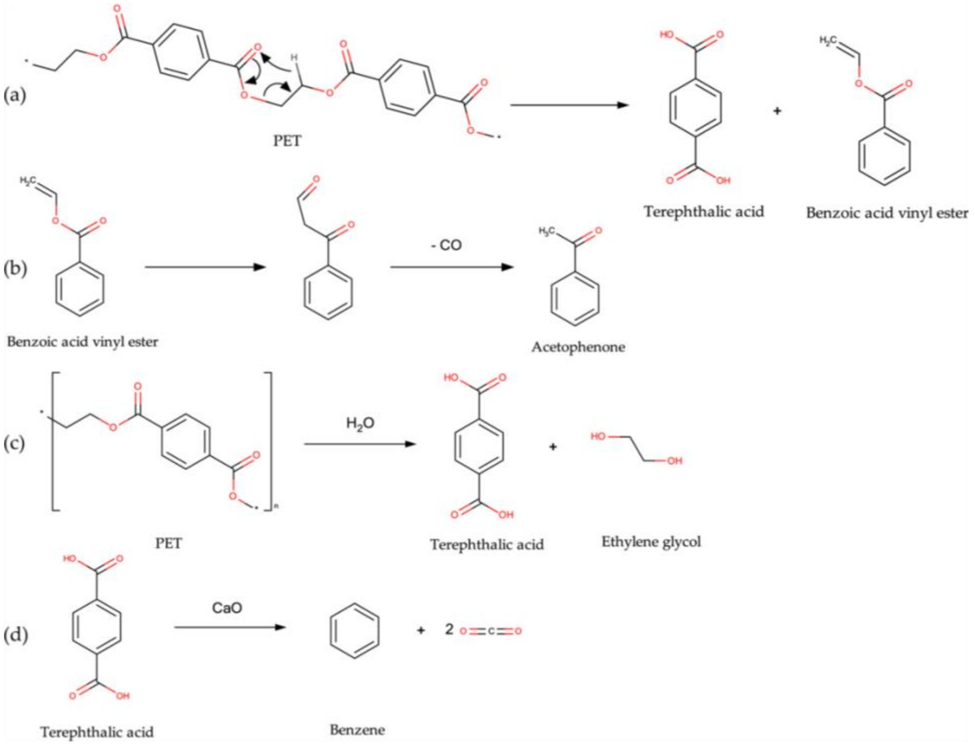


Figure 2.15 Mechanism of (a), (b), and (c) thermal degradation of PET (beta scission), (d) degradation mechanism in the presence of CaO catalyst. Adaptation of[127].

Plastic pyrolysis was also examined with metal impregnated zeolite catalysts, this study has been conducted by Akubo et al.[128] to improve the production of pyrolysis oil. In this study, HDPE was pyrolyzed in a fixed bed reactor (two stage reactor), using zeolite-impregnated metals such as nickel (Ni), iron (Fe), molybdenum (Mo), gallium (Ga), ruthenium (Ru), and cobalt (Co). Applying these metals on a Y-zeolite catalyst improved the production of aromatic hydrocarbons (80-95 %) in the product oil and increased hydrogen gas yield. The aromatic hydrocarbons in the oil were mainly toluene, ethylbenzene and xylene and the two ring aromatic hydrocarbons were naphthalene and alkylated naphthalenes. Metal impregnated zeolite produced relatively lower pyrolysis oil yields than zeolite alone. However, it showed less carbon deposition on the catalysts. Park et al.[129] investigated the catalytic pyrolysis in the presence of a palladium metal catalyst (5 wt.% Pd loaded on activated carbon) in a Pd/PET ratio of 0.01 to 0.05, using a tubular furnace with an operating temperature range of 400-700 °C, the gas yields produced at a catalyst concentration of 0.01 were approximately 43% and increased to 49% at 0.05, while the liquid yield was 39% and decreased to 33%. Using a moderate quantity of Pd catalyst reduced the synthesis of polycyclic hydrocarbons and benzene derivatives during pyrolysis. This effect occurred via a free radical mechanism and ring-opening reaction, and increasing the Pd catalyst resulted in lower amine species production. Naphthalene, benzoic acid fluorenone, triphenylene, biphenyl-4-carboxylic acid, p-terphenyl, and o-terphenyl were the main compounds that were produced in the oil. That suggests that using metal catalysts such as Pd to pyrolyze PET and other polymers might lead to more environmentally sustainable waste disposal.

2.4.2.2 Influence of plastic types on products from the pyrolysis – catalysis process

Vyas et al.[130] had carried out the pyrolysis-catalysis (two-stage process) of PP using three natural types of catalysts which were ZSM-5 and Zeolite, sludge from pickling liquor (SPS), and red brick sand (RB) in a fluidized bed reactor at temperature ranging from 100-800 °C. They used different ratios of PP to catalyst which was between 1:1 and 5:1 respectively. Figure 2.16 shows the total liquid yield that produced from the pyrolysis of PP with different catalysts. It was found that the ratio PP to catalyst (3:1) at the optimum temperature of 420 to 510 °C with a ZSM-5 catalyst obtained the highest conversion of PP waste with a maximum liquid yield that increased from 70.69 wt.% to 84.67 wt.%, and subsequently decreased from 84.67 wt.% to 57.25 wt.%. Using Zeolite, the liquid yield increased from 51.32 wt.% to 60.10 wt.% then dropdown from 60.10 wt.% to 53.15 wt.%, while using the RB as catalyst the liquid yield increased from 38.40 wt.% to 47.85 wt.% then decreased from 47.85 wt.% to 30.91wt.%, but with SPS the amount of liquid yield increases as feed to catalyst ratio was increased but the yield of obtained liquid was very low. Catalytic pyrolysis of PP yielded a complex liquid oil which included aromatics, olefins, and naphthalene chemicals such as benzene, 1,1-(2-butene-1,4-diyl)bis-, 1,1-(1,3-propanediyl)bis-, anthracene, 9-methyl-, naphthalene, 2-phenyl-, 1,2,3,4-tetrahydro-1-phenyl-, naphthalene, and phenanthrene, which was also reported by Miandad et al.[64]

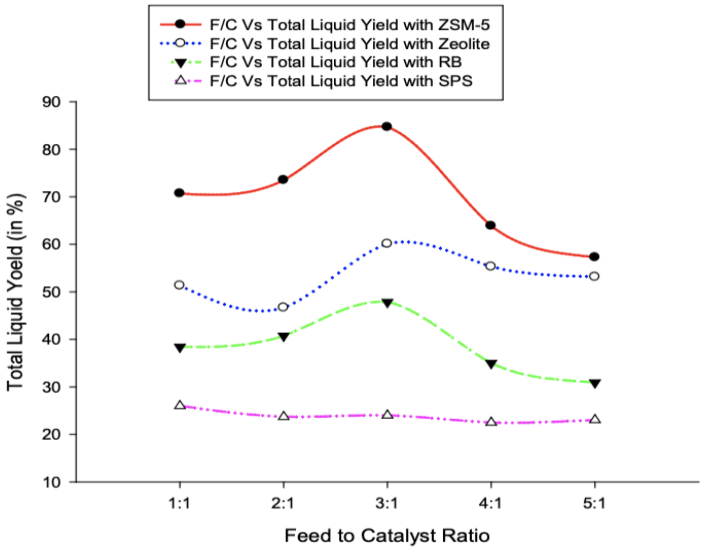


Figure 2.16 Total liquid yield produced from the pyrolysis of PP with different Catalysts. Adaptation of [130].

Miandad et al.[64] have studied the catalytic pyrolysis (catalyst is mixed with the feedstock) of individual PS and PE using a small pilot scale reactor and with natural zeolite (NZ) applied as catalysts after the modification by thermal (TA) and acidic (AA) treatment to promote the catalytic properties. Figure 2.17 shows the products yield of catalytic pyrolysis of individual PS and PE using TA-NZ and AA-NZ. The liquid oil consisted of aromatic hydrocarbons with some paraffins, naphthalene and olefin compounds. As PS has the cyclic structure, that may explain the production of high oil yield and the PS degradation occurred via both random-chain and end chain scissions, thus leading to the production of the stable benzene ring structure, which increases the potential for further cracking which leading for more oil production. PS produced liquid oil with TA-NZ and AA-NZ, and the main compounds are alpha-methylstyrene, benzene, 1,1 -(2-butene-1,4-diyl) bis-, bibenzyl, benzene, (1,3-propanediyl), phenanthrene, 2- phenylnaphthalene. In the case of PE with TA-NZ and AA-NZ catalysts produced the oil (40 and 42%). However, the highest yield of gas was produced (50.8 and 47.0%) using AA-NZ and TA-NZ respectively. This can be attributed to high cracking between PE and catalysts (high acidity). The oil produced from the catalytic pyrolysis of PE, with both catalysts, contained mainly naphthalene, phenanthrene, napthalene-2-ethenyl-, 1-pentadecene, anthracene, 2-methyl-hexadecane.

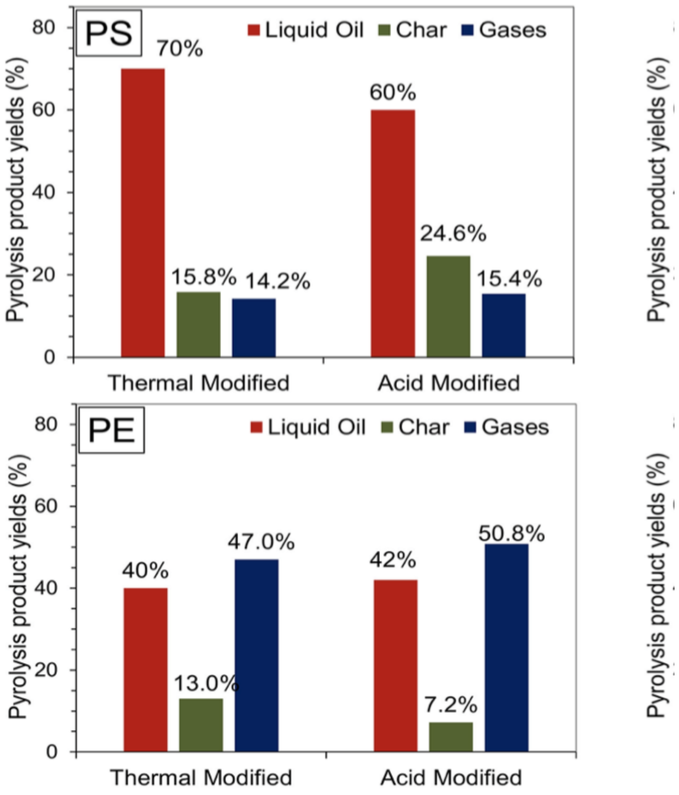


Figure 2.17 The products yield of catalytic pyrolysis of individual PS and PE using natural zeolite catalyst modified by thermal treatment (TA-NZ) and natural zeolite modified by acid treatment (AA-NZ). Adaptation of[64].

The oil produced from the pyrolysis-catalysis of waste plastics has been shown to contain high aromatic content, related to the high selectivity of the catalysts toward the target products. For example, the catalytic-cracking of HDPE over mesoporous MCM-41 and microporous ZSM-5 zeolites resulted in producing oil yields of up to 83.15 wt.% and 97.72 wt.% gasoline range hydrocarbons[103]. Similarly, Dai et al.[131] conducted the catalytic pyrolysis of LDPE using multiple catalysts that worked in tandem, improving the selectivity of C_5-C_{12} alkanes/olefins and monoaromatics by up to 100%. The MCM-41 formed C_5-C_{23} olefins, which were transformed into aromatics by Diels-Alder, cyclization, aromatization, and polymerization processes in the micropores of the ZSM-5.

Yoshioka et al.[132] found maximum gas and char production, while the liquid oil production was low from the catalytic pyrolysis of PET. The high production of char formation from PET pyrolysis was attributed to the carbonization and condensation reactions that occurred during its high-temperature decomposition as well as the presence of an oxygen atom promotes the large formation of char from catalytic pyrolysis of PET[132–134].

2.4.2.3 Influence of temperature

The effect of degradation temperature on the catalytic pyrolysis of LDPE was carried out by Abbas-Abadi et al.[135]. They examined the catalytic pyrolysis of LDPE at different temperatures of 420, 450, 480, and 510 °C, with an FFC catalyst in a semi-batch stirred reactor. The maximum condensed oil yield was achieved at 450 °C with FCC/polymer 10% (w/w) which was 91.5 wt.%. At 450°C, the pyrolytic liquid product contained olefins (53.8 wt.%), paraffins (28.1wt.%) and aromatics (14.7 wt.%). At 480 °C, it was shown that the quantity and composition of olefins in the oil were increased by 55.3 wt.%. However, the reduction in naphthene and paraffin yields was observed due to their tendency to form double bonds as well as the potential of, cyclization, unsaturation and aromatization that can take place at 480 °C. Higher temperature and the presence of catalyst can improve LDPE cracking, which can lead to the conversion of oil to aromatic and gases.

The catalytic pyrolysis of polystyrene was conducted by Wang et al.[136], using a fixed-fluidized bed reactor to investigate the effects of temperature and reaction time on product distribution. The catalytic pyrolysis of polystyrene was carried out with γ-Al_2O_3 as basic catalyst and silica sand as support, at temperatures ranging from 430 °C to 510 °C. Figure 2.18 displays the product distribution of PS catalytic pyrolysis. The results showed that increasing the temperature from 430 °C to 490 °C resulted in a considerable increase in oil yield, reaching 94.60 wt.%. At temperatures reaching 510 °C, the production of styrene increased from 27.15 to 32.58 wt.%, while decreasing yields of toluene, ethylbenzene, cumene, and α-methyl styrene. That was because the catalyst limits both intramolecular and intermolecular hydrogen transfer processes. Consequently, the solid base catalyst may hinder the synthesis of toluene and ethylbenzene while increasing the selectivity of styrene. Furthermore, as the temperatures increased, the secondary reactions increased, and more gases produced which mainly consisted of C_1-C_5 alkanes and alkenes, with a low concentration of hydrogen.

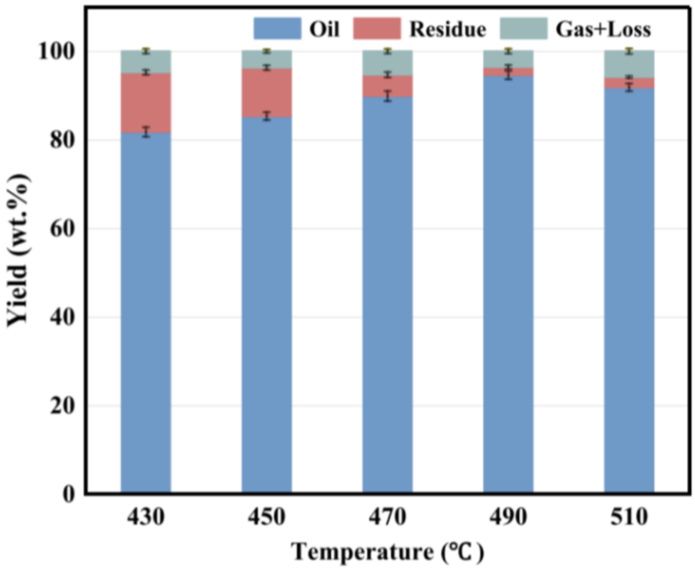


Figure 2.18 Product yield distribution of polystyrene catalytic pyrolysis at different temperatures. Adaptation of [136].

2.4.2.4 Influence of the reactor type

Currently, the most common plastic pyrolysis reactors on the laboratory and pilot scale are (i) fluidized bed reactors; (ii) fixed bed reactors (kettle type, batch and semi-batch reactors); and (iii) spouted bed reactors [5], among others. In fluidized-bed reactors, Lee et al.[137] and Imani Moqadam et al.[138] produced *the* conversion rates of over 95% by utilizing Fe_2O_3 and silica-alumina as catalysts in pyrolysis-catalysis of PS, while Liu et al.[77] reached a maximum styrene yield of 78.7 wt.*%.* Pyrolysis reactions of polystyrene in a conical spouted bed with speed fast to produce additional styrene monomers. Artetxe et al. [86] achieved, 70.57 wt.% styrene yields at, 500 °C. Abadi et al.[91] carried out PP pyrolysis in a semi-batch reactor at 450oC using an FCC catalyst. The experiment resulted in a very high liquid yield of 92.3 wt.%. Some batch and semi batch reactors were also outfitted with stirrers that ran at varying speeds depending on what was required. Seo et al.[90] investigated the pyrolysis of HDPE using a batch reactor with a stirrer at 450 °C (the stirrer's speed was 200 RPM). Higher liquid oil yields were achieved than in thermal pyrolysis, which was about 84.0 wt.%. Furthermore, the quantity of liquid product produced by catalytic pyrolysis utilizing a comparable silica-alumina catalyst was more significant, at 78 wt.%, compared to 74.3 wt.%.

2.4.3 Summary of pyrolysis-catalysis of waste plastics literature

The pyrolysis- catalysis of waste plastic have been investigated for high oil production as well as upgrading the oil quality which can be used as fuel or chemical feedstock. Temperature, and the type of catalyst are the most influential parameters on products yield. Using MCM-41 and ZSM-5 zeolite catalysts can produce oil that contains a high yield of gasoline range hydrocarbons (C_8 –C_{12}) reaching 97.72 wt.% of yield. Applying metal impregnated zeolite catalysts improved the production of aromatic hydrocarbons (80-95 %) in the product oil and increased hydrogen gas yield. It was found that optimum temperature for the catalytic pyrolysis of waste plastics was around 430 °C to 490 °C to produce high oil yield as compared to the thermal pyrolysis temperature in the range of 500-550 °C. The amount of oil produced and the catalyst's selectivity for additional BTEX chemicals are significantly improved in the two-stage fixed bed reactor.

2.5 Waste tires

A typical car or truck tire is composed of polymeric material that generally contains 14% natural rubber (NR), 27% synthetic rubber (SR), 14% high carbon steel wire, 28% carbon black and 16% fabric, fillers and other materials[3]. The main rubbers found in tire manufacture consist of a mixture of natural rubber (NR), styrene rubber (SR,) butyl rubber (BR) and styrene–butadiene copolymer (SBR)[4]. It has been reported that more than the one hundred different compounds and materials can be used in the manufacture of tires depending on the specific purpose of use[4]. For example, a mixture of aromatic, naphthenic and paraffinic hydrocarbons can be added to soften the rubber. The sulphur content of rubber from tires is around 1.5wt.%, and it is added to crosslink between the elastomer molecular chains and the formation of a three-dimensional chemical network, also, this addition of sulphur gives the tires more strength and flexibility[4,139]. In addition, carbon black, zinc, and metals are used in tire manufacturing[139]. Carbon black is used to add strength and abrasion resistance to the rubber, while zinc is used as zinc oxide to manage the vulcanisation process and improve the physical qualities of the rubber, and metal is utilized for strength in steel belts and cable[4,139].

Table 2.4 summarizes the proximate and ultimate of waste tire [109]. The proximate analyses of the tire samples show considerable variations. The formulation includes carbon black, which contributes to the fixed carbon content of 20-30 wt.%. Finally, the ash content varies depending on the additives found in the original tire and the steel removal procedure. The high carbon content (over 80 wt.%) and hydrogen concentration (about 7 wt.%) increase hydrocarbon formation during pyrolysis. However, the high sulfur content, which ranges between 1.5 and 2.5 wt.%, limits the direct use of pyrolysis products as fuel[109].

Table 2.4 The proximate and ultimate analysis of waste tire [109]

	Proximate analysis (wt.%)				**Ultimate analysis (wt.%)**				
Tire	**Moisture**	**Volatile matter**	**Fixed carbon**	**Ash content**	**C**	**H**	**O**	**N**	**S**
	0.4	62.9	27.2	18.6	84.9	7.3	4.0	1.1	2.6

2.5.1 Pyrolysis of waste tires

Pyrolysis is the technique of converting the waste tire to valuable products such as, oil, gas, and char[140–142 4,143]. That allows several reactions to take place that include cracking, dehydrogenation, aromatisation, and condensation[4]. Essentially, pyrolysis of feedstock and solid wastes produce high calorific fuels, chemicals, and valuable materials[4,140]. For example, pyrolysis releases the volatile gases which include condensable high-molecular-weight compounds as well as non-condensable low-molecular-weight products which can be used as process fuel to provide the energy for the pyrolysis process, while the high-energy-density carbonaceous solid char is produced that can be used as a solid fuel[4].

2.5.1.1 Pyrolysis mechanism and thermal degradation of waste tires

Li et al.[144] identified the reactions that occurred in tire pyrolysis into three groups (i) primary pyrolysis reactions occurs at temperatures ranging from 250 to 520 °C and involves a radical chain reaction in which dehydrogenation occurs concurrently with the decomposition of the main polymer chain; (ii) secondary subsequent-cracking reaction of volatiles occurring at 550 to 800,°C, which promotes the development of aromatic and polycyclic aromatic compounds that are attributed to a Diels–Alder cyclization reaction as shown in Figure 2.19 [145,146]. (iii) pyrolytic carbon black gasifying reaction in the presence of $CO_2/H_2O/O_2$ gases occurring at 750 to 1000°C [4].

The gas contains H_2, CO, CO_2, CH_4, C_2–C_5 paraffin compounds, C_3–C_5 olefin compounds, and low concentrations of sulphur (H_2S, SO_2), carbonyl sulphide (COS), carbon disulphide (CS_2), and nitrogen (NH_3) [145,146]. The liquid portion of waste tires pyrolysis yields a mixture of paraffins, olefins, and aromatic chemicals with high heating values of 40–45 MJ kg1[147].

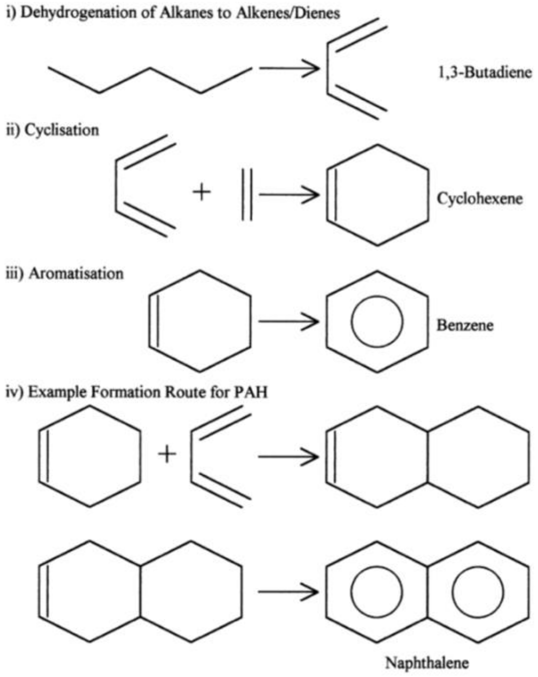


Figure 2.19 The Diels–Alder cyclization reaction for the production of polycyclic aromatic hydrocarbons from waste tires. Adaptation of [146].

A study on the pyrolysis mechanism and products distribution of waste bicycle tire (WBT) was investigated by Xu et al.[148], WBT composition was mostly containing NR, SBR, and BR. The major process of waste tire pyrolysis is described as polymer depolymerization, which produces various monomer radical fragments[149]. Figure 2.20 shows the pyrolysis mechanism of NR, SBR, BR and main products[148].

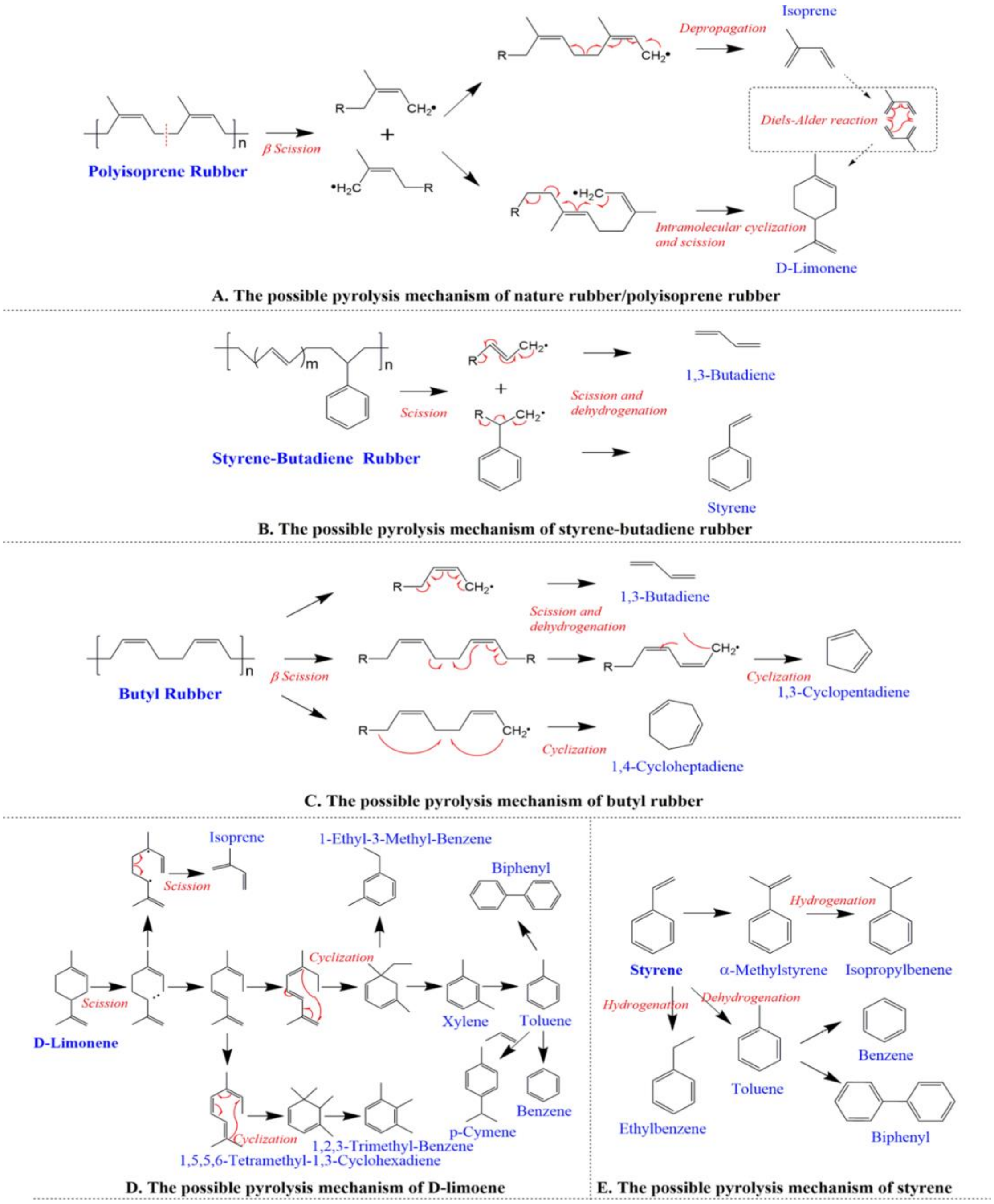


Figure 2.20 The possible pyrolysis mechanism of Waste bicycle tire (WBT) and main products. Adaptation of [148].

The pyrolysis of the rubbers contained in the tire decompose at different temperatures due to different rubbers in tire. Figure 2.21 shows TG and DTG curves of tire pyrolysis at different heating rates[150]. Bikova and Straka[151] demonstrated the two stages of waste tire degradation over a temperature range of 300–485 °C. However, Kan et al.[152] reported that waste tire pyrolysis involved three stages: the first stage (around 200–350 °C) was associated to the decomposition of volatile matter such as, oil, plasticizer, and additives) in rubbers, the mass loss at around 300–450 °C and that was related to the decomposition of NR component, and the third stage (in the range 400–500 °C) was observed due to the degradation of SBR and/or BR components. Islam et al.[153] concurred that the breakdown temperature of oils, plasticizers, and other organic additives in tires was around 150–350 °C for NR, 330–400 °C for SBR, and 400–480 °C for BR and SBR. Han et al.[150] have reported that derivative thermogravimetric (DTG) analysis of waste tire and observed a bimodal peak at 250–500 °C and a minor peak at 600–800 °C. According to some previous results, NR, SBR/BR decomposition obtained at 300–500 °C[152,153].

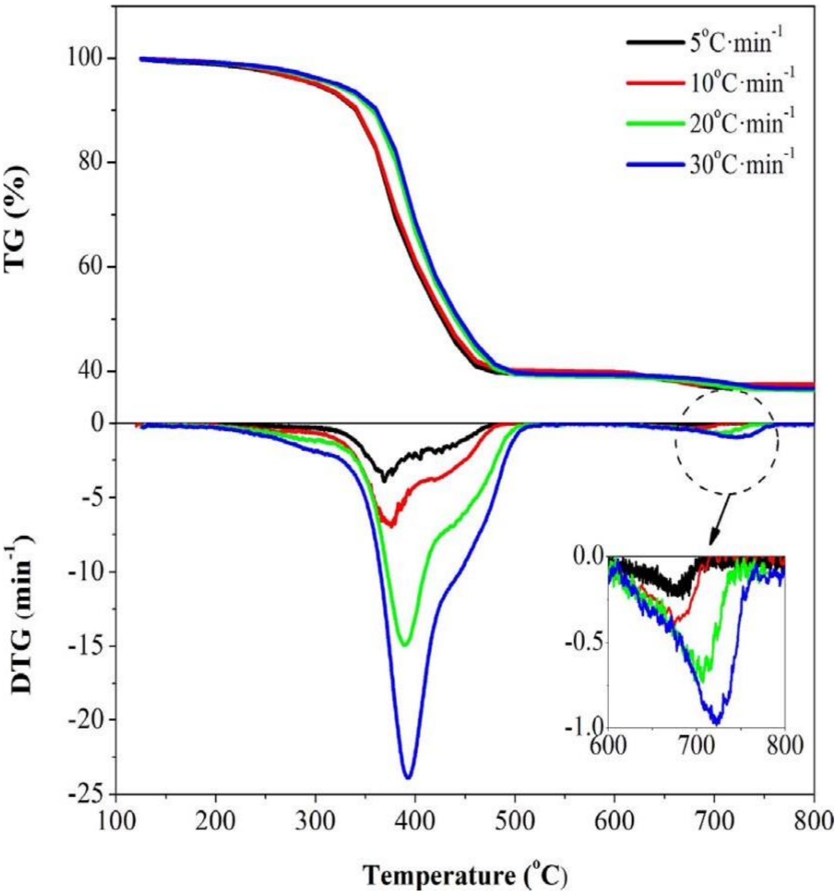


Figure 2.21 TG and DTG of tire pyrolysis with different heating rate. Adaptation of [150].

2.5.1.2 The product yield distribution of pyrolysis of waste tires

The product yield distribution of pyrolysis of waste tires has been investigated in different studies. For example, Rada et al.[154] conducted the pyrolysis of tire in a fixed bed batch reactor, and the oil yield obtained was 40 wt.% while the gas and char yields were reported at 20 and 40 wt.%, respectively. Williams et al. [155] observed that increasing the heating rate revealed a rise in gas yield, which was 6.6 wt.% at 5 °C/min heating rate and 14.8 wt.% at 80 °C/min heating rate.

Islam et al.[153] reported similar results for the pyrolysis of waste tire in a fixed-bed reactor and reported a high oil yield of 55 wt.% at 475 °C pyrolysis temperature, with char and gas yields of 36 wt.% and 9 wt.%, respectively. Different parameters such as, temperature, heating rate, reactor type, residence time, and flow rate of inert carrier gas all have an impact on the pyrolysis products distribution [143]. It is critical to discuss the main parameters which include the effect of feedstock composition, temperature, and the reactor types on the pyrolysis products.

2.5.1.3 Influence of the tire composition

Many studies on the differences in characteristics and yields of the product oil and gas composition from different types of tires have been documented in the literature on waste tire pyrolysis[4]. For example, the pyrolysis of waste tires was investigated by Lopez et al.[156] in a pilot plant equipped with a conical spouted bed reactor, at temperatures ranging from 425 to 600 °C, by utilizing two types of tire materials containing varying amounts of natural and synthetic rubber. The content of natural rubber and styrene-butadiene rubber in the tire has a considerable impact particularly on the oil composition (contents of aromatics, styrene and limonene). As a result, olefin yields were obtained in the gaseous fraction (2.95 wt.% of 1,3-butadiene at 600 °C for tire synthetic rubber, with styrene-butadiene content of 29.59 wt.%). At 425 °C, the liquid fraction has mainly limonene, which was 20.4 wt.%.

The effect of the tire composition on the product distribution and composition was also investigated by Singh et al.[157], they studied the co-pyrolysis of three different types of tires waste: light vehicle tire (LVT), medium vehicle tire (MVT) and heavy vehicle tire (HVT). In their experiments, the effect of the tire composition on the products yield was reported at 750 °C, in a semi-batch reactor. Due to the presence of natural rubber in the LVT which reduced the degradation temperature of the tire. Thus, LVT produced an oil yield of 47 wt.% and char yield of 38.9 wt.% at 750 °C. The results obtained showed that a higher fraction of HVT increased the degradation temperature due to the major presence of butadiene rubber. Also, a higher amount of styrene in the mix caused a larger fractional residue. Consequently, HVT produced the lowest char and maximum oil yields (62.67 wt.%) because of the presence of natural rubber and butadiene rubber, which was also reported by Ucar et al.[158]. MVT contained more styrene butadiene rubber (SBR) which produced the lowest oil yield (45.17 wt.%) due to very low presence of natural rubber and butadiene rubber. It was demonstrated that synthetic rubber with natural rubber, pyrolysis when the SBR degraded the cross-linked structure inhibited the breakdown of cyclised and cross-linked components and resulted in a more char yield[159]. The gas was largely composed of hydrogen and methane, with minor amounts of other gases such as C_2- C_6, CO, and CO_2 present. The oil fractions were found to be quite close to gasoline range hydrocarbons.

Muriel et al.[160] studied the fast pyrolysis of tire, using an analytical micro-pyrolysis reactor at a temperature range between 400 and 500 °C, the tire sample included waste tire, natural rubber, polybutadiene rubber, and styrene–butadiene rubber. The results obtained the higher production of D, L-Limonene and isoprene at ~60 wt.% and ~25 wt.%, respectively because of natural rubber depolymerization. Furthermore, styrene-butadiene and polybutadiene rubber mostly produced 4-vinylcyclohexene at ~80 wt.% through intramolecular cyclization of radical polymer fragments. The yield of BTXs, p-cymene, and p-cymenene, are found in very low concentrations in waste tires and natural rubber as shown in Figure 2.22.

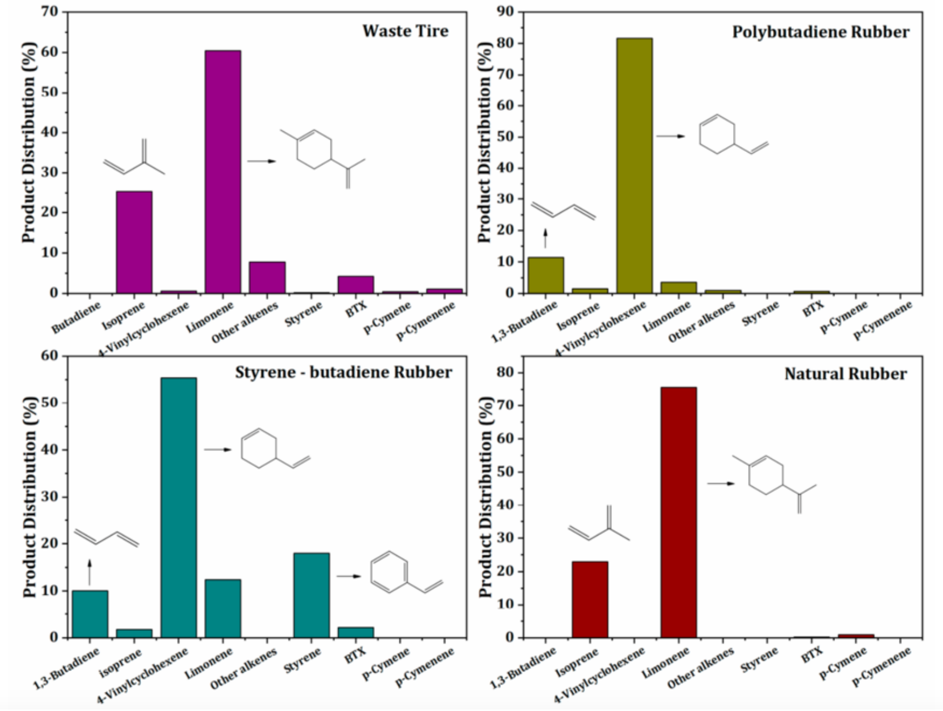


Figure 2.22 The product distribution obtained from waste tires pyrolysis. Adaptation of[160] .

2.5.1.4 Influence of temperature

Pyrolysis of used tire rubber was examined by Nisar et al.[161] to study the effect of the temperature on the products yield. Tire rubber was pyrolyzed at temperatures ranging from 500 to 800 °C. As the total volatile matter increased, char yield decreased, and it was also reported that increasing the temperature from 500 to 770 °C increased the amount of oil. When the temperature was increased from 570 to 770 °C, it was observed that the increase in gas, particularly C_1–C_5 yield from 24.39 to 75.69 wt.%. The oil fraction contained hydrocarbons ranging from (C_{16}-C_{19}) such as, hexadecanoic acid and methyl octadecanoic acid (methyl stearate).

The influence of temperature on product yields was examined by Pradhan and Singh[162] .Their experiment was carried out in a batch reactor utilising bicycle tire. The temperature effect was investigated between 450 and 650 °C. When the temperature was raised from 450 to 600 °C, the char production decreased significantly. However, only a slight reduction in char yield was noticed after 600 °C. Oil yield was constantly increased at 600 °C, while the increase of temperature above 600 °C no significant alteration in oil yield was reported. At higher temperatures, strong cracking as well as secondary reaction occur, resulting in an increase in gas product[146,163]. The main component of pyrolytic oil includes benzene, aromatic, and aliphatic compounds. Kaminsky et al.[164]found that pyrolyzing tires in a fluidized bed increased the gas yield from 20 wt.% at 598 °C to 33 wt.% at 700 °C. They also reported an increase in hydrogen yield and methane, C_2 hydrocarbons and C_3 hydrocarbons when the pyrolysis temperature was increased from 598 to 700 °C. Carbon dioxide and carbon monoxide also increased as the pyrolysis was temperature increased.

The effect of temperature on product distribution was investigated by Lopez et al. [165]. Pyrolysis temperature was in the range of 425- 575 °C using waste truck tires. It was found that char formed at 425 °C with a yield of 37.9 wt.% and contained a high amount of volatile matter; on the other hand, the char yield decreased to 35.9 wt.% at 475 °C. At 425 and 475°C, the maximum oil yield of 58 wt.% was reported. Furthermore, the maximum limonene production of 14.1 wt.% was obtained at 475°C. When the temperature raised to 575 °C, the gas yield increased from 3.6 to 10.2 wt.%, while the oil yield was decreased to 54 wt.%, and limonene yield was reduced to 7.1 wt.%. This action can be attributed to the secondary cracking reactions at higher temperatures which encouraged the gas production at the expense of liquid production[4].

Lopez et al.[166] pyrolysis of scrap tires was carried out in a conical spouted bed reactor, and the results (yields, volatile fraction composition, and carbon black characteristics) were obtained at temperatures ranging from 425 to 600 °C. Figure 2.23 shows the development of the product distribution as a function of temperature and carbon atom number. For the lighter hydrocarbons, the components have been classified as C_1 through C_{10}. Heavy hydrocarbons are classified as C_{11}-C_{13}, C_{14}-C_{16}, and > C_{17} according to their low yields. The classification of the components demonstrates the suitability of the gas and liquid fractions for producing various commercial fuels. Furthermore, increasing temperature increased the gases (C_1-C_4) and low molecular weight oil fraction (C_5-C_9) yields with temperature. The C_{10} fraction yield decreases significantly at high temperatures, particularly 600°C, due to thermal cracking of the major compound (limonene).

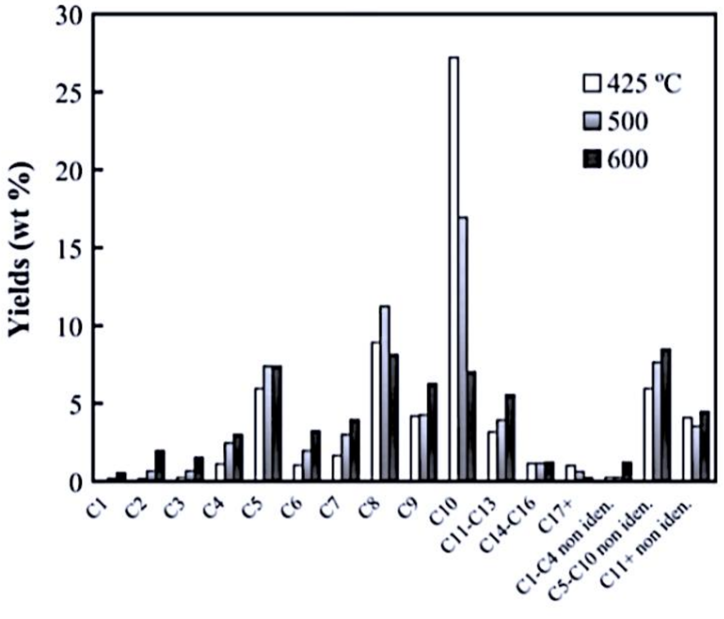


Figure 2.23 Product distribution according to the carbon atom number in the 425–600 °C temperature range. Adaptation of [166].

Pyrolysis temperature has significant effect on the limonene concentration. For example, Cunliffe and Williams [146] conducted the pyrolysis of tire in a fixed bed reactor at temperatures ranging 450- 600 °C, and they reported that limonene was the predominant component of the tire oil, forming 3.1 wt.% at 450 °C and decreasing to 2.5 wt.% of the total liquid at 600 °C. Zhang et al. [167] demonstrated that limonene concentration is very sensitive to pyrolysis temperature. When the pyrolysis temperature increased from 450 to 550°C, the limonene concentration decreased from 11.97 to 4.72 wt.%. Likewise, Li et al. [144] determined a limonene content in the pyrolysis liquid of 5.4 wt.% at 450 °C using a rotary kiln reactor, they found that limonene concentration decreased to 0.07 wt.% at 650 °C.

Xu et al.[168] investigated the influence of temperature on tire pyrolysis oil composition, using a laboratory-scale downdraft tube reactor. The aromatic formation increased dramatically after 500 °C, at the expense of D-Limonene. Long-chain olefins were formed as unstable intermediates at higher temperatures through ring-oping, trans-alkylation, and rearrangement reactions of D-Limonene, and then converted into monoaromatics, via the Diels-Alder reaction and aromatization reaction. The secondary reactions produced initially aromatics and then produced further benzene derivatives (BTXs). As the temperature was increased to around 600 °C, light polycyclic aromatic hydrocarbons such as naphthene and indene were released through hydrogen transfer and vinyl radical addition of monoaromatics and aliphatic hydrocarbons. Figure 2.24 shows the results of the main tire pyrolysis oil (D-Limonene and BTXs) at different pyrolysis temperatures[168].

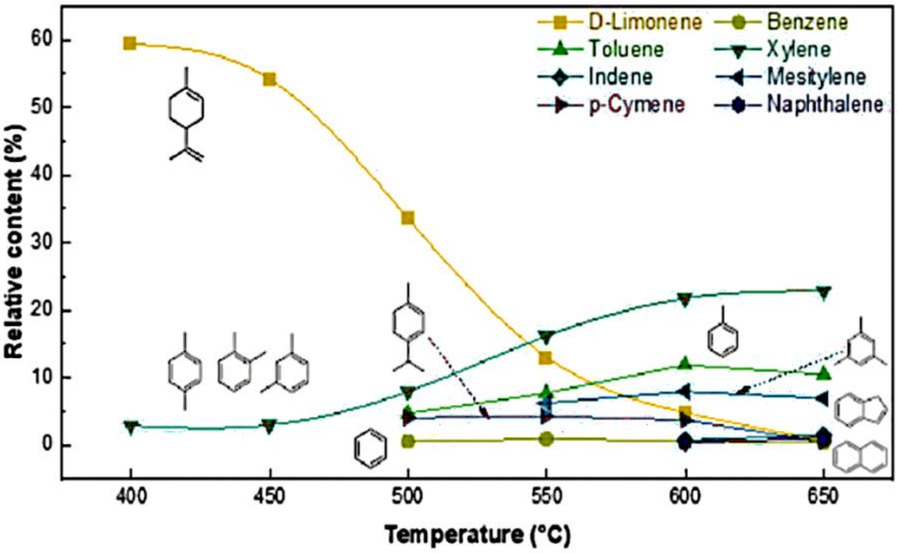


Figure 2.24 The influence of temperature on the composition of tire pyrolysis oil. Adaptation of [168] .

2.5.1.5 Influence of the reactor type

As the temperature affects the product distribution in pyrolysis of waste tire, reactor type and configuration have a significant impact on product distribution[169]. Pyrolysis reactors that include fixed bed reactors, both batch and semi-batch reactors, rotary kilns, auger reactors, and stirred tank reactors involve slow pyrolysis (low temperatures, low heating rates, and long residence times) for the products generated. The other types of reactors include fluidized bed reactors (bubbling and circulating), rotary kilns, spouted reactors, and ablative reactors. These reactors carry out the fast pyrolysis process with a very short residence time and temperatures ranging from 600 °C to 800 °C[142,143,169]. Conical spouted bed reactor has been criticized for high production and ability to deliver innovative, high-quality products. Conical spouted bed reactor produces a higher liquid yield ranging from 44.5 to 55.0 %. The higher operating temperatures in this reactor boost the aromaticity content which has been reported by many researchers[142].

Taleb et al.[170] investigated the thermal behaviour of pyrolysis products in a fixed bed reactor. They reported that liquid yield of 32% was attained at 500 °C, and the liquid product contained high levels of aromatic chemicals such as benzene, toluene, xylene, and limonene, as well as a complex mixture of C_5-C_{16} organic compounds. The gas yield was 26%, while the char yield was 42% at 500 °C.

Mkhize et al.[171] conducted the influence of reactor configuration where three types of reactors investigated: a fixed bed reactor, a bubbling fluidized bed reactor, and a conical spouted bed reactor with two condensation systems, a shell and tube and a quenching condenser type configuration were examined. It was noticed that a bubbling fluidized bed reactor and a quenching condenser were efficient for producing a high oil yield (50 wt.% at 475 °C) and limonene.

2.5.2 Summary of pyrolysis of waste tires literature

The pyrolysis of waste tires was investigated by many researchers. The results show that NR, SBR/BR decomposition was obtained at temperature between 300–500 °C[152,153]. The effect of the tire composition on the product distribution were reported particularly the content of natural rubber and styrene-butadiene rubber in the tire which has a considerable impact on the liquid oil composition with high contents of aromatics, styrene and limonene products. The influence of temperature on product distribution can be explained that at lower temperatures of ~450 °C, the decomposition was incomplete, which resulted in high char yields, while the liquid and gas yields were low. At higher temperatures of ~550 °C, strong cracking as well as secondary reactions occur, which encouraged gas production compared to oil. Moreover, it was reported that at 475 °C, the product oil contained high concentration of limonene, while the aromatic content in the oil was increasing at 575 °C[165]. The gas products were C_1- C_5 hydrocarbons, CO, CO_2, and H_2S. Pyrolysis reactors affect the product distribution in pyrolysis of waste tires. It was found that a bubbling fluidized bed reactor, a quenching condenser, and conical spouted bed reactors were efficient for producing a high oil yield around 50 and 55 wt.%, respectively.

2.5.3 Pyrolysis-catalysis of waste tires

As the catalysts can speed up the chemical reactions and the presence of certain catalysts, pyrolysis reactions can be accelerated. Catalytic pyrolysis has the ability to create a more constant product distribution than thermal pyrolysis and produces high valuable products [169]. From the literature review, several studies[114,172–175] reported the advantages of using catalysts in waste tire pyrolysis in terms of increasing the yield of the target products and their quality. Pyrolysis-catalysis can be selective to produce valuable chemicals, such as lighter aromatic hydrocarbons, and BTXE (benzene, toluene, xylene and ethylbenzene), it may also reduce the sulphur content in liquid oil or increase H_2 content in the gas yield[176,177].

Using catalysts in tire pyrolysis effects the pyrolysis rate, oil quality, product yields, and composition, such as aromatics content for chemical production[109,143]. To summarize the reviews of the catalytic tire pyrolysis which include; (i) the type of catalyst investigated such as (acid, basic, or metallic) have a significant impact on the characteristics and/or dispersion of the product; (ii) the selection of a catalyst is heavily influenced by the prospective applications of the target product; (iii) it is also found that the acid catalysts such as those found in the zeolites family, promote the degradation of liquid yield to produce compounds such as aromatics and light olefins,(iv) the reduction of the liquid oil yield can occur in the presence of these catalysts, while, increasing the gas product yield; (v) base catalysts such as MgO, Na_2CO_3, and NaOH can increase the liquid oil production, while the sulphur concentration in the liquid oil can be reduced by CaO and $Ca(OH)_2$.

2.5.3.1 Influence of the catalyst type

Miandad et al.[178] investigated the catalytic pyrolysis of waste tires in a fixed bed reactor at 450 °C. They used natural and H-SDUSY zeolites, $Ca(OH)_2$ and Al_2O_3 catalysts. The maximum liquid yield was obtained with Al_2O_3 (32 wt.%), while the minimum liquid yield with zeolite (H-SDUSY) was reported (20 wt.%) followed by natural zeolite (22 wt.%) and $Ca(OH)_2$ (26 wt.%). High liquid yield as well as high yield of gases were produced when Al_2O_3 was used, this can be associated to the mild acidity of Al_2O_3. However, zeolite catalyst produced lower liquid yield, while higher gas yield was obtained and can be attributed to the higher surface activity and relatively large pore size of the zeolite catalyst. In the case of use $Ca(OH)_2$ catalyst which produced the maximum char (55.6 wt.%), less amount of liquid was reported (26 wt.%) and less gas yield (18.4 wt.%). On the other hand, the non-catalytic pyrolysis of tire reported the maximum liquid yield 40 wt.%, while the char and gas yields were 40 wt.% and 20 wt.% respectively. The results of gas chromatography-mass spectrometry indicated that the pyrolysis liquid produced without a catalyst contains up to 93.3 wt.% mixed aromatic chemicals. Catalysts reduced the concentration of aromatic compounds in the oil to 60.9 wt.% when activated calcium hydroxide was used, and around 71.0 wt.% when natural zeolite was used, and about 84.6 wt.% when activated alumina was used, with the exception of synthetic zeolite, which produced 93.7 wt.% aromatic compounds.

Kordoghli et al.[179] investigated the effect of powdered acid (ZSM-5 and Al_2O_3) and base ($CaCO_3$ and MgO) catalysts on oil yield, a fixed-bed reactor was used at a of temperature of 550 °C. It was reported that oil yield was 63.1 wt.% and 62.5 wt.%, with $CaCO_3$ and Al_2O_3 catalysts. They concluded that $CaCO_3$ and Al_2O_3 are the best catalysts for enhancing gas yield, while MgO promotes oil production. Similarly, Shah et al.[180] have reported waste tires degradation via catalytic pyrolysis in a batch reactor using basic catalysts (MgO and $CaCO_3$) tires produced gas, liquid, and char 24.4, 39.8, and 35.8 wt.% respectively for MgO and 32.5, 32.2, and 35.2 wt.% for $CaCO_3$ after 2 hours of catalytic pyrolysis at 350°C. They found that both catalysts produced approximately 25 wt.% of aliphatic hydrocarbons in the liquid fraction, however the usage of MgO produces a high quantity of aromatic hydrocarbons (55 wt.%).

2.5.3.2 Influence of temperature

Kar[181] investigated the effect of temperature applied in the range 350 to 500 °C in a batch reactor, with expanded perlite which was used as an additive. In the examined range, there was a significant rise in tire conversion. The oil yield at 425°C reached the maximum yield of 60 wt.%. As a result, the high oil yield in the presence of the catalyst was caused by the catalyst preventing repolymerisation and the formation of gases products during thermal degradation.

The increase in temperature and Na_2CO_3 catalyst increased the rates of catalytic conversion which was conducted by Demirbas et al.[139]. They used a stainless-steel vertical reactor at temperatures ranging from 400 to 600°C. They found at 458 °C, without the addition of Na_2CO_3, the oil yield was 39.6 wt.%. The maximum oil yield of 54.8 wt.% was produced in the presence of Na_2CO_3 at 452°C. The gas yield included C_1–C_4 hydrocarbons, carbon dioxide, carbon monoxide, nitrogen, oxygen, hydrogen sulphide, hydrogen, and other substances, while the liquid yield contained the main chemicals which were styrene (28.1wt.%) and butadiene (10.7 wt.%). The high amount of valuable light olefins such as ethylene and propylene, as well as light aromatics such as benzene, toluene, xylene, and naphthalene derivatives, have been reported in the produced fuel-oil.

Williams and Brindle[182] demonstrated the product yield for Y-zeolite (CBV-400) and zeolite ZSM-5 catalysts in relation to catalyst temperature for pyrolysis–catalysis of tires. It was clear that increasing the temperature of the catalyst bed had the effect of significantly increasing gas production at the expense of oil yield. For the Y-zeolite (CBV-400) catalyst, for example, increasing the catalyst bed temperature from 430 to 600 °C raised total gas yield from 16.3 to 21.8 wt.%, while decreasing oil yield from 38.7 to 32.2 wt.%. These results show a drop in oil production compared to the thermal pyrolysis, which produced an oil yield of 55.8 wt.% and a gas yield of 6.1 wt. %. As expected, the char yield remained consistent at roughly 38.0 wt.%. When compared to the Y-zeolite (CBV-400) catalyst, the oil yield was higher, and the gas production was lower when the zeolite ZSM- 5 catalyst was utilised. For example, in the absence of a catalyst, oil yield decreased from 55.8 wt.% to 42.9 wt.%, followed by a further decline to 34.6 wt.% as the catalyst temperature was increased from 430 to 600°C. Furthermore, the gas yield increased from 6.1 to 15.1 wt.% at 430 °C catalyst temperature to 20.0 wt.% at 600 °C catalyst temperature. The zeolite ZSM-5 catalyst increased the gas yield significantly at higher temperatures, rising from 4.0 wt.% at 430 °C to 7.6 wt.% at 600°C. It has been demonstrated that tire pyrolysis oils include large concentrations of alkenes and aromatic compounds. Figure 2.25 (a and b), show the effect of temperature on yields of high value chemicals using Y-zeolite and ZSM-5 as catalysts. The presence of the catalyst increased the concentrations of single ring aromatic hydrocarbons, benzene, toluene, and xylenes in the oils. Naphthalene and alkylated naphthalenes were also studied, and their concentrations increased significantly when a catalyst was present. When compared to the ZSM-5 catalyst, the Y-type zeolite catalyst with bigger pore size and better surface activity produced higher quantities of aromatic chemicals. The concentrations of benzene, toluene, xylenes, naphthalene, and alkylated naphthalenes changed significantly as the catalyst temperature was raised.

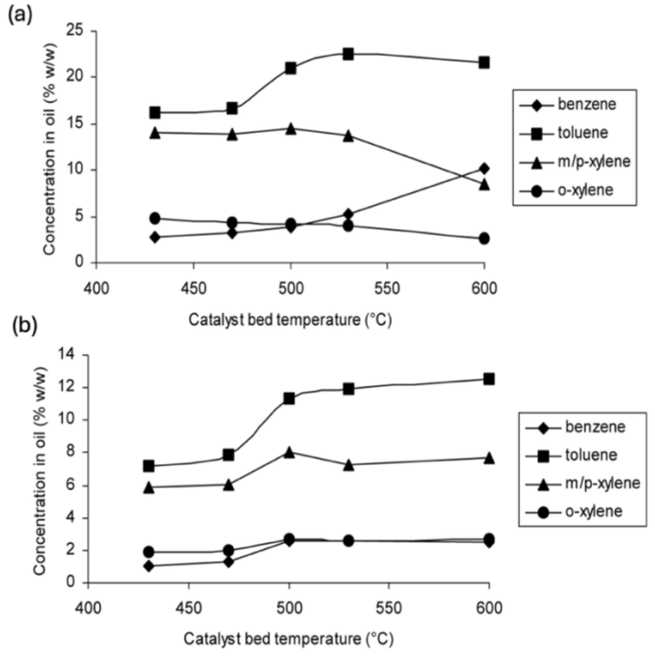


Figure 2.25 Effect of catalyst bed temperature on yields of high value chemicals (benzene, toluene, and xylene), using, (a) Y-zeolite (CBV-400), and (b) ZSM-5 as catalysts. Adaptation of [182].

2.5.3.3 Influence of reactor types

Catalytic pyrolysis can take place in different type of reactors such as, fixed-bed and fluidized-bed reactors[183]. The catalysts are usually utilised in situ and mixed with the tire material in catalytic pyrolysis tests performed in fixed bed reactors [109]. This approach, however, has significant limitations, including high coke deposition and problems in separating the catalyst and solid product at the end of the reaction[38]. A two-stage fixed bed reactor pyrolysis was successfully applied for the pyrolysis-catalysis of waste tire[142]. In the first chamber of the reactor, tire samples were pyrolyzed in an inert gas atmosphere (N_2) [142]. Following that, gaseous products were passed into the second section of the reactor, where catalytic reactions occur [142].

Furthermore, the study by Yuwapornpanit and Jitkarnka[184] catalytic pyrolysis was carried out in the fixed bed reactor. In this experiment, the sample was placed in the reactor in a specially designed, readily removable cage. In trials without a catalyst, pyrolytic gases were transported by an inert gas onto a zeolite catalyst or ceramic beads placed in a wire container mounted above the pyrolysis zone. The results showed that the catalyst in the pyrolytic process boosted gas yield and decreased oil yield. However, the zeolite catalyst enhanced the yield of single ring aromatic compounds.

2.5.4 Summary of pyrolysis-catalysis of waste tires literature

The catalytic pyrolysis of waste tires conducted reported the advantages of using catalysts for increasing the yield of the target products and their quality. Using catalysts such as Na_2CO_3, MgO, $CaCO_3$, Al_2O_3, and zeolite can enhance the produced oil with more aromatics and light olefins contents. Increasing the catalyst bed temperature from 430 to 600 °C increased the gas yield, while decreasing oil yield. However, the presence of the catalyst increased the concentrations of single ring aromatic hydrocarbons, benzene, toluene, and xylenes in the oils. Catalytic pyrolysis has been investigated in different type of reactors such as, fixed-bed and fluidized-bed reactors. A two-stage fixed bed reactor pyrolysis was applied with catalyst which can enhance the aromatic compounds.

The large-scale research has been conducted on the pyrolysis and pyrolysis-catalysis of individual waste tires and plastics, there remains a significant gap in understanding the co-pyrolysis and co-pyrolysis-catalysis of combined tire/plastic feedstocks. The interaction between thermally decomposed tire and plastic fractions during co-pyrolysis has not been comprehensively investigated, particularly in terms of product yield, quality, and the influence on catalytic upgrading. This research project will extensively focus on the thermal and catalytic co-pyrolysis of waste tire and plastic mixtures. Moreover, the synergistic effects of co-processing on product distribution (gas, oil, char) as well as the composition and fuel quality of pyrolysis oils will be thoroughly evaluated and characterized.

Chapter 3: Methodology

3.1 Introduction

This chapter explains the experimental methodology that was used for the pyrolysis and the pyrolysis-catalysis of waste tires and plastics. It provides the materials or feedstocks (tire and plastic) and explains the characterisation of the materials in terms of determining the thermogravimetric analysis (TGA), proximate and ultimate analyses. This chapter also describes the experimental reactor set up procedures and the validation of the pyrolysis and the pyrolysis-catalysis systems, which includes the reactor configurations and the operational conditions. Furthermore, it demonstrates in detail the calculations of the products yield, the gas and the oil analysis. The oil analysis is the main portion in this project, and it is conducted using standards and samples preparation, peaks identification, and the analysis instruments.

3.2 Materials

The waste tires and plastics were selected for this project as the feedstocks that were inherently high hydrocarbon content due to the long-chain molecular structures. The produced oil from these materials through thermal and catalytic pyrolysis can provide valuable compounds such as gasoline (C_5-C_{12}) and diesel (C_{13}-C_{20}) hydrocarbons[185]. This study investigates the pyrolysis and co-pyrolysis of plastics and tires as viable waste management options.

3.2.1 Waste plastics

In this project, the common waste plastics that included high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) were used for the pyrolysis and the pyrolysis-catalysis experiments. These plastics were supplied from a waste plastics recycling company, Regain Polymers Ltd., Castleford UK, in the form of 2 mm sized pellets as shown in Figure 3.1.

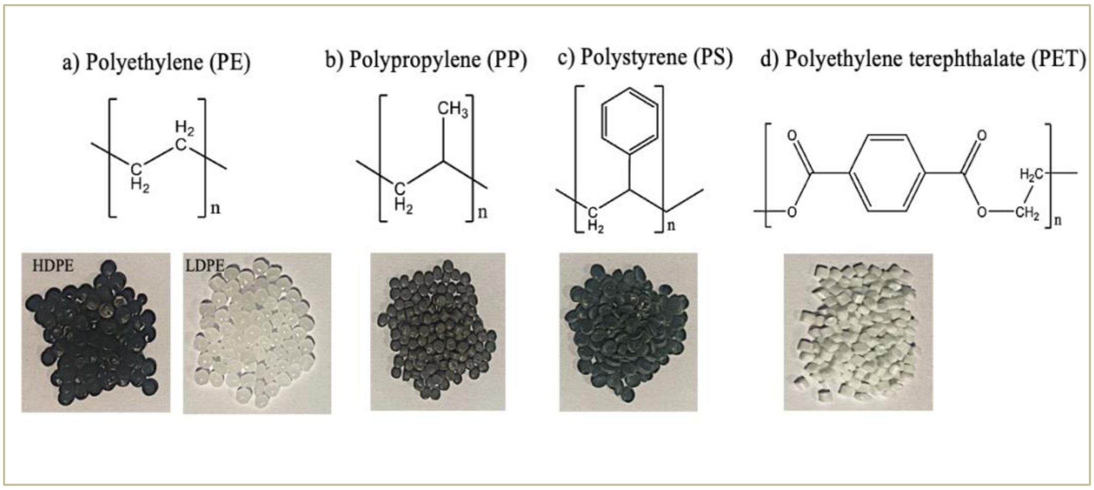


Figure 3.1 Plastic samples and the chemical structures of each type.

3.2.2 Waste tires

The tire sample was produced from truck tires and was the rubber component only and was shredded to produce a particle size of 6 mm as shown in Figure 3.2.

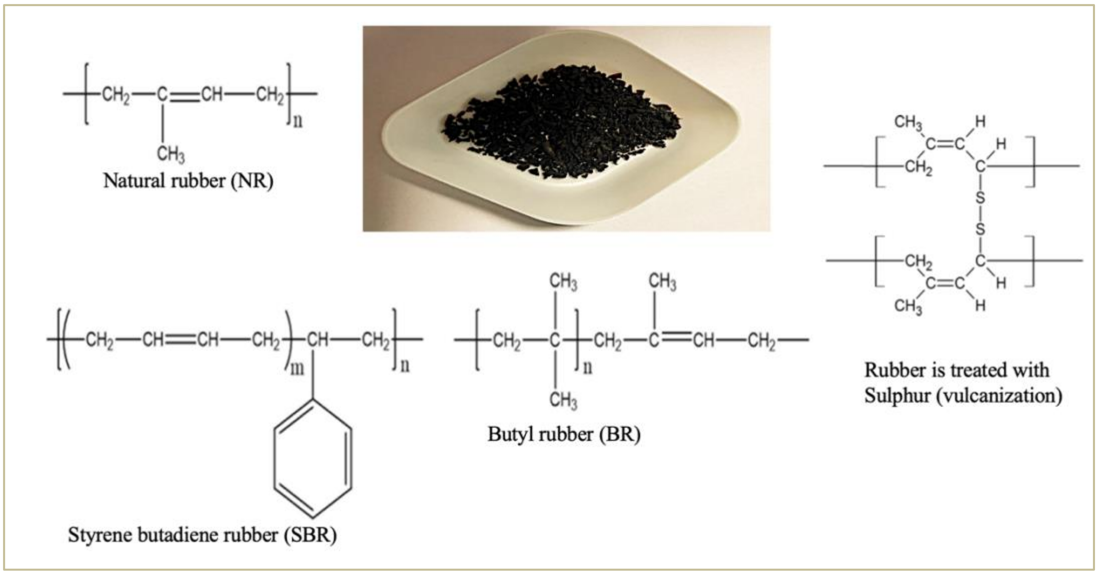


Figure 3.2 Tire sample and the chemical structures of the main tire composition.

3.2.3 Catalysts

Zeolite Catalysts in the form of ZSM-5 and MCM-41 (~1–2 mm spheres) were supplied from Nankai University Catalyst Plant, China as shown in Figure 3.3. These catalysts were examined to investigate their properties, which includes Si:Al ratio, BET surface area, and the pore volume. Table 3.1 shows the properties of these catalysts.

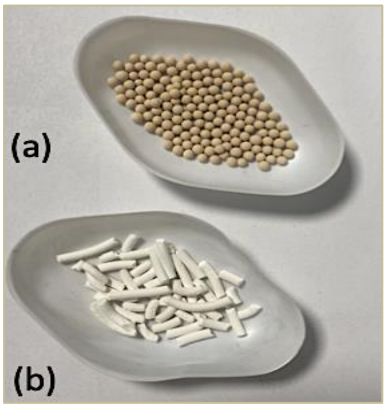


Figure 3.3 Catalysts samples (a) ZSM-5, and (b) MCM-41.

Table 3.1 Characterizations of the zeolite catalysts[103].

Catalyst	Si:Al ratio	BET Surface Area ($m^2\ g^{-1}$)	Pore Volume ($cm^3\ g^{-1}$)		Average Pore Width (nm)
			Micropore	Mesopore	
ZSM-5	38	233	0.23	0.12	5.2
MCM-41	4	734	0.38	0.33	3.95

3.3 Materials analysis and characterizations

The waste plastics and tire samples were characterised by ultimate analysis of the samples for C, H, N and S and was conducted using a Thermos EA-2000 elemental analyser. The proximate analysis of the samples was conducted by using thermogravimetric analysis (TGA) of the individual waste plastics and tire using a Shimadzu TGA-50 analyser.

3.3.1 Ultimate analysis

The examination of raw materials in the plastics and tires samples was performed using a Flash EA2000 elemental analyser. Figure 3.4 depicts the instrument schematic diagram. The operating concept of this instrument is based on a dynamic of the combustion method, which is combined with gas chromatography and consists of three major steps: high temperature combustion, product separation, and detection. Approximately ~ 3mg of the sample is precisely weighed with a microbalance and sealed in a tin foil capsule. The prepared sample is then loaded into the automated sampler tray. The software allows for the selection of the optimum settings such as the temperature program and the carrier gas flow rate. The instrument automatically carries the sample to a combustion furnace, where it combusts quickly at high temperatures and in the presence of oxygen. This requires a specified quantity of sample in a tin capsule in the presence of a specified quantity of an oxidising agent, such as vanadium pentoxide (V_2O_5). At 1000°C, combustion converts all carbon, nitrogen, and sulphur atoms into CO_2, NO_2, and SO_2 through the oxidation process. These gases were separated and delivered by helium to a gas chromatographic column where each gas is separated and analysed based on retention time by a thermal conductivity detector (TCD) which allows to determine the element concentrations of each sample according to the response of the known standards. The samples were injected twice and the average was taken for all the elements. The results for the elemental analysis are shown in Table 3.2. The results indicted high C and H contents for HDPE, LDPE, PS, and PP, while PET and tire produced more oxygen content.

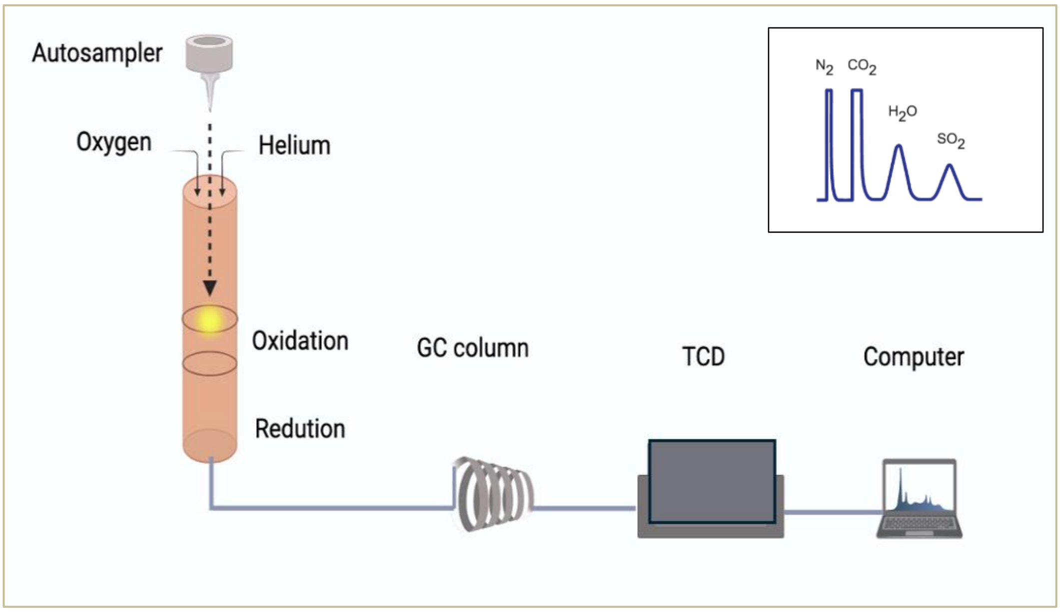


Figure 3.4 Flash EA2000 elemental analyser diagram. Adaptation of [186].

Table 3.2 Ultimate analysis of the tire and individual plastic samples.

Ultimate analysis (wt.%)							
Feedstock	**Carbon**	**Hydrogen**	**Nitrogen**	**Oxygen**	**Sulfur**	**Total**	**Standard deviation**
Tire	80.01	7.22	0.98	6.89	2.42	97.52	0.78
HDPE	85.01	13.10	0.68	0.57	0.00	99.36	1.01
LDPE	85.19	14.15	0.66	0.00	0.00	100	0.74
PP	82.32	15.12	0.68	1.35	0.00	99.47	1.11
PS	90.39	8.95	0.66	0.00	0.00	100	1.05
PET	62.03	5.02	0.52	30.93	0.00	98.50	1.13

3.3.2 Proximate analysis

A Schimadzu TGA-50 thermogravimetric analyser (TGA) was used to evaluate the tire and plastic moisture, volatiles, ash, and fixed carbon content. The thermal decomposition properties and composition of the sample are determined by measuring the change in mass with temperature or time under regulated temperature and atmospheric conditions. Samples of ~10 mg were accurately weighed and placed in the thermogravimetric analyser sample crucible. The heating programme was, starting from room temperature to 105 °C in an inert atmosphere to determine moisture content, then raising temperature to 900 °C to determine volatile content, and finally, the addition of air to combust the char and determine ash content. The TGA continuously records the change in sample mass. Figure 3.5 illustrates a typical analysis thermogram of the polypropylene sample which shows the volatile and ash contents. Table 3.3 shows the results of all the samples, and it indicates that the plastics samples produced high amount of the volatile content and low quantities of the moisture and fixed carbon. This is due to the high carbon and hydrogen ratio in the plastics samples, particularly PE, PP, and PS compared to PET and tire.

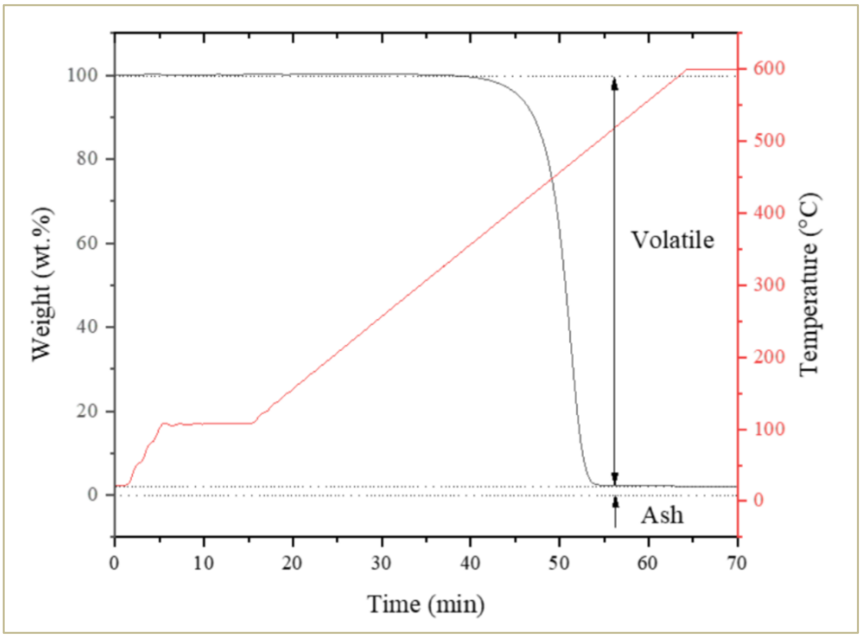


Figure 3.5 A proximate analysis of polypropylene by TGA.

Table 3.3 Proximate analysis of the tire and individual plastic samples.

Proximate analysis (wt.%)						
Feedstock	**Moisture Content**	**Volatile Matter**	**Fixed Carbon**	**Ash Content**	**Total**	**Standard deviation**
Tire	0.36	62.30	25.57	2.48	90.71	0.36
HDPE	0.88	93.15	0.07	0.64	94.74	0.65
LDPE	0.78	96.04	0.09	0.53	97.44	0.50
PP	0.48	94.07	0.06	1.14	95.75	0.50
PS	0.77	95.88	0.09	1.08	97.82	0.70
PET	0.73	82.33	14.38	1.50	98.94	0.73

3.4 Experimental set-up

In this study, two reactors were used for the experiments, firstly, a single stage fixed-bed reactor was conducted for all the pyrolysis experiments including, the pyrolysis of individual plastics (HDPE, LDPE, PP, PS, and PET), the pyrolysis of individual tires, and the co-pyrolysis of mixtures of plastics and tires. The single stage reactor was modified with the addition of a second stage fixed-bed rector to produce a two-stage pyrolysis-catalysis experimental reactor set-up. The two-stage reactor was used for the pyrolysis-catalysis experiments for individual tires and plastics as well as the mixtures of plastics and tires; the catalysts used were zeolite ZSM-5 and the two layer MCM-41/ ZSM-5 catalyst system.

3.4.1 Fixed-bed reactor for the pyrolysis experiments

The fixed bed single stage pyrolysis reactor was constructed of stainless steel with an inner diameter of 4 cm and an outer diameter of 6 cm, and a height of 30 cm. Figure 3.6 shows a schematic diagram of the single stage fixed-bed reactor. The nitrogen purge gas inlet are set up on the top of the reactor. The waste sample (plastics, or tire) was placed in a stainless-steel sample boat with a diameter of 2.3 cm and a height of 5.5 cm which was located inside the reactor. The reactor was heated externally by a 1. kW electrical furnace, and the temperature measurement of the feedstock sample was measured by a thermocouple (type K stainless steel thermocouples 2.5 mm diameter with temperature measurement range is from 0ºC -1100ºC). During the pyrolysis experiments nitrogen (carrier gas), enters the reactor and purges the product gases through the condenser system. Three condensers in series, cooled by firstly air and then dry ice were used to collect the liquid oil products, while the uncondensed gases were collected by a 25 L Tedlar gas sample bag. The solid residue char produced from the pyrolysis remains in the sample boat where it can be collected and weighed. Figure 3.7 shows a photograph of the experimental set up.

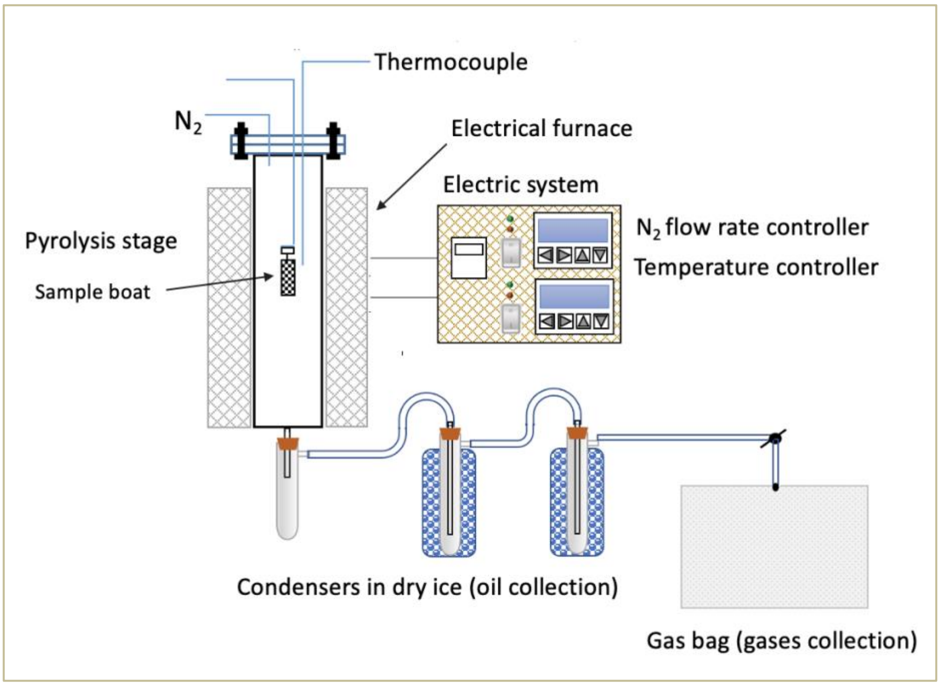


Figure 3.6 A schematic diagram of the single stage fixed-bed reactor.

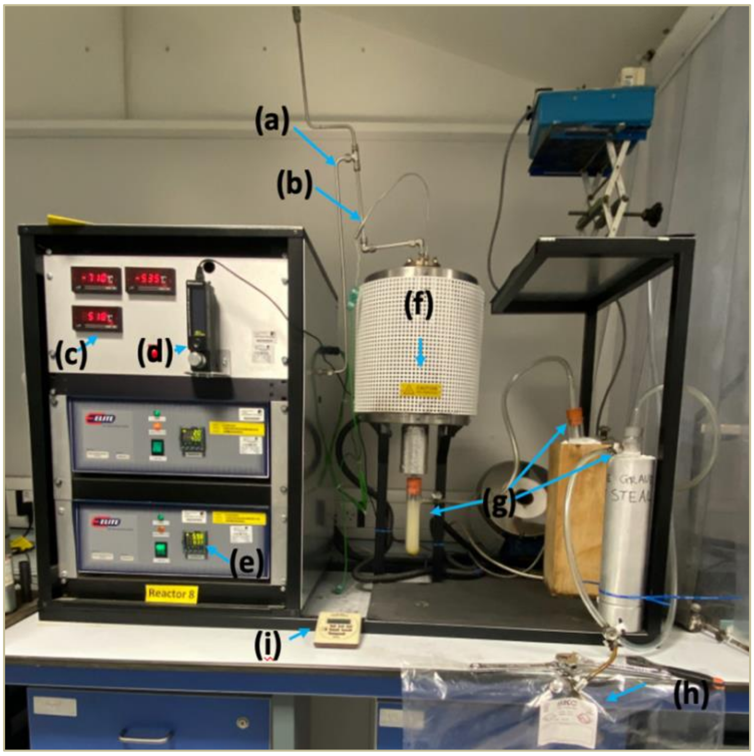


Figure 3.7 A photograph of the pyrolysis experiment set up.
Nitrogen, (b) Thermocouple, (c) Temperature display, (d) N_2 flow rate controller, (e) Temperature controller, (f) Temperature controlled furnace (pyrolysis stage), (g) Condensers system, (h) gas bag, (i) timer.

3.4.2 Fixed-bed reactor for the pyrolysis-catalysis experiments

The two-stage, fixed bed reactor system was used for the pyrolysis-catalytic processing of waste plastics and waste tires the mixtures (plastics/tires) with downstream catalytic processing. The fixed bed pyrolysis-catalysis reactor was constructed of stainless steel with an inner diameter of 4 cm and an outer diameter of 6 cm., and a height of 48 cm. Figure 3.8 shows a schematic diagram of the two-stage fixed-bed reactor. This fixed bed reactor is surrounded by the two electric furnaces that is linked to the heating control system which provided the temperature controlled heating of the first and the second stages. In the pyrolysis stage, the sample of waste is placed in the stainless-steel sample boat and in the catalysis stage, the catalyst is located on a quartz wool support bed above a metal mesh plate. All the product yields of gas, oil, and char were collected as before. Figure 3.9 shows a photograph of the experimental set up.

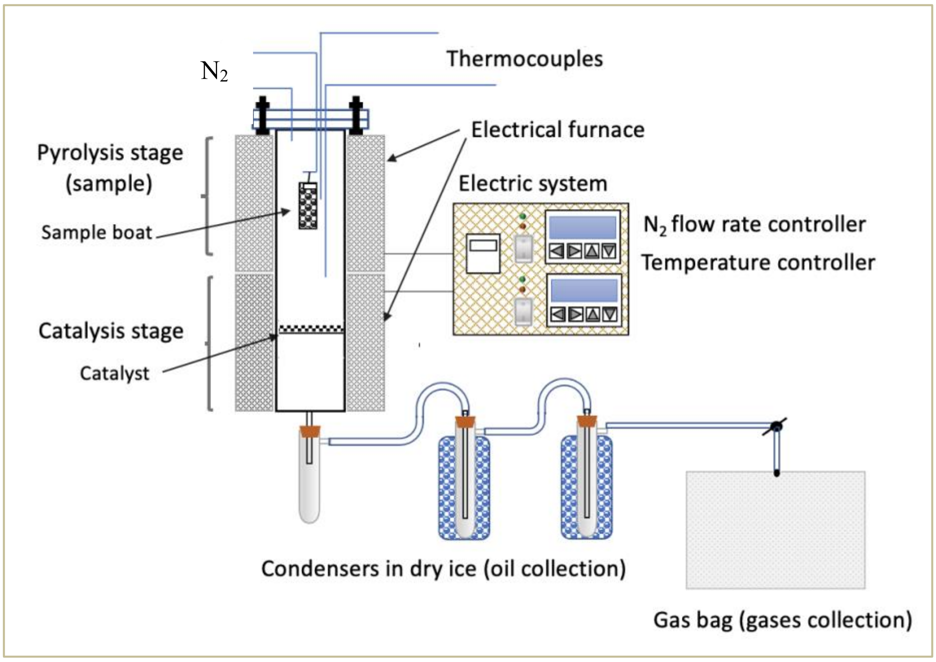


Figure 3.8 A schematic diagram of the two-stage fixed-bed reactor.

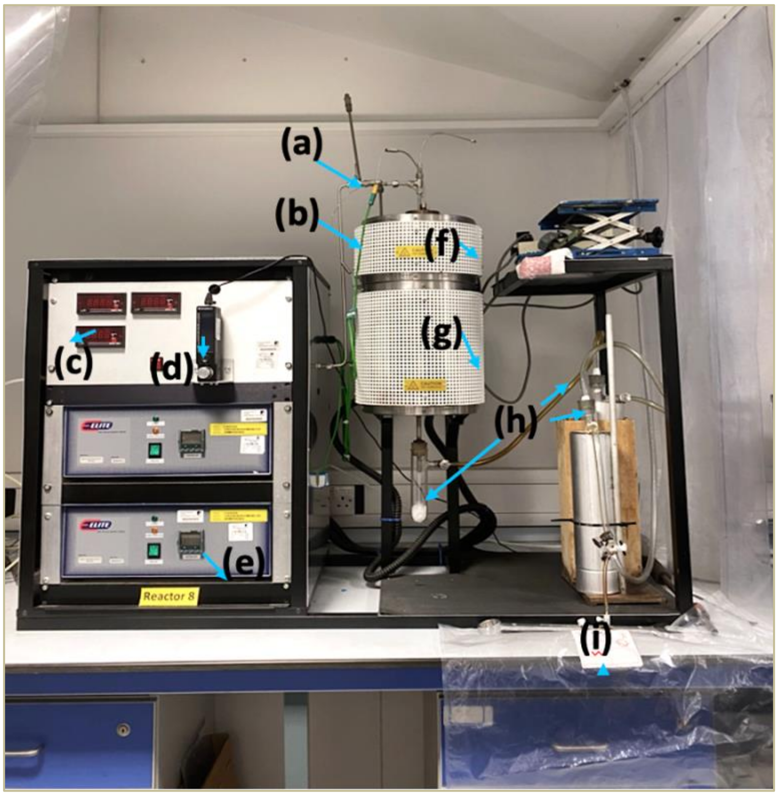


Figure 3.9 A photograph of the pyrolysis-catalysis experiment set up (a) Nitrogen, (b) Thermocouples, (c) Temperature display, (d) N_2 flow rate controller, (e) Temperature controller, (f) Temperature controlled furnace (pyrolysis stage), (g) Temperature controlled furnace (catalysis stage), (h) Condensers system, (i) gas bag.

In the case of the pyrolysis-catalysis, one layer of ZSM-5 or two layers of catalysts (MCM-41 followed by ZSM-5) were applied to investigate the influence of different catalyst properties on the products composition.

3.4.3 Pyrolysis experimental procedure and the operating conditions

The pyrolysis of the tire and plastics and their mixture (co-pyrolysis) was carried out using the fixed bed pyrolysis reactor system. Initially, the sample boat, reactor, and condensers were weighed. Then, the waste sample of plastics, and/or tire (6.0 g total feedstock mass) was placed in a stainless-steel sample boat and placed centrally inside the reactor. For the co-pyrolysis experiments an equal 1:1 mass of 3.0 g of plastic and 3.0 g tire was used to give a total feedstock mass of 6.0 g. This feedstock mass ratio was used to show the essential influence of tire addition on the products composition. Nitrogen was used as a purge carrier gas to ensure flow of the product gases and volatiles that exhaust from the sample boat through the reactor at flow rate of 200 ml/min, which was adjusted by the flow meter. The heating regime for pyrolysis consisted of heating from ambient temperature to a final temperature of 650 °C, at a heating rate of 20 °C min^{-1}. When the experimental temperature reached 200 °C the product gas collection into the gas sample bag was started. When the pyrolysis temperature reached 650 °C it was held at that temperature for 20 mins to ensure complete collection of pyrolysis gases. Three condensers were used to collect the liquid products, and uncondensed gases were collected into a 25 L Tedlar gas sample bag. The solid residue char produced from the pyrolysis remained in the sample boat where it was collected and weighed after each experiment. After the experiments the sample boat, reactor, and condensers system were weighted in order to calculate the products yield. oil is stored in the freezers for oil analysis, while the gas analysis should be analysed directly after the experiment. These conditions were applied in different studies by Li et al. [144]Xu et al.[168]and Ratnasari et al. [103]

3.4.4 Pyrolysis-catalysis experimental procedure and the operating conditions

For the two-stage pyrolysis-catalysis experiments, the sample boat, reactor, and condensers are weighed prior the experiment as before. However, the catalyst was pre-loaded into the second stage catalytic reactor, support on a quartz wool support bed. The quartz wool bed is inserted into the reactor column and weighted together.

For the pyrolysis-catalysis experiments 4 g of the tire or plastic was used with 4 g of catalyst. The catalyst stage was heated to 550 °C, and held at that temperature for 30 minutes prior to the pyrolysis heating, which was to heat up to 650 °C, with a heating rate of 20 °C/min. Similarly to the pyrolysis experiments, at 200 °C the gas yield is started to be collected into the gas sample bag. During this time the condensed liquid is collected in the three condensers.

3.4.5 Repeatability of the pyrolysis system

The fixed bed reactor was examined to investigate its efficiency and repeatability. Three experiments were carried out under the same conditions for the pyrolysis. Table 3.4 shows the repeatability of the reactor system and the experimental conditions, the repetitions of the experiments using the truck tires, which also shows the mass balance as well as the product yields.

Table 3.4 The repeatability of the pyrolysis reactor and the experimental conditions.

Experimental conditions					
Sample/weight	6 g of the shredded truck tires				
Pyrolysis temperature	650 °C				
N_2 flow rate	200 ml/min				
Heating rate	20 °C/min				
Products yield wt.%	**Experiments**			**Average**	**Standard deviation**
	1	**2**	**3**		
Gas yield	6.98	6.92	8	7.30	0.61
Liquid yield	55	58.5	58	57.2	1.89
Char yield	37.2	36.7	37.5	37.11	0.40
Mass balance	99.14	102.1	103.51	101.6	2.23

3.4.6 Repeatability of the pyrolysis-catalysis system

Table 3.5 shows the repeatability of the pyrolysis -catalysis system was also examined similar to the pyrolysis process. Three experiments were carried out under the same conditions, and the repetitions of the experiments using the high-density polyethylene in the first stage, while the addition of catalyst was applied in the second stage at the ratio of 1:1.

Table 3.5 The repeatability of the pyrolysis-catalysis reactor and the experimental conditions.

Experimental conditions					
Sample/weight	4 g of the high density polyethene				
Catalyst	4 g of the zeolite catalyst				
Pyrolysis stage	650 °C				
Catalytic stage	550 °C				
N_2 flow rate	150 ml/min				
Heating rate	20 °C/min				
Products yield wt.%	**Experiments**			**Average**	**Standard deviation**
	1	**2**	**3**		
Gas yield	32.23	30	29	30.41	1.65
Liquid yield	51.66	53.33	56.50	53.83	2.46
Char yield	1	0	0.5	0.5	0.5
Mass balance	84.90	83.88	86.39	85.06	1.26

3.5 Gas analysis

The pyrolysis process produced a gas which was collected in the gas sample bag and was analysed by using packed column GC using different Varian 3380C gas chromatographs. The permanent gases (H_2, N_2, O_2, CO and CO_2), alkanes and alkenes are also analysed. A photograph of one of the Varian GC is shown in Figure 3.10 This gas was analysed off-line using three GC instruments. The first instrument, a Varian CP-3380 analysed the permanent gases (H_2, O_2, N_2 and CO) with using argon as the carrier gas and a 2 m x 2 mm column packed with a 60-80 mesh molecular sieve and a thermal conductivity detector (TCD). The second instrument was also a Varian CP-3380 but with a Haysep column and was configured to measure carbon dioxide also using a TCD. The third instrument was used to determine hydrocarbon gases (C_1-C_4), used nitrogen as a carrier gas and a 2m x 2mm stainless steel column packed with Hysesp, 80-100 mesh using a flame ionisation detector (FID). Calibration was achieved using known standards these were used to calculate response factors (RF) for each gas. Each gas sample was injected three times with the average used to calculate the gas yield[187].

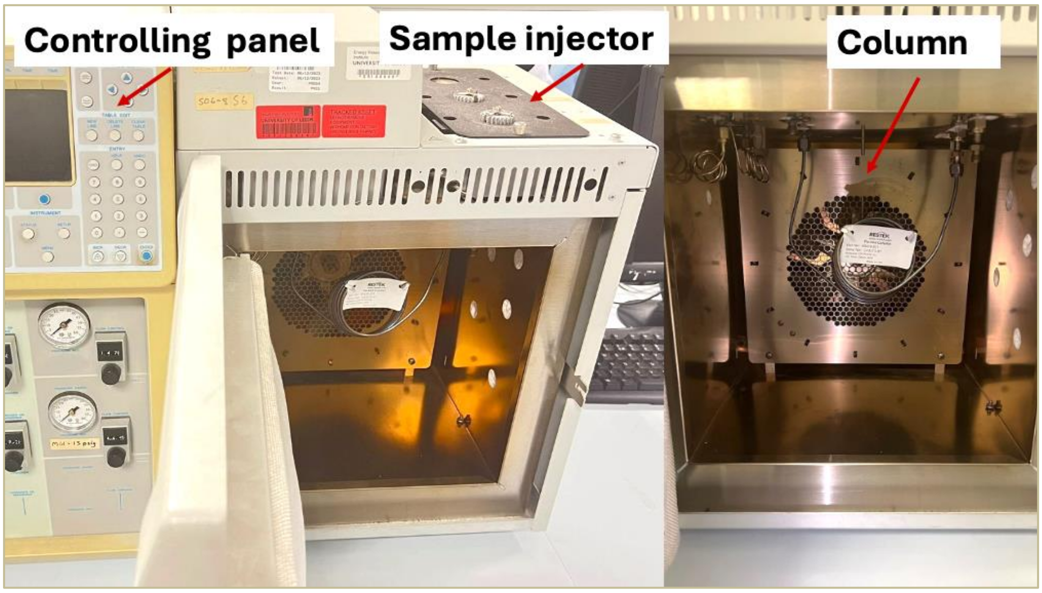


Figure 3.10 A photograph of the Varian 3380 gas chromatography.

3.5.1 The Gas concentration calculation

The gas concentrations were calculated using the standards of permanent and hydrocarbon gases concentrations at approximately 1.0% of each gas. Table 3.6 presents the standard of these gases. The concentrations of the detected gases by the GC can be calculated through the following equation.

$$C_s = \frac{P\ area\ s}{P\ area\ std} \times C_{std} \quad (mg/l) \tag{3.1}$$

Where;

C_S presented the concentration of the gas sample.

$P_{area\ s}$ is presented the sample peak area.

$P_{area\ std}$ is presented the peak area of the gas standard.

C_{std} is presented the concentration of the gas standard.

The injection of the gas sample through the GC was repeated three times, then the average of the gas concentrations was taken for calculation. The moles of each gas are also calculated and that can be achieved by calculating the total volume, which is taken into consideration that N_2 flow rate is constant during the experiments, the following equation presents the calculation of the total volume

$$Total\ volume = \frac{Flow\ rate\ of\ N2 \times Gas\ collection\ time}{volume\ \%\ of\ N2} \times 100 \qquad (vol.\%) \qquad (3.2)$$

By obtaining the total volume, then the concentration in moles for the gases can be calculated through the following equation

$$Moles\ of\ gas = \frac{volume\ \%\ of\ gas \times total\ volume}{100 \times 22.4\ (L)} \qquad (mole) \qquad (3.3)$$

The mass of each gas is also calculated in the equation below;

$$Mass\ of\ gas = Moles\ of\ gas \times Molecular\ weight\ of\ gas \qquad (wt.\%) \qquad (3.4)$$

Table 3.6 The standard gas used for the GC calibration of permanent and hydrocarbon gases.

Gases	Retention time (min)	Concentration (Vol.%)	Peak area	Standard deviation
Permanent gases				
Hydrogen	3.67	1	209276	0.013
Oxygen	4.75	1	22133	0.001
Nitrogen	5.78	96	1688069	0.106
Carbon monoxide	11.18	1	15972	0.001
Carbon dioxide	6.62	1	11149	0.001
Hydrocarbon gases				
Methane	1.39	1	623419	0.039
Ethene	4.46	1	1289616	0.081
Ethane	5.42	1	1151363	0.072
Propene	10.91	1	1868906	0.117
Propane	11.10	1	1792476	0.113
Butene and butadiene	17.14	2	4770611	0.299
Butane	17.40	1	2486641	0.156

3.5.2 Calculations of the product yield

The pyrolysis products which consisted of the gas, liquid and char were collected and measured. Gas was collected in the gas sample bag and was directly analysed by packed column gas chromatography (GC). The mass of liquid collected from the three condensers was calculated by taking the weight difference (before and after the experiment). The calculations of products yields are shown below;

$$\text{Gas yield, (GY\%)} = \frac{W\ gas}{W\ sample} \times 100 \qquad (3.5)$$

$$\text{Liquid yield, (LY\%)} = \frac{W\ condensed\ oil}{W\ samples} \times 100 \qquad (3.6)$$

$$\text{Char yield, (CY\%)} = \frac{W\ (sample\ boat\ 1) - W\ (sample\ boat\ 2)}{W\ sample} \times 100 \qquad (3.7)$$

$$\text{Mass balance, MB (\%)} = GY + LY + CY \qquad (3.8)$$

Where; W is presented the weight in gram unite.

3.6 Oil analysis

In this work, all the oil samples were analysed to identify the oil composition, and determine the chemical compounds obtained from the pyrolysis of the tire and plastics and their mixture (co-pyrolysis). This section will explain in detail all the experimental steps, starting from the samples preparation until the analysis process.

3.6.1 Samples and standards preparation

After the experiments the oil yield was collected and transferred to glass vials. Then dichloromethane (DCM) was used as the solvent to dissolve all the oil samples, and it was found that these non-polar compounds were completely dissolved in DCM. The wax was produced from the pyrolysis of the plastics samples as shown in Figure 3.11(a). A yellow powder was produced from the pyrolysis of PET, which showed less solubility compared to the other plastics. However, DCM was used to dissolve the powder and was left for two days in the fridge prior to analysis (Figure 3.11 (b)). Tire and PS produced an oily liquid. The mixture of tire and plastic samples produced less wax because of the tire addition as 50% of the produced oil from tire, and they fully dissolved in DCM as shown in Figure 3.11(c). Similarly, pyrolysis-catalysis of both individual plastics and tire/plastic mixtures produced oil rather than wax due to the high cracking rate. Thus, all the oil samples were dissolved easily in DCM. Samples and standards were prepared in specific concentrations on the same day of analysis to avoid in loss of the oil due to devolatilisation that may affect the results. Samples and standards were all prepared in specific concentrations prior to injection through the gas chromatography mass spectrometry (GC/MS) system. Figure 3.12 shows a schematic diagram of the main oil analysis steps.

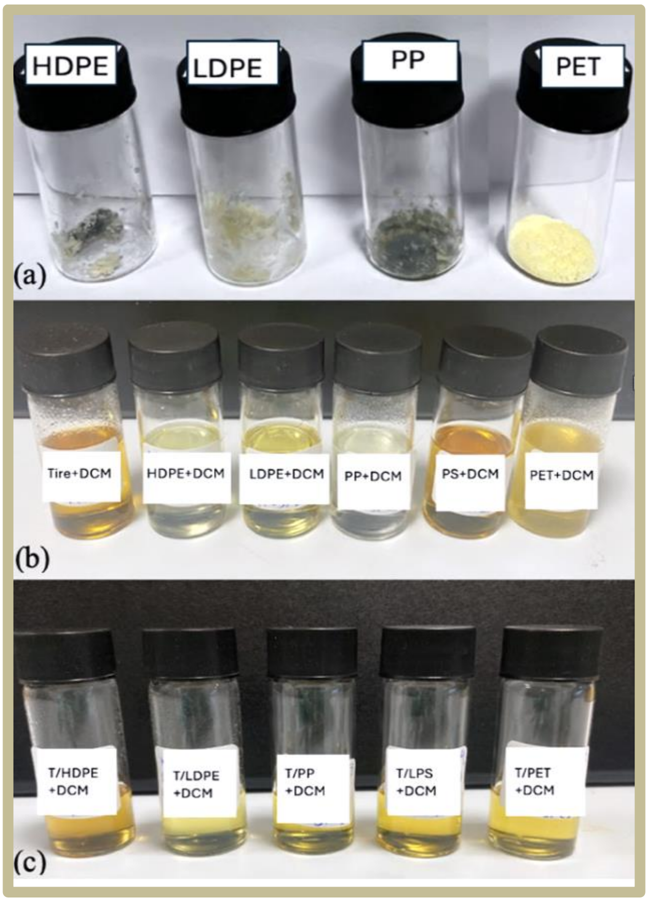


Figure 3.11 Preparation of the oil samples, (a) wax produced from the pyrolysis of HDPE, LDPE, PP, and PET, (b) individual pyrolysis samples dissolved in DCM, (c) mixtures pyrolysis samples dissolved in DCM.

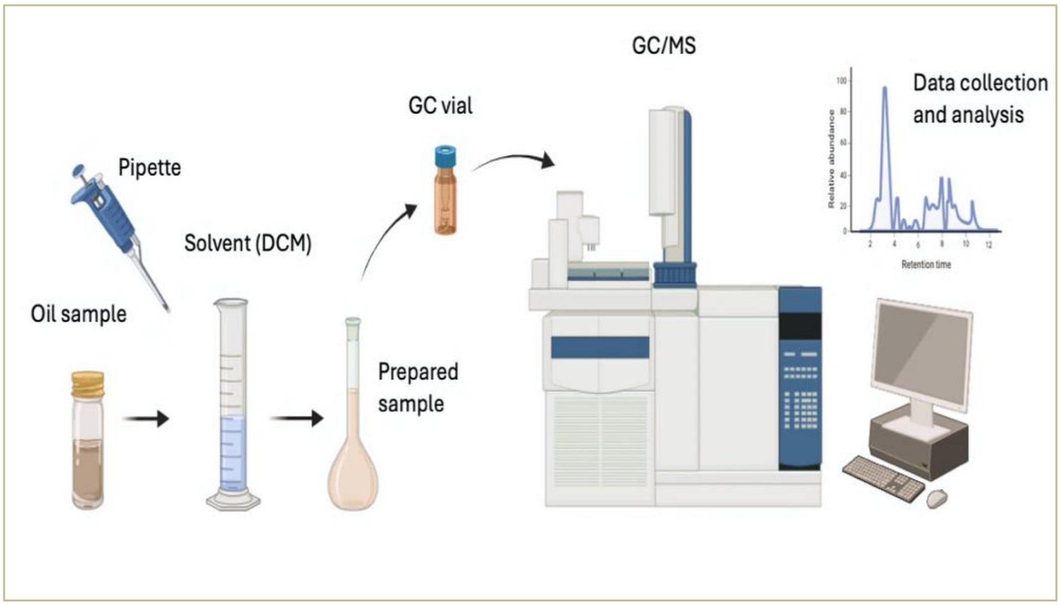


Figure 3.12 A schematic diagram of the main oil analysis steps. Created with BioRender.com

The standards were injected into the GC/MS to record the retention times of the main compounds. According to the retention times and using the spectral library of the GC/MS then it will be possible to identify the expected compound in the oil samples. Table 3.7 shows the main compounds that were injected as standards, which included aliphatic compounds, which were refenced as alkanes ranging from C_8-C_{32}, aromatic compound such as benzene, toluene, xylene, styrene, limonene, naphthalene, phenanthrene, and pyrene. Furthermore, the main oxygenated compounds were also injected to identify the oil composition that produced from the pyrolysis and the pyrolysis-catalysis of PET, which includes benzoic acid, phenol, and acetophenone.

Table 3.7 Standards of the main expected compounds obtained from the oil composition.

Aliphatic compounds	Retention time (min)	Peak area (average)	Standard deviation
C8	4.213	252640	0.119
C9	5.999	659720	0.866
C10	7.957	626960	0.822
C11	9.883	614130	0.892
C12	11.786	585260	0.471
C13	13.563	600500	0.254
C14	15.239	630400	0.627
C15	16.679	628550	0.848
C16	18.299	590860	0.842
C17	19.742	1282520	0.682
C18	21.057	1116940	0.551
C19	22.322	507920	0.435
C20	23.554	499330	0.742
C21	24.726	477930	0.174
C22	25.854	451430	0.346
C23	26.925	451840	0.500
C24	27.961	436000	0.606
C25	28.958	401660	0.212
C26	29.916	399110	0.194
C27	30.843	363470	0.538
C28	31.734	339260	0.097
C29	32.616	278350	0.189
C30	33.601	2036860	0.199
C31	34.674	1373090	0.424
C32	35.813	1030190	0.096

Table 3.7 Standards of the main expected compounds obtained from the oil composition (Continued).

Aromatic compounds	**Retention time (min)**	**Peak area**	**Standard deviation**
Benzene	2.710	528687	0.104
Toluene	4.720	932867	0.012
Xylene	9.150	1406000	0.246
Styrene	10.370	2919000	0.015
Limonene	19.330	738397	0.020
Naphthalene	27.170	2569797	0.031
Biphenyl	33.606	6745788	0.009
Fluorene	38.767	3390085	0.021
Phenanthrene	43.360	12030000	0.592
Anthracene	43.399	2143088	0.033
Pyrene	49.890	15501472	0.457
m-terphenyl	50.296	1497000	0.478
Chrysens	55.470	2737882	0.514
Oxygenated compounds	**Retention time (min)**	**Peak area**	**Standard deviation**
Phenol	16.123	1174213	0.348
Acetophenone	21.755	5249000	0.029
Dimethylphenol	25.876	1925653	0.326
Benzoic acid	26.514	2437330	0.237
Trimethylphenol	28.004	2455857	0.197

3.6.2 Gas chromatography mass spectrometry (GC/MS)

The oil collected in the condenser system was analysed using coupled gas chromatography with mass spectrometry (GC/MS). The GC/MS used was a Varian, CP-3800 GC/Varian with Saturn 2200 MS instrument equipped with a DB-5 capillary column. The GC column was heated from a temperature of 40 °C to 310 °C, at a heating rate of 5 °C min^{-1}. The oil samples were loaded into a GC sample vial, then an auto-sampler was used to inject 2 μL into the GC/MS column. The samples were analysed in the GC-MS and optimized to maximize the separation of compounds and to avoid any overlaps between the peaks whilst ensuring elucidation of a wide a range of compounds. The system was calibrated using known compounds as standards (Table 3.7). The analysis consisted of analysis of the full range of aliphatic compounds aromatic compounds and oxygenated compound identification [187].

3.6.3 Peaks identification

The dentification of unknown GC/MS-peaks was achieved by injection of a wide range of standard chemicals to determine response factors and retention times as presented in Table 3.7. For example, tire oil sample presented the highest peak at 19.2 min (Figure 3.13(a)), while the oil sample of the HDPE did not observe any peak at 19 min (Figure 3.13(b)). In the case of the mixture oil sample (Tire/HDPE), the high abundance peak is presented similar to the tire oil sample at 19.2 min as shown in (Figure 3.13(c)). Limonene was injected as the standard and it presented at the retention time of 19.1 min (Figure 3.13(d). This can confirm the identification of limonene as the peaks obtained from the individual tire and HDPE oil samples, and their mixture correspond to the observed peak in the standard.

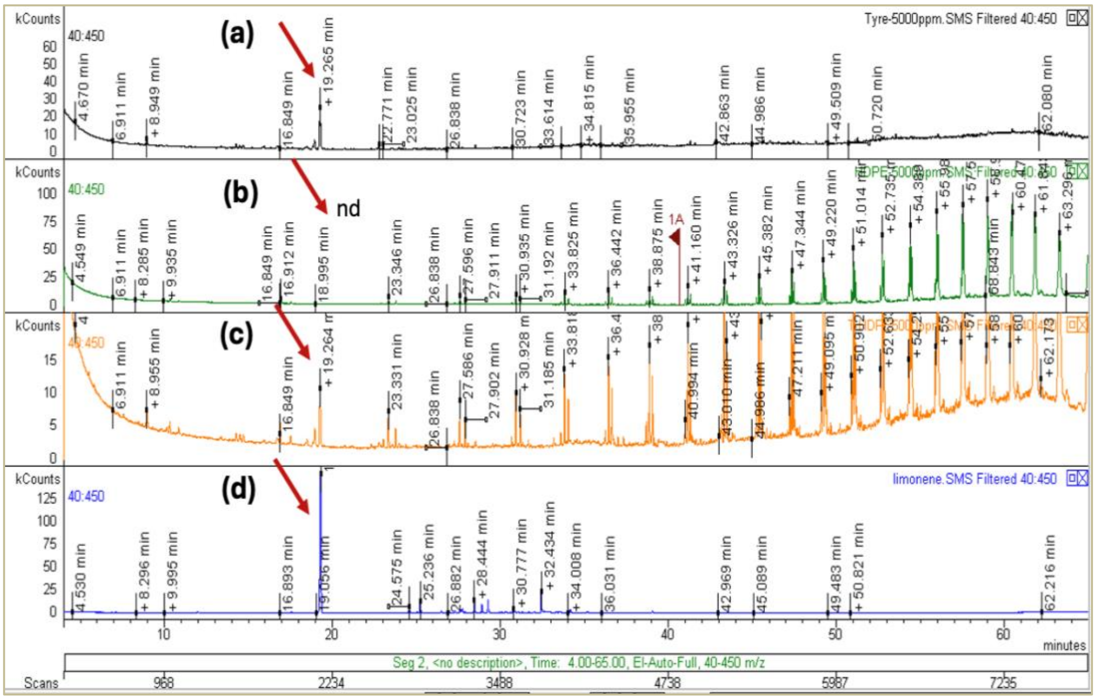


Figure 3.13 The identification of limonene GC/MS peak, (a) tire oil sample, (b) HDPE oil sample, (c) T/HDPE oil sample, and (d) limonene standard.

In addition, the GC/MS NIST library was used to aid peak identification of compounds but also the use of calculated relative retention indices. The use of calculated retention indices for identifying and quantifying the other compounds, particularly the polycyclic aromatic hydrocarbons, this method was developed by Lee[188]. A retention index for a compound indicates where the compound will elute in a chromatogram, under specific experimental GC conditions. For temperature programming, the calculation for the retention indices I, of a compound x, is presented in the following formula[189].

$$Ix = 100\frac{T_n - T_x}{T_{n+1} + T_n} + 100_n \tag{3.9}$$

where T, is the retention time of compound x. T, and T_{n+l} are the retention times of selected polycyclic aromatic hydrocarbons, with ring number n and n+l, respectively, n is the carbon or ring number of the reference compound eluting prior to compound x, such that the n+l reference compound elutes after compound x, bracketing the compound of interest. Nevertheless, GC/MS system was able to identify and quantify the major compound peaks present in the pyrolysis and co-pyrolysis oils[189].

3.6.4 Oil yield calculation

The known standards were injected to calibrate the GC/MS with retention times and response factors (RF). Then, it will be possible to calculate the mass of each compound produced in the oil composition.

$$Concentration\ of\ oil\ compound\ x = \frac{peak\ area\ of\ compound\ x}{peak\ area\ of\ std} \times concentration\ of\ std$$

(mg/ml) (3.10)

$$RF = \frac{\text{Peak area}}{\text{Concentration mg/ml}} \tag{3.11}$$

$$Mass\ of\ compound\ x = Peak\ area\ of\ x \times RF \times volume \quad (mg) \tag{3.12}$$

$$Wt.\% = \frac{mass\ of\ compound\ x}{total\ oil\ mass} \times 100 \tag{3.13}$$

Synergistic effect calculation:

To demonstrate the synergistic effect, comparing co-pyrolysis product yields to theoretical values calculated by using the additivity equation from individual component yields [190].

$$y = (x_1.w_1 + x_2.w_2) \tag{3.13}$$

In this equation, y represents the theoretical yield value, x_1 and x_2 represent the experimental value, of the compounds obtained from individual tire and plastics pyrolysis oil, and w_1 and w_2 are the mass fractions of tire/plastics mixtures. Co-pyrolysis provides synergistic effects when the experimental value exceeds the theoretical value[190].

$$y = y_{experimental} - y_{theoretical} \tag{3.14}$$

3.7 Summary

The experimental methodology that was used for the pyrolysis and the pyrolysis-catalysis of waste tires and plastics was examined in this chapter. The ultimate analysis results show high content of carbon and hydrogen for all the plastics, with high oxygen content observed from PET. The proximate analysis indicates that the plastics samples produced high amount of the volatile content and low quantities of the moisture and fixed carbon. The experimental reactor set up procedures show high efficiency and constant repeatability of the pyrolysis and the pyrolysis-catalysis systems. The calculations of the products yield, the gas and the oil analysis were explained to investigate the wt.%. The oil analysis is conducted using standards and samples preparation, peaks identification, and the analysis instruments, GC for gas analysis and GC/MS for the oil analysis.

Chapter 4: Co-pyrolysis of waste plastics and tires: Influence of interaction on product oil and gas composition

4.1 Introduction

Incorrect disposal of waste plastics is associated with negative impacts on the environment [191,192]. Although recycling of waste plastics via mechanical methods can generate recycled products, they are generally for low grade applications. Also, the other main treatment options of waste landfill and incineration are associated with land and air pollution and represent a waste of resource[120,193]. Many researchers have investigated the use of waste plastics as an essential resource to create new fuels and raw chemical materials through chemical recycling to extract value from the waste plastics [39,48,75]. Plastic waste can be converted to a secondary raw material such as monomers or pyrolysis oil through the process of pyrolysis[194]. The product pyrolysis oil can be used as a liquid fuel, a source of chemicals or as a feedstock to produce new plastics. The chemical composition of the derived pyrolysis oil is dependent on the type of plastic polymer being pyrolyzed. The main plastics found in municipal solid waste are the thermoplastics, low and high density polyethylene, polystyrene, polypropylene and polyethylene terephthalate[195]. Low density polyethylene has a high level of branching and crosslinking in the polymer structure compared to high density polyethylene [48]. However, their product pyrolysis oil composition is very similar as they are both based on polymeric ethylene and consists of mainly n-alkanes, alkenes and alkadienes. Pyrolysis of polypropylene also produces alkenes in the product oil but the oil composition is more complex compared to polyethylene due to the branched structure of the polymer. Since polystyrene has a polymer structure based on aromatic styrene, the oil obtained from pyrolysis of polystyrene is aromatic consisting of mainly styrene, styrene oligomers and single ring aromatic compounds. The polymer structure of polyethylene terephthalate is aromatic and contains oxygenated groups and consequently produces an oil product containing oxygenated compounds including terephthalic acid and benzoic acid[48].

Another high-volume waste material associated with negative environmental impact and difficulties in effective disposal, are waste tires[196]. In recent years, waste tire management options have included mechanical recycling and shredding of the tire rubber for use in sports fields, and for civil engineering applications and via combustion of the tires. Waste landfill for the disposal of tires is also practised in some countries, but is a waste of the resource. Pyrolysis has also been proposed as an effective management option for waste tires for the production of liquid fuels in high yields[141,197,198]. The pyrolysis oil from waste tires is mainly aliphatic and aromatic in composition, but also contains sulfur and nitrogen and oxygenated species [141]. Several different types of rubber may be used in the formulation of a tire, including, styrene–butadiene rubber, natural rubber (polyisoprene), nitrile rubber, chloroprene rubber and polybutadiene rubber. The pyrolysis of the different types of rubber will influence the product oil composition. For example, pyrolysis of styrene-butadiene-rubber produces an oil containing styrene and other single ring aromatic compounds. Pyrolysis of natural rubber generates an oil containing isoprene, dipentene, single-ring aromatic and polycyclic aromatic hydrocarbons as well as aliphatic alkane and alkene hydrocarbons up to C_{16}.

Several million tonnes of both waste plastics and waste tires are generated each year, representing an acute management problem to ensure environmental sustainability[39,198]. The potential for recovery of high yields of product oil from the pyrolysis of waste plastics and tires has been demonstrated. However, there is interest in the co-pyrolysis of these fossil-fuel derived polymeric wastes as a route to recovering the hydrocarbons rather than loss of the resource through combustion or landfilling. There have been some recent studies on the co-pyrolysis of waste plastics and tires [199]. For example, Hu et al [199], used coupled thermogravimetric analysis with Fourier transform infra-red spectrometry to study the co-pyrolysis of waste tires with low and high density polyethylene, polystyrene and polypropylene. They reported that the addition of tire to the co-pyrolysis process resulted in a wider thermal decomposition range for the plastics and evidence of interaction of the tire and plastic volatiles was observed influencing the composition of the product oils and gases. Hussain et al.[200], conducted co-pyrolysis experiments involving tire and polyethylene and reported interaction between the waste polymers during co-pyrolysis which influenced the chemical composition of the product oil. Li et al.[201], investigated the co-pyrolysis of waste tires, with polypropylene, polyethylene, polyvinyl chloride and mixed plastic waste using a thermogravimetric analysis - Fourier transform infra-red/mass spectrometry reaction system (FT-ir/MS). They reported synergistic interaction between the tire and the plastic waste, with polyethylene demonstrating the highest interaction with the tire. Dewi et al.[202], investigated the synergistic interaction between tires and plastics with the main aim of determining the effect of the sulfur content of the tire on the product oil composition from the co-pyrolysis process. They reported that the sulfur content of the product oil could be effectively eliminated by mixing polystyrene or low density polyethylene with the tire. In addition, they showed that mixing polypropylene or polyethylene with the tire produced a pyrolysis oil with enhanced concentrations of lighter hydrocarbons. Miranda et al.[203] used an autoclave closed batch reactor system to study the co-pyrolysis of tires and different plastics, polyethylene, polypropylene and polystyrene. They concluded that pyrolysis temperature has a significant effect on the reaction mechanism of the pyrolysis of tire and plastic waste mixtures.

The literature demonstrates that there has been only limited research into the co-pyrolysis of waste tires and plastics. Consequently, there is a need to understand the advantages or disadvantages of co-processing of these abundant waste polymers to produce product oils via the pyrolysis process. In this respect detailed analysis of the product oils and by-product gases is required to understand the interactions of tires and plastics during co-pyrolysis as to how their interaction influences the end-product oil composition. In this chapter the interaction of waste tires with several different plastics commonly found in municipal solid waste, comprising, high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) is reported. The co-pyrolysis was investigated in a fixed bed reactor and detailed compositional analysis of the product oils and gases is presented to determine the extent of interaction and the influence on product gas and oil yield. The aim of the work was to show how the individual plastics found in mixtures of plastics derived from municipal solid waste influence the overall yield and composition of the product oils and gases.

4.2 Thermogravimetric analysis of tires and plastics

Initial experiments were carried out to determine the thermal decomposition characteristics of the tire, the individual plastics and the mixtures of tire and plastic. The samples were cryogenically crushed to achieve a fine powder particle size to ensure homogeneity. A Schimadzu TGA-50 thermogravimetric analyser (TGA) was used for the analysis, using 10 mg of sample, with heating rate and temperature programme identical to the fixed bed reactor to replicate the pyrolysis reactor experiments (as presented in chapter three). The thermograms and derivative thermograms which measured the rate of decomposition were analysed to determine, the onset of pyrolysis, the peak decomposition and end-point temperatures.

4.2.1 Results of thermogravimetric analysis

Figure 4.1 shows the thermogravimetric analysis (TGA) and the derivative thermograms (DTG) of the tire and individual plastics. The plastics all showed a single weight loss peak decomposition temperature, whereas the tire decomposition occurred over two weight loss peaks, which may be attributed to a mix of rubbers used in the tire formulation[155]. The thermal decomposition of the tire occurred over a temperature range from 230 to 510 °C with a large DTG peak occurring at 387 °C and a smaller DTG peak at a temperature of 445 °C. Dewi et al.[202], also reported the thermal decomposition of tire to be over a broad range from 240 °C to 500 °C, with two distinct peaks, but a smaller peak at a temperature of 375 °C and a much larger peak at 423 °C. The differences in the thermal degradation profile from their work to that reported here are most probably due to the different types of rubber used in the formulation of the tires.

The thermograms were analysed to determine the temperatures related to the on-set of pyrolysis, the peak decomposition and end-point of pyrolysis. The results are shown in Table 4.1. The order of thermal degradation in terms of the main peak degradation temperature was PS<PET<PP<LDPE<HDPE with tire decomposition occurring over a range of 230 - 510 °C.

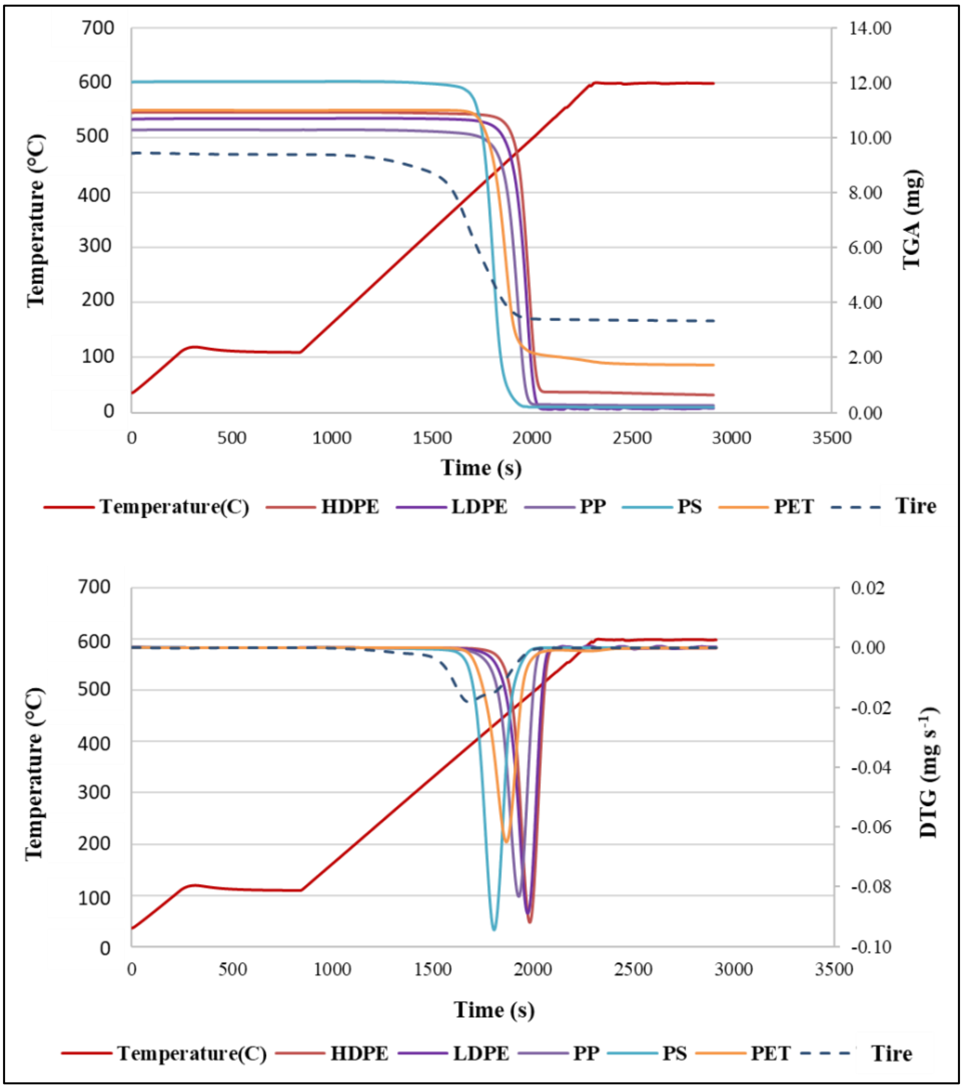


Figure 4.1 (a) Thermogravimetric analysis (TGA) and (b) derivative thermograms (DTG) of the tire and individual plastics.

Table 4.1 Temperatures of thermogravimetric decomposition of the individual plastics and tire.

	HDPE	LDPE	PP	PS	PET	Tire
On-set temperature (°C)	405	430	400	380	380	230
Peak temperature (°C)	495	491	478	434	441	387
End-point temperature (°C)	518	519	511	480	485	510
Mass loss (wt.%)	92.7	98.7	98.0	98.6	81.0	61.0

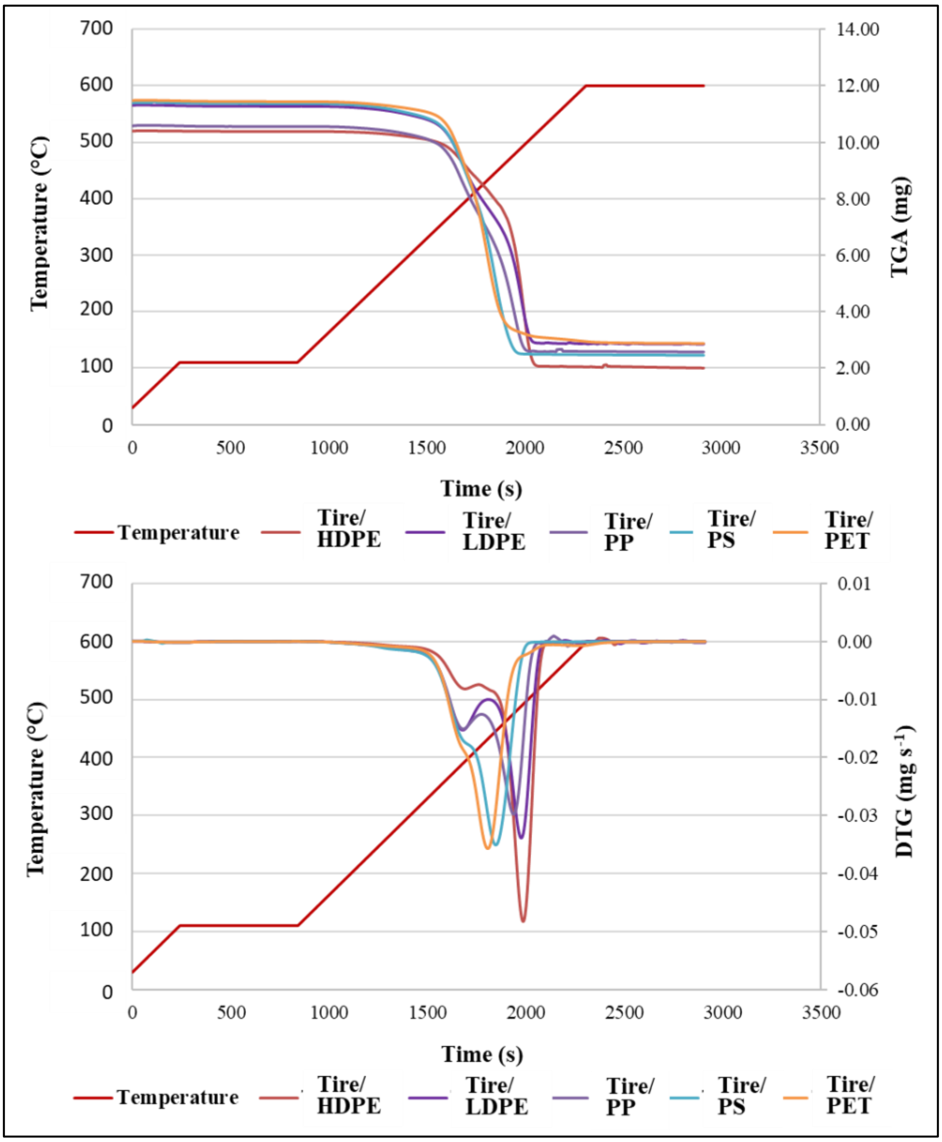


Figure 4.2 (a) Thermogravimetric analysis (TGA) and (b) derivative thermograms (DTG) of the tire/plastic mixtures.

Table 4.2 Temperatures of the thermogravimetric decomposition of the tire/individual plastic mixtures.

	Tire/HDPE	**Tire/LDPE**	**Tire/PP**	**Tire/PS**	**Tire/PET**
Experimental					
On-set temperature (°C)	255	255	255	255	255
Peak Temperature (°C)	(1) 394 (2) 492	(1) 390 (2) 489	(1) 391 (2) 477	(1) 390 (2) 446	(1) 390 (2) 432
End-point temperature (°C)	520	505	515	500	530
Mass loss (wt.%)	80.6	74.7	75.2	78.1	73.2
Individual additive data					
Peak temperature (°C)	(1) 387 (2) 495	(1) 387 (2) 491	(1) 387 (2) 478	(1) 387 (2) 434	(1) 387 (2) 441
Mass loss (wt.%)	76.9	79.8	79.5	79.8	71.0

Figure 4.2 shows the thermogravimetric analysis (Fig. 4.2a)) and derivative thermograms (Fig. 4.2(b)) of the tire/plastic mixtures. Figure 4.2 shows that when tire was added to the plastic during co-pyrolysis, the onset temperature of the thermal degradation for the plastics was shifted to lower temperatures compared to the thermal decomposition of the individual plastic components (Figure 4.1). This phenomena has also been reported by Hu et al. [199]. The mixtures of tire and the polyalkene plastics (Tire/HDPE, Tire/LDPE and Tire/PP) show thermograms that have two distinct peaks of mass loss, the first attributed to the degradation of the tire and the second due to the degradation of the plastic component of the mixture. Hu et al.[199], undertook co-pyrolysis of tires and different plastics using a thermogravimetric analyser and also reported two DTG peak, a lower peak at ~380 °C due to tire decomposition and second higher peaks due the decomposition of the plastic, 460 °C for Tire/PP and 480 °C for Tire/HDPE and Tire/LDPE. The interaction of the tire with the polystyrene and polyethylene terephthalate (Figure 4.2) is influenced by the presence of an aromatic ring in the plastic polymer structure. The thermal decompositions for the mixture of these plastics with tire (Tire/PS, Tire/PET) show clear interaction with the tire, resulting in a single thermal decomposition peak.

Table 4.2 shows the on-set temperature, peak temperature and end-point temperature for the decomposition of the tire/plastic mixtures and also the overall mass loss, for the experimental results. The calculated results, based on the additive data for the individual TGA analysis for the tire and plastics from Table 4.1 are also shown in Table 4.2. The results show that for the polyalkene plastics there is only a small change in the peak temperatures for the first stage tire decomposition and second stage plastic decomposition temperatures. However, the experimental mass loss for the plastics are quite similar to those expected from additive calculation of the individual weight loss data. For the tire/polystyrene and tire/polyethylene terephthalate, Table 4.2 also shows two peak mass losses for the tire and plastics, at 390 °C and 446 °C for Tire/PS and at 390 °C and 432 °C for Tire/PET respectively. Hu et al.[199], investigated TGA co-pyrolysis of Tire/PS and reported two DTG peaks with peaks at ~380 °C and ~ 445 °C, representing tire and PS decomposition. However, Li et al.[201], also reported that only one peak of thermal decomposition was observed for co-pyrolysis of tire and PS using a TGA-FTir/MS system.

4.3 Pyrolysis of the tire and individual plastics

The tire sample and HDPE, LDPE, PP, PS and PET plastics were pyrolyzed individually to determine, the product yield, gas composition and detailed oil analysis. This data can then be used when experiments were conducted using mixed tire/plastic co-pyrolysis to determine any interaction between the waste tire and plastics.

4.3.1 Pyrolysis product yield and gas composition from the tire and individual plastics

Table 4.3 shows the experimental product yield distribution between gas, oil and char from the pyrolysis of the tire sample and the individual waste plastics. The tire and all the plastics produced a hydrocarbon gas and oil/wax, while tire and PET also produced a significant amount of char. The results show a high oil yield compared to gas and char yields. The product yield from the pyrolysis of waste tires showed a high product yield of 54.83 wt.% for the oil, 8.69 wt.% gas, and 37.33 wt.% char. Islam et al.[204], reported similar results for the pyrolysis of waste tire in a fixed-bed reactor and reported a high oil yield of 55 wt.% at 475 °C pyrolysis temperature, with char and gas yields of 36 wt.% and 9 wt.%, respectively. For the plastic pyrolysis experiments polystyrene produced the maximum oil yield at 99.20 wt.%, which is comparable to the results reported by others[205]. The pyrolysis of HDPE and LDPE produced largely a wax product at a yield of 85.50 wt.% and 90.17 wt.% respectively (Table 4.3).

Marcilla et al.[68], conducted pyrolysis of HDPE at 550°C, and observed an oil yield of 84.7 wt.% predominantly (C_5–C_{20}), and gas yield of 16.3 wt.%. Pyrolysis of PP produced a high oil yield of 89 wt.%, similar to that reported by Fakhrhoseini and Dastanian [74]. The pyrolysis of PET produced a mainly yellow coloured wax/solid powder rather than an oil with a yield of 53.0 wt.% in comparison to the other plastic types with a large gas yield of 33.60 wt.%, mostly carbon dioxide and carbon monoxide, as well as a high char yield of 10.17 wt.%, similar to that reported previously[206].

Table 4.3 Product yield from the pyrolysis of individual waste plastics and tire.

	Feedstock sample					
	Tire (wt.%)	**HDPE (wt.%)**	**LDPE (wt.%)**	**PP (wt.%)**	**PS (wt.%)**	**PET (wt.%)**
Gas yield	8.69	6.45	6.17	4.34	1.68	33.60
Oil yield	54.83	85.50	90.17	89.00	99.20	53.00
Char yield	37.33	5.33	0.00	0.67	1.00	10.17
Mass balance	100.85	97.28	96.34	94.01	101.88	96.77

The main gases produced from tire pyrolysis were hydrogen, methane, ethane, ethene, propane, propene, butane, butene, butadiene, carbon dioxide and carbon monoxide as shown in Figure 4.3 and as also reported in several other studies. Figure 4.3 also shows the gases produced from the pyrolysis of HDPE, LDPE, PP, PS, and PET. A low gas yield was produced from the pyrolysis of all the types of plastics except PET, which, unlike the other plastics, produced lower hydrocarbons and more CO_2 and CO due to the presence of oxygen in the polymer structure, which was also reported by other researchers[74,207]. Also the ultimate analysis results (Chapter 3) indicated high oxygen content in PET and tire which was then released during the pyrolysis as CO and CO_2, unlike PE, PP and PS, which produced only hydrocarbon gases. The CO_2 and CO are formed through the random scission of the chain, which occurred at the ester linkages, resulting in carboxyl and vinyl ester groups in the decarboxylation process[55]. The thermal degradation of HDPE, LDPE, and PP primarily produced alkane and alkene gases through the random scission process[55,194].

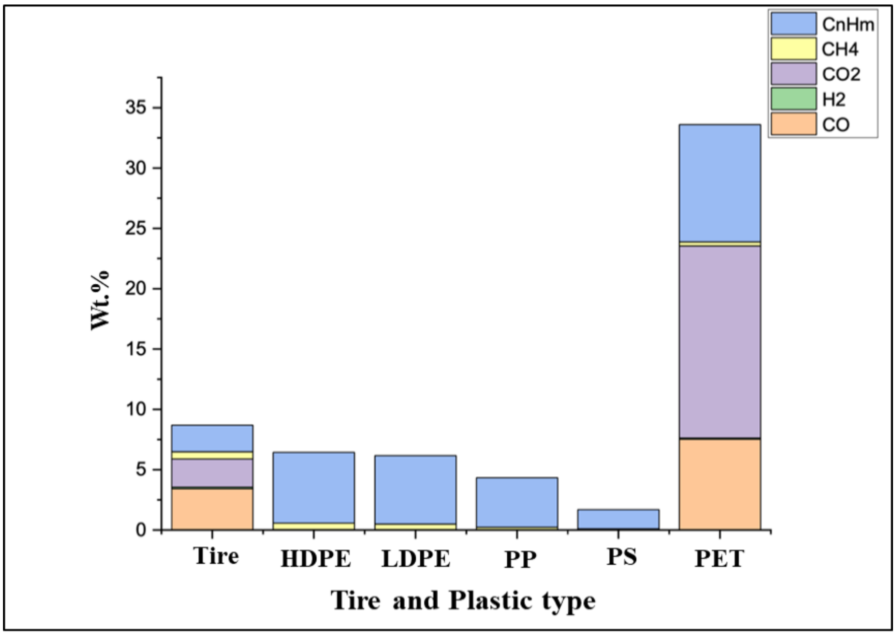


Figure 4.3 Gas composition of the pyrolysis of individual tire and plastic (wt.% of the total product yield).

4.3.2 Oil composition from pyrolysis of individual waste tires and plastics

Table 4.4 and 4.5 show the yield of compounds in the product oil from the pyrolysis of waste tire, high density polyethylene and low density polyethylene determined by GC/MS. The major compounds presented in Table 4.4 and 4.5 consisted of over 95 % of the compounds identified in the oil. There were also other minor peaks observed in the GC/MS chromatogram. For the identified compounds yields are expressed as wt.% in the pyrolysis oil.

Table 4.4 Composition of oil obtained from the pyrolysis of waste tires.

Tire		
Compound	**RT (min)**	**Mass (wt.%)**
limonene	19.31	39.7
benzene,1-methyl-4-(1-methylethenyl)	18.97	6.35
xylene	8.98	4.73
cyclohexene,1-methyl	22.79	4.18
benzothiazole	28.51	3.92
4-methylbiphenyl bibenzyl	36.18	3.65
1,2-dimethylcyclohexane	6.87	3.47
cyclobutane,12-bis(1-methylethenyl)	14.29	3.31
unknown	6.80	3.27
unknown	36.69	3.14
toluene	4.71	2.99
2,3,6-trimethylnaphthalene	37.33	2.92
c-3 naphthalene	36.99	2.89
2-ethylnaphthalene	33.18	2.65
benzene, 1-ethyl-3-methyl	14.71	2.07
1-methylfluorene	41.31	2.05
benzen,1-methyl-4-(methylpropyl)	23.97	1.45
dibenzyl or dibenzofuran	36.64	1.31
1h-indene,1,3-dihydro-1,6-dimethyl	27.49	0.91
9-methylfluorene	38.77	0.87
fluorene	38.19	0.85
ethylbenzene	8.28	0.53
Total		97.21

Table 4.5 Composition of oil obtained from the pyrolysis of high density polyethylene and low density polyethylene.

High density polyethylene			**Low density polyethylene**		
Compound	**RT (min)**	**Mass (wt.%)**	**Compound**	**RT (min)**	**Mass (wt.%)**
C14	14.93	12.52	C15	16.54	12.79
C13	13.23	11.47	C14	14.94	12.26
C15	16.54	10.74	C16	18.06	11.53
C12	11.43	9.42	C13	13.24	10.44
C16	18.00	9.24	C12	11.44	8.90
C11	9.54	8.80	C11	9.54	7.75
C10	7.58	7.52	C19	22.17	6.46
C19	22.16	4.92	C10	7.58	5.51
C20	23.41	3.66	C20	23.41	4.75
C9	5.64	3.65	C17	19.5	4.43
C17	19.49	3.36	C18	20.87	4.04
C18	20.86	2.96	C21	24.60	3.63
C21	24.59	2.62	C9	5.61	2.68
C22	25.73	2.11	C22	25.75	2.19
C8	4.30	1.30	C23	26.89	1.40
C23	26.88	1.12			
C28	31.62	1.01			
C24	27.92	0.70			
C25	28.92	0.57			
Total		97.69			98.76

Tires: The main compounds present in the tire pyrolysis oil were mainly single-ring aromatic compounds and polycyclic aromatic hydrocarbons (PAHs) as shown in Table 4.4. The concentrations of the PAH, naphthalene, fluorene, and phenanthrene and their homologues were around 14 wt.%. According to several studies, tire pyrolysis oil comprises aromatic compounds, but also present are reported to be aliphatic compounds such as alkanes and alkenes[141]. The largest concentration compound was limonene (39.70 wt.%), while the other identified compounds were styrene, cyclohexane, cyclobutene, indene, cyclohexene, and benzothiazole.

Limonene has also been reported as the major product in the oil from the pyrolysis of waste tires by Pakdel et al.[208]. However, limonene yield in tires is dependent on the type of rubber used in the formulation of the tire and also the pyrolysis process conditions. For example, Kwon and Castaldi[209], attributed the presence of limonene to the presence of decomposition of polyisoprene found in natural rubber[147]. In addition, Zhang et al.[167] demonstrated that limonene concentration is very sensitive to pyrolysis temperature, where they reported that increasing the pyrolysis temperature from 450 to 550°C, decreased the limonene concentration from 11.97 wt.% to 4.72 wt.%. The production of high yields of aromatic compounds in the tire pyrolysis oil reported here has also been reported by others [144,156]. For example, Li et al.[144], found that the benzene, toluene, ethylbenzene, and xylene (BTEX) concentration in tire pyrolsis oil produced at a temperature of 650 °C was 11.17 wt.%. Also, Lopez et al.[156], reported high aromatic content oil for the pyrolysis of truck tires at a pyrolysis temperature of 500 °C, at 33.4 wt.% and for pyrolysis of car tires at 43.7 wt.%. The aromatic content found in tire pyrolysis oils has also been attributed to the thermal degradation of styrene-butadiene rubber[147]. Aromatic compounds are also reported to be due to secondary reactions in the pyrolysis hot zone[209].

Tires may be manufactured using several different types of rubber, however, the most commonly used are, natural rubber, styrene-butadiene-rubber and polybutadiene rubber[141]. The formation of products in the oil will depend on the thermal degradation mechanism of the different rubbers and the process conditions of pyrolysis. For example, natural rubber is a polyisoprene polymer and is thermally degraded through depolymerisation of the bonds of the rubber polymer to produce isoprene which may be followed by intramolecular cyclization or Diels-Alder type reaction to produce dipentene and other isoprene oligomers. Further reaction to produce other aliphatic and aromatic hydrocarbons occurs via chain propagation and intramolecular hydrogen transfer [210]. The thermal degradation of styrene-butadiene rubber involves degradation of the butadiene groups of the rubber polymer at lower temperatures and the styrene groups at higher temperature, leading to the formation of mainly ethylbenzene, styrene and isopropylbenzene [159]. Polybutadiene rubber decomposes in a two-stage process with depolymerisation at lower temperatures producing butadiene and dipentene and a range of hydrocarbons at higher temperature. Importantly, the process conditions of tire pyrolysis, will also influence the product oil and gas composition. For example, secondary reactions of the produced hydrocarbons are greatly influenced by high temperature and/or long residence times. For instance, increased single ring and polycyclic aromatic hydrocarbon concentrations may be produced by Diels-Alder reactions, involving the reactions of alkenes such as butadiene to produce cyclic alkenes which subsequently form aromatic compounds via dehydrogenation[210]. In addition, thermal decomposition of major compounds produced from tire pyrolysis widen the range of possible compounds found in the oil. For example, limonene is known to thermally decompose to give benzene, xylene, toluene, trimethylbenzene, styrene and methylstyrene[141].

High and low density polyethylene: Table 4.5 shows the concentration of compounds in the oil obtained from the pyrolysis of high density polyethylene and low density polyethylene. The pyrolysis of HDPE and LDPE produced wax instead of oil, with a high abundance of heavier molecular weight compounds. The composition of the wax/oil produced from the pyrolysis of HDPE and LDPE included mostly linear alkanes, with essentially no aromatic compounds generated. The GC/MS total ion chromatograms for HDPE and LDPE, showed the presence of aliphatic long- chain hydrocarbons from carbon number C_8 to C_{28} for HDPE and from C_8 to C_{25} for LDPE, including alkadiene, 1-alkene, and n-alkane, respectively. Triple peaks were detected for each of the carbon numbers, with the 1-alkene as the largest peak, and the separation of these peaks occurred clearly in the chromatogram for the low carbon numbers from $C_8 – C_{22}$. At higher molecular weights, the resolution from the GC/MS column decreased, and heavier compounds with a carbon number $>C_{23}$ presented as one peak, (1-alkene). The thermal decomposition of the polyalkene plastics, HDPE and LDPE involves a series of reactions, including free radical initiation, secondary decomposition via random scission and chain-end scission and then recombination of different chains[211]. The C — C bonds which are the weakest bonds in the polyethylene structure and are break to form radicals which are then stabilised via the formation of C = C double-bond alkenes, leading to the formation of alkenes as the main compounds in the product oil [207]. Others have also reported that the oil produced from the pyrolysis of polyethylene was mostly aliphatic and with similar carbon number ranges to that shown in this work[62,212,213].

Table 4.6 shows the yield of compounds in the product oil (wt.%) derived from the pyrolysis of polypropylene.

Table 4.6 Composition of oil obtained from the pyrolysis of polypropylene.

Polypropylene		
Compound	**RT (min)**	**Mass (wt.%)**
2,4-diethyl-1-methyl-cyclohexane	7.53	27.33
1,1'-bicyclohexyl, 2-(1-methylethyl)-, trans-	31.12	11.89
1,2-dicyclohexylbutane	31.62	9.43
dodecane, 5-cyclohexyl-	36.96	5.33
1-undecene, 7-methyl-	22.4	4.39
cyclohexane, 1,1,3-trimethyl-2-(3-methylpentyl)-	31.37	4.29
1,19-eicosadiene	38.66	4.06
2-methyl-7-octadecene	37.63	3.12
1,7-nonadiene,4,8-dimethyl-	22.63	2.86
cyclohexane, 1,1'-(1,2-dimethyl-1,2-ethanediyl)bis-	33.13	2.71
9-eicosene	41.86	2.53
2,3,3- trimethyl-1-hexene	10.25	2.34
1-docosene	42.49	2.20
3-eicosene	41.63	2.14
cyclodecane, octyl-	37.20	1.95
cyclohexane, 1-(cyclohexylmethyl)-4-ethyl-, trans-	32.41	1.77
cyclodopentane,(4-octyldodecyl-)	43.39	1.64
1-tetradecene	25.72	1.47
decane, 4-methyl	8.28	1.37
unknown	37.99	1.33
cyclopentane,1-butyl-2-2propyl	16.82	1.24
dodecane, 2,6,10-trimethyl-	30.63	1.07
cyclohexane, 1,3,5-trimethyl	7.120	1.01
1-nonadecene	37.39	0.97
2-undecene, 4,5-dimethyl-	24.74	0.98
1-tetracosene	43.17	0.84
2-tetracosene	46.22	0.76
heneicosane	42.07	0.65
Total		101.67

Polypropylene: Table 4.6 shows that the thermal degradation of the polypropylene produced a significant concentration of unsaturated hydrocarbons (alkenes) with a carbon number range from C_6 - C_{25}. Thermal degradation of polypropylene is promoted by random scission of the polymeric chain; as a result, the degradation products are distributed over a wide range of molecular weights. Due to the CH_3 side group in the polypropylene structure, a considerable number of compounds with carbon double bonds (C=C) are formed in polypropylene cracking products [207].

Table 4.7 shows the yield of compounds in the product oil (wt.%) derived from the pyrolysis of polystyrene

Table 4.7 Composition of oil obtained from the pyrolysis of polystyrene.

Polystyrene		
Compound	**RT (min)**	**Mass (wt.%)**
styrene	10.28	70.08
methyl fluorene	41.51	12.12
dibenz[a,c]anthracene	54.99	3.86
xylene	8.84	3.22
benzene, 3-cyclohexen-1-yl-	31.66	1.70
1,3-diphenyl-3-methylcyclopropene	42.06	1.70
2-methylfluorene or unknown	40.21	1.61
C-3 naphthalene	37.06	1.16
methylacenaphthalene	37.80	0.84
benzene	2.73	0.50
1-methylphenanthrene	45.28	0.50
toluene	4.69	0.50
Total		97.79

Polystyrene: Table 4.7 also show the product oil composition from the pyrolysis of polystyrene. The main product in the oil was styrene at 70.08 wt.%, and also benzene, xylene, toluene and ethylbenzene at ~4 wt.%. The polycyclic aromatic hydrocarbons, naphthalene, biphenyl, fluorene, phenanthrene, and anthracene were also identified in the oil composition. Liu et al. [77], also reported that styrene and monoaromatic compounds such as, benzene, toluene, ethylbenzene, and methyl styrene, were the most significant compounds present in the oil, accounting for approximately 80% of the total. The thermal degradation mechanism of the aromatic structured polystyrene polymer has been demonstrated to involve scission, hydrogen abstraction, hydrogen transfer, radical recombination and disproportionation [211]. Thereby, leading to the formation of the monomer styrene and other single ring aromatics and also polycyclic aromatic hydrocarbons in high concentration[212].

Table 4.8 shows the yield of compounds in the product oil (wt.%) derived from the pyrolysis of polyethylene terephthalate.

Table 4.8 Composition of oil obtained from the pyrolysis of polyethylene terephthalate.

Polyethylene terephthalate		
Compound	**RT (min)**	**Mass (wt.%)**
benzoic acid	27.11	41.1
ethanone, 2-(formyloxy)-1-phenyl-	25.07	21.9
ethanone, 2,2-dihydroxy-1-phenyl-	21.47	2.96
benzene, 1,4 dimethyl-2,5bis(1-methylethyl)	38.00	2.93
methanol, oxo-, benzoate	26.56	2.74
benzoic acid, 4-ethyl	32.56	1.97
acetophenone	26.72	1.83
biphenyl	33.31	1.75
benzoic acid, 4-methyl	30.27	1.68
trimethylphenol	29.56	1.36
benzoylformic acid	14.41	1.13
phthalic acid, di-(1-hexen-5-yl) ester	39.01	0.76
phthalic acid, ethyl 4-isopropylphenyl	39.04	0.55
Total		82.66

Polyethylene terephthalate: Table 4.8 shows the products identified in the waxy/solid powder produced from the pyrolysis of polyethylene terephthalate. The waxy/solid was dissolved in dichloromethane (DCM), but required sonication and an extended time period to dissolve the sample. Benzoic acid was present in high concentration at 41.10 wt.%, while the main aromatic compounds were also observed, such as xylene, styrene, biphenyl, and terphenyl. The chemical structure of PET consists of aromatic, aliphatic and oxygenated groups, leading to the formation of a complex mixture of products during thermal degradation of the polymer. It has been reported that the mechanism for PET thermal degradation include polymer bond scission and retro-hydoalkoxylation to produce benzoic acid and vinyl (CH_2 =CH—) based compounds. Simultaneously the ester groups of the PET polymer decompose to form carbon monoxide, carbon dioxide and ethene[211]. The pyrolysis of PET produced oxygenated compounds in the product oil, in contrast to the other plastics investigated in this work. Cepeliogullar and Putun[93], also reported that almost 50 wt.% of the oil produced during the pyrolysis of PET contained benzoic acid. Other oxygenated compounds present include carboxylic acids, phthalic acid and phenols as well as aromatic compounds.

4.4 Co-pyrolysis of tire and plastic mixtures

The tire sample and each of the plastics were mixed in a 1:1 ratio to produce a Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS and Tire/PET mixture which were then co-pyrolysed in the fixed bed reactor system. The product yield, gas composition and detailed oil analysis were used to determine any interaction between the waste tire and plastics.

4.4.1 Product yield and gas composition from the co-pyrolysis of tire and plastics

Table 4.9 shows the product yield distribution of gas, oil and char produced from the co-pyrolysis of the tire and plastic mixtures. Also shown are the addive yields, calculated based on the predicted yields calculated from the individual tire and plastic pyrolysis data. The results demonstrate a certain interaction between the plastics and tires, resulting in a significantly higher gas yields than predicted for all the mixtures. The tire/polystyrene co-pyrolysis produced the lowest gas yield (7.61 wt.%), but higher than predicted, while the oil yield was consequently slightly lower (69.67 wt.%) than expected. Co-pyrolysis of the tire/polypropylene mixture produced the highest oil yield (73.50 wt%) of all the other tire/plastic mixtures. The char yields were slightly lower than predicted for all the mixtures, suggesting that there was interaction between the tire and plastics during the co-pyrolysis process. This could be via gas-solid (char) interacion or interaction of the evolved volatiles. It has been reported that the release of radicals during pyrolysis promotes depolymerisation of plastics[214]. Also, the char itself can react with the decomposition products from the pyrolysis of plastics[215].

Table 4.9 Product yield from the mixtures of the tire and waste plastics, experimental and additive data (results calculated based on the additivity data of the individual samples).

	Experimental (wt.%)				
	Tire/HDPE	**Tire/LDPE**	**Tire/PP**	**Tire/PS**	**Tire/PET**
Gas yield	13.94	12.13	12.77	7.61	24.58
Oil yield	70.50	71.67	73.50	69.67	56.33
Char yield	16.50	15.83	18.33	20.17	21.67
Mass balance	100.94	99.63	104.60	97.45	102.58
	Additive data (wt.%)				
	Tire/HDPE	**Tire/LDPE**	**Tire/PP**	**Tire/PS**	**Tire/PET**
Gas yield	7.57	7.43	6.52	5.19	21.15
Oil yield	70.17	72.50	71.92	77.01	53.92
Char yield	21.33	18.67	19.00	19.17	23.75
Mass balance	99.07	98.60	97.44	101.37	98.82

Figure 4.4 shows the gas composition obtained from the pyrolysis of the tire and plastic mixtures. Mixing the tire with each plastic produced the main gases of methane, C_2-C_4 hydrocarbons, carbon monoxide and carbon dioxide, which all have a higher gas yield than the calculated additive prediction. The gas analyses of Tire/HDPE, Tire/LDPE, and Tire/PP revealed significant concentrations of CO, CO_2, and hydrocarbon gases due to the addition of tire as the individual HDPE, LDPE, PP, and PS did not produce CO and CO_2 (Figure 4.3). Whereas, the Tire/PS mixture showed lower concentrations of these gases. The Tire/PET mixture gave high gas yields of mainly CO, CO_2, which reflected the high oxygen content of PET compared to the other mixtures.

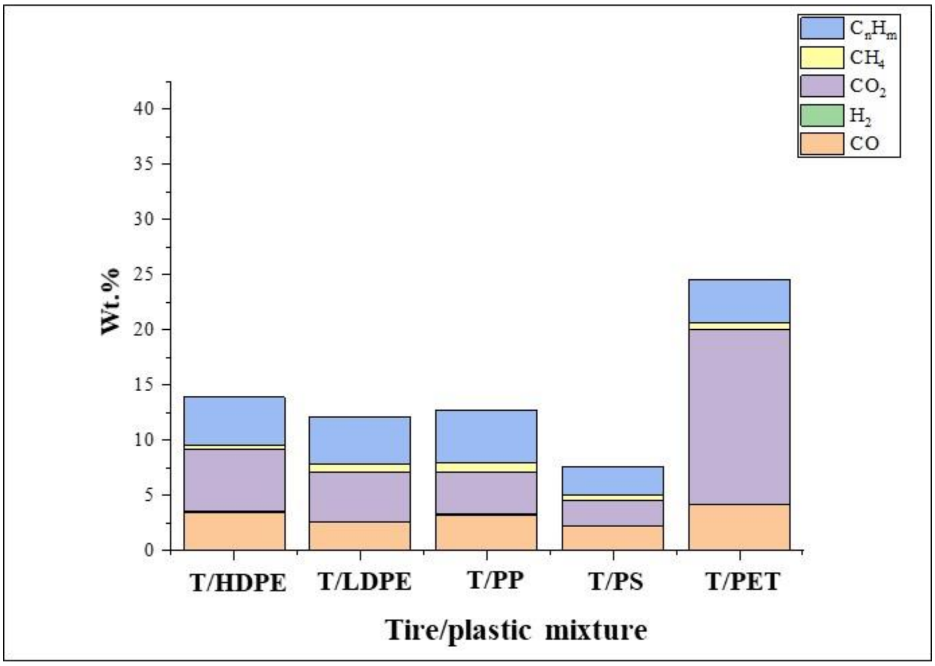


Figure 4.4 Gas composition derived from the pyrolysis of tire/high density polyethylene (T/HDPE), tire/low density polyethylene (T/LDPE), tire/polypropylene (T/PP), tire/polystyrene (T/PS) and tire/polyethylene terephthalate (T/PET).

4.4.2 Composition of oil obtained from the co-pyrolysis of the tire/plastic mixtures

Table 4.10 and Table 4.11 show the composition of the product oil obtained from the co-pyrolysis of Tire/HDPE and Tire/LDPE. The results represent the yield of compounds present in the oil obtained from the pyrolysis of tire/plastic (wt.%).

Table 4.10 Composition of oil obtained from the pyrolysis of tire/high density polyethylene.

Tire/High density polyethylene		
Compound	**RT (min)**	**Mass (wt.%)**
C32	61.83	16.19
C33	63.28	15.34
C31	60.47	15.12
C30	59.05	13.35
C26	54.38	9.22
C24	52.73	8.01
C29	57.5	4.4
C28	56.05	4.37
C21	47.34	2.65
C20	45.37	2.37
C19	43.32	2.00
limonene	19.26	1.41
unknown	41.15	1.36
9-methylfluorene	38.87	1.11
dibenzofuran	36.43	0.97
unknown	23.33	0.9
1,3 dimethyl naphthalene	33.81	0.78
C25	53.06	0.68
1-methylnaphthalene	30.92	0.57
naphthalene	27.58	0.51
C23	51.00	0.51
Total		101.82

Table 4.11 Composition of oil obtained from the pyrolysis of tire/low density polyethylene.

Tire/Low density polyethylene		
Compound	**RT (min)**	**Mass (wt.%)**
C31	59.07	15.15
C32	60.49	14.99
C30	57.53	14.28
C33	61.86	13.90
C27	54.41	8.34
d-limonene	19.34	6.15
C28	55.99	3.90
C24	51.03	2.81
C25	52.75	2.43
anthracene	43.35	1.78
1-methylfluorene	41.18	1.42
C29	56.13	1.42
C26	53.10	1.39
benzene,1-methyl-2-(1 methylethenyl	19.01	1.18
9-methylfluorene	38.89	1.17
unknown	23.37	1.08
dibenzofuran	36.46	1.05
1,3 dimethyl naphthalene	33.84	0.94
methyl styrene	16.94	0.81
cyclohexene,1-methyl-4-(methyl ethenyl	14.33	0.68
1-methylnapthalene	30.95	0.68
naphthalene	27.62	0.63
C22	49.24	0.57
C21	47.36	0.50
Total		97.25

Tire/HDPE and Tire/LDPE: Tables 4.10 and 4.11 show the composition of the oil obtained from the co-pyrolysis of tire/high density polyethylene and tire/low density polyethylene. The main influence of mixing tire with HDPE in relation to the product oil composition was a decrease in the concentration of the aliphatic compounds, represented as triple alkane, alkene and alkadiene peaks from carbon number C_{19} – C_{33}. For each carbon number hydrocarbon group, not all three of the alkane, alkene and alkadiene hydrocarbons were present in the oil. While the lighter aromatic compounds present in the product oil were essentially produced from the tire pyrolysis contribution, such as toluene, xylene, and limonene. Additionally, PAHs that included naphthalene, fluorene, and anthracene and their derivatives were also found in the oil, as was expected based on the tire pyrolysis oil composition (Table 4.4). In relation to the co-pyrolysis of Tire/LDPE, Table 4.11 also shows that the major effect of mixing tires with LDPE was to also produce a pyrolysis oil with a decreased concentration of aliphatic compounds in the carbon number range C_{20} – C_{33}, compared with LDPE pyrolysis alone (Table 4.5). As was the case for HDPE, the co-pyrolysis of tire and LDPE also showed that not all of the alkane, alkene and alkadiene hydrocarbons for each carbon number were identified in the oil. The presence of toluene, xylene, and methyl styrene, and PAHs, illustrate the contribution from pyrolysis of the tire.

Tables 4.12 and 4.13 show the composition of the oil determined by GC/MS derived from the co-pyrolysis of tire/polypropylene and tire/polystyrene. The results represent the yield of compounds present in the oil obtained from the pyrolysis of tire/plastic (wt.%).

Table 4.12 Composition of oil obtained from the pyrolysis of tire/polypropylene.

Tire/Polypropylene		
Compound	**RT(min)**	**Mass (wt.%)**
toluene	4.64	20.16
benzene, 1,2,4-trimethyl-	16.61	13.9
o-xylene	8.9	5.88
cyclohexene,1-methyl-5-(1-methylethenyl	14.41	5.09
benzene,1,2,3-trimethyl-	14.99	4.84
p-xylene	8.91	4.33
benzene, 1,2,4,5-tetramethyl-	24.3	3.98
benzene, 2-ethyl-1,4-dimethyl-	22.58	3.42
cyclohexene, 4-methyl-1-(1-methylethyl)-	20.93	3.28
cyclopentane, 1,1,3,4-tetramethyl	7.13	2.89
naphthalene, 1,4-dimethyl-	34.38	2.78
m-xylene	10.1	2.76
benzene, 1-ethyl-2,4-dimethyl-	25.62	2.66
cyclohexane, 1,1,3-trimethyl-2-(3-methylpentyl)-	31.27	2.48
ethylbenzene	8.42	2.19
naphthalene, 2,3,6-trimethyl-	37.27	2.00
decane, 4-methyl-	18.2	1.78
benzene, 1-ethyl-3-methyl-	15.51	1.73

Table 4.12 Composition of oil obtained from the pyrolysis of tire/polypropylene (Continued).

Tire/Polypropylene		
Compound	**RT(min)**	**Mass (wt.%)**
naphthalene, 1,7-dimethyl-	34.49	1.68
cyclohexene, 1-butyl-	23.36	1.50
2,4-dimethylstyrene	25.13	1.34
cis-.beta.-methyl styrene	19.27	0.92
naphthalene, 1,2,3,4-tetramethyl-	40.49	0.88
9-eicosene	41.84	0.81
naphthalene, 1,6,7-trimethyl-	37.97	0.77
benzene, 1-methyl-4-(1-methyl-2-propenyl	27.13	0.70
7-heptadecene	36.94	0.55
naphthalene	26.94	0.52
7-tetradecene	31.10	0.50
benzene, pentamethyl-	30.28	0.50
undecane, 4,6-dimethyl-	35.28	0.50
benzene	2.70	0.50
1,2,3-trimethylindene	33.13	0.50
azulene, 4,6,8-trimethyl-	38.39	0.50
naphthalene, 2-(1-methylethyl)-	36.44	0.50
naphthalene, 1-methyl-7-(1-methylethyl)-	39.34	0.50
Total		101.36

Tire/polypropylene: Table 4.12 shows the oil composition and yield obtained from the pyrolysis of the tire/polypropylene mixture. The addition of the tire to the plastic had a significant effect on the product oil, producing more aromatic compounds in high concentrations. It also revealed a low abundance of compounds with a higher molecular weight, particularly the aliphatic compounds (alkenes) as well as the alicyclic hydrocarbon compounds, which were mostly formed from the polypropylene. Benzene, toluene, ethylbenzene and xylene (BTEX) compounds were found in high concentrations with toluene found in very higher concentration compared to other compounds. There was also a significant production of benzene, naphthalene, and their derivatives. Wong and Broadbelt [216], also reported that interaction occurs when polyalkene polymers are co-pyrolyzed with aromatic polymers.

Table 4.13 Composition of oil obtained from the pyrolysis of tire/polystyrene.

Tire/Polystyrene		
Compound	**RT (min)**	**Mass (wt.%)**
styrene	10.18	11.44
cis-beta-methyl styrene	15.91	6.25
2,4-dimethyl-1-heptene	7.53	6.08
benzene, 1,1-(1,3-propanediyl) bis	40.22	5.90
limonene	19.23	4.72
benzene, 1-methyl-2-(1-methylethyl)-	18.91	4.42
dibenzo[a,c]anthracene	54.94	4.32
benzene, 1-ethyl-4-methyl-	12.02	4.09
benzene, propyl-	13.92	3.82
benzene, 3-cyclohexen-1-yl-	31.61	3.79
benzene, 1,1'-(3-methyl-1-propene-	41.66	3.67
ethylbenzene	8.48	2.86
1-pentene, 1,5-diphenyl-	45.93	2.83
unknown	56.74	2.78
benzene, (2-methyl-1-propenyl)-	21.01	2.62
benzene, 1,1'-(1,2-dimethyl-1,2-ethanedi	37.74	2.54
toluene	4.66	2.47
1-propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	53.77	2.47
o-xylene	8.92	2.43
7-tetradecene	22.97	2.00
benzene, 1,1'-(1-butene-1,4-diyl) bis-	43.84	1.94
p-xylene	8.91	1.92
benzene, 1,1-(1,2-propanediyl) bis	40.54	1.85
unknown	49.19	1.56
benzothiazole	28.45	1.40
1,2,3-trimethylindene	33.12	1.32
unknown	51.42	1.30
1,5-diphenyl-1,5-hexadiene	47.39	1.07
diphenylmethane	34.73	0.96
benzene, 1,1'-(1-methyl-2-cyclopropene-1,2-diyl)	42.02	0.86
1,3,5 triphenyl benzene	62.12	0.82
5,5-dimethyl-1,3-hexadiene	6.74	0.72
(1-methylpenta-1,3-dienyl) benzene	30.15	0.68
naphthalene, 1-phenyl-	44.53	0.62
1,2-diphenylethylene	36.85	0.60
2,6-diphenyl-1,7-heptadiene	46.04	0.56
Total		99.68

Tire/polystyrene: Table 4.13 shows the composition of the oil obtained from the co-pyrolysis of the tire/polystyrene mixture. The major compounds listed in Table 9 show that styrene was detected in the highest concentration (11.44 wt.%) compared to the other compounds. However, the pyrolysis of polystyrene alone, produce an oil with

70.08 wt.% of styrene (Table 4.7), indicating that interaction between the tire and PS promoted degradation reactions of the styrene to produce other aromatic compounds. Moreover, BTEX compounds were identified in high concentration. PAHs were also found in the oil derived from the pyrolysis of the Tire/PS mixture, which included naphthalene, diphenyl, terphenyl, and anthracene. The highly aromatic product oil from Tire/PS pyrolysis is also linked to their individual pyrolysis oil composition which was mainly aromatic. Because of the structure of polystyrene and the presence of a phenyl group in the structure, aromatic compounds account for more than 90% of the pyrolysis products from polystyrene[79,217]. Pyrolysis products from tires are also dominated by aromatic compounds[141] and mixing PS with tires increased the percentage of these compounds, which produced a highly aromatic oil. Miranda et al.[218], investigated the co-pyrolysis of tires with plastic (30% rubber tires and 70% plastics (20% PE, 30% PP, and 20% PS)). They found that the product oil had a complex composition consisting of 47% alkanes, 14% alkenes, and 39% aromatics. The aromatic compounds were obtained in high concentration at the expense of the alkane fraction.

Table 4.14 shows the composition of the oil determined by GC/MS derived from the co-pyrolysis of tire/polyethylene terephthalate. The results represent the yield of compounds (wt.%) present in the product oil.

Table 4.14 Composition of oil obtained from the pyrolysis of tire/polystyrene and tire/polyethylene terephthalate.

Tire/Polyethylene terephthalate

Compound	**RT(min)**	**Mass (wt.%)**
benzoic acid	27.33	17.34
benzene, 1-methyl-4-(1-methylethyl)-	18.91	7.92
toluene	4.69	7.18
unknown	25.09	6.57
xylene	8.94	6.35
benzene, 1-ethyl-3-methyl-	14.46	5.47
limonene	19.24	4.25
benzoic acid, ethyl ester	26.58	3.98
unknown	22.99	3.91
cyclohexene, 1-methyl-4-(1-methylethylid	22.74	3.26
unknown	21.50	3.21
ethylbenzene	8.47	2.59
benzene, 1,3,5-trimethyl-	16.67	2.18
biphenyl	33.32	1.97
benzene	2.70	1.76
benzothiazole	28.48	1.73
6-methyl-6-hepten-4-yn-3-ol	6.78	1.57
1-(2-methylphenyl)	17.07	1.41
2h-indeno[1,2-b] oxirene, octa hydro-	20.97	1.40
benzene, 1,2,3-trimethyl-	18.45	1.37
unknown	26.91	1.35
2-cyclohexen-1-ol, 4-ethyl-1,4-dimethyl-	13.86	1.21
fluorene	38.04	1.05
benzene, 1-methyl-4-(1-methylpropyl)-	23.92	1.04
diphenylmethane	34.74	0.63
(1-methylbuta-1,3-dienyl) benzene	29.52	0.62
benzene, 1,2,4,5-tetramethyl-	24.33	0.58
2,4-dimethylstyrene	25.51	0.55
benzophenone	39.60	0.52
octadecane, 6-methyl-	41.26	0.47
Total		93.44

Tire/polyethylene terephthalate: Table 4.14 shows the composition of the oil produced from the pyrolysis of the tire/polyethylene terephthalate mixture. The main compounds produced from PET pyrolysis was benzoic acid, while tire pyrolysis produced mainly limonene. On the other hand, PAHs compounds, such as naphthalene, fluorene, and phenanthrene were indicated in this mixture. Furthermore, oxygenated compounds were identified in the product oil as a part of the PET pyrolysis oil. In addition, more BTEX and aromatic contents were produced compared to the individual PET pyrolysis oil.

4.5 Tire-plastic co-pyrolysis interaction effects

The impact of mixing waste tire with different plastics in relation to the yield and composition of the product oils and gases may be seen by comparing the co-pyrolysis product yields to the value predicted using the additivity rule from the yields of the separate feedstock components. Any interaction between tire and plastic may be identified when the experimental value exceeds (positive) or is less than (negative) the calculated additive value [199]. The calculated interaction data for the product yields are shown in Figure 4.5, which includes gas, oil, and char yields for the tire/plastic mixtures investigated in this study. Gas yields for all the mixtures of Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS, and Tire/PET revealed positive values at 6.37, 4.70, 6.26, 2.43, and 3.44 wt.%, respectively. This demonstrated that the volatile materials increased with temperature which led to an increase in gas yield at the expense of oil yield. The char yields observed a positive value for Tire/PS at 1.0 wt.% compared to the other mixtures that showed negative values at -4.83, -2.84, -0.67, and -2.08 wt.% for Tire/HDPE, Tire/LDPE, Tire/PP, and Tire/PET, respectively.

The oil yields of Tire/HDPE, Tire/PP, and Tire/PET showed higher values than calculated by feedstock addition at 0.36, 1.59, and 2.42 wt.%, which was considered as a very slight difference between the co-pyrolysis experimental and calculated additive oil yields. That may be explained by the minimum interaction that can be seen between HDPE and tire during the co-pyrolysis process. Whereas the co-pyrolysis of Tire/PP and Tire/PET obtained a significant and higher interaction effect. Tire/LDPE and Tire/PS obtained lower, negative values at -0.83 and -7.35 wt.%, respectively, as the experimental results were less than the calculated additive results. This is due to the high gaseous products evolved from the co-pyrolysis at the expense of oil formation. Furthermore, changes in the branched chain of the plastic polymer may result in distinct pyrolysis breakdown behaviour when interacted with natural and synthetic rubber components in tires, which may explain the variation in interaction effects during the co-pyrolysis process[199]. Hu et al.[199], investigated the co-pyrolysis of Tire/HDPE, Tire/LDPE, Tire/PP and Tire/PS using a coupled thermogravimetric analyser with Fourier transform infra-red spectrometry and reported synergistic interaction between the tire and plastic which influenced the composition of product oils and gases.

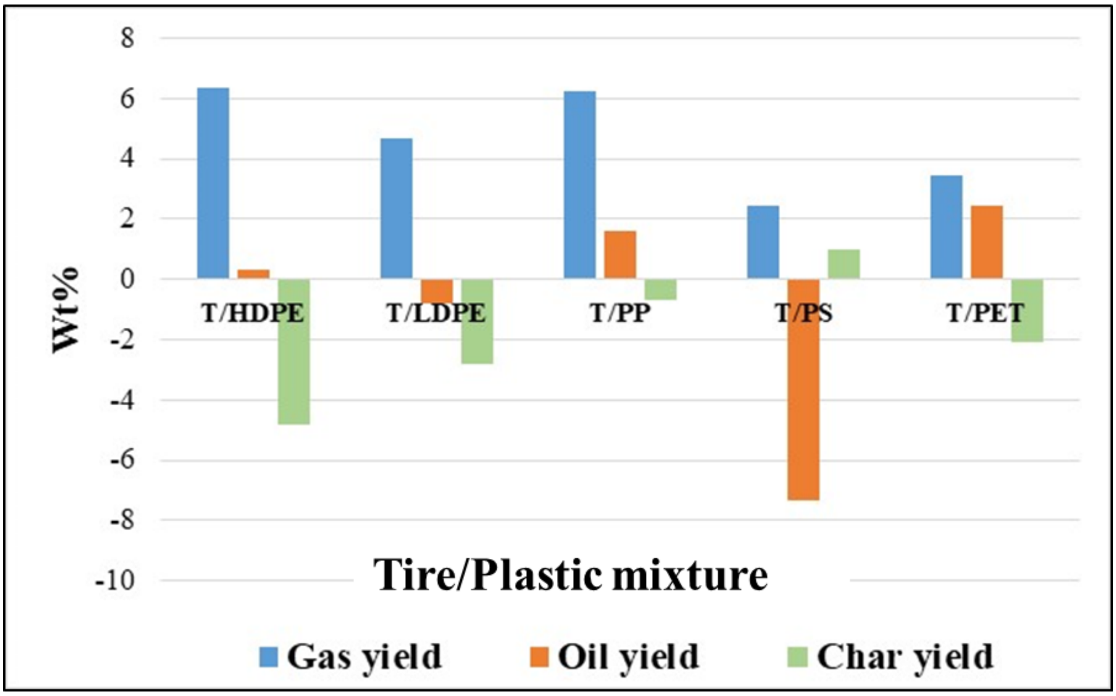


Figure 4.5 Interaction effect of mixing tire/plastic on product yield from the pyrolysis of tire/high density polyethylene (T/HDPE), tire/low density polyethylene (T/LDPE), tire/polypropylene (T/PP), tire/polystyrene (T/PS) and tire/polyethylene terephthalate (T/PET).

The main investigated gases in the co-pyrolysis of tires and plastics were, hydrogen, methane, C_nH_m hydrocarbons (C_2-C_4), carbon monoxide and carbon dioxide. Figure 4.6 shows the interaction results, which showed higher values of CO_2 were produced experimentally than would be expected from additive calculation based on the pyrolysis of the individual feedstocks for all the mixtures. For example, Tire/PET was associated with high yields of gas species generated from the individual tire and PET. While the CO yield revealed a lower than expected value for the Tire/PET mixture compared to the other mixtures. Moreover, the hydrocarbon gases (C_nH_m), showed a negative interaction effect for Tire/PET representing a lower yield of hydrocarbons that were generated by the pyrolysis of the individual tire feedstock. Hydrogen and methane showed low calculated interaction values which make it difficult to assess their interaction effects. Hu et al.[199], reported that the co-pyrolysis of Tire/HDPE, Tire/LDPE, Tire/PP and Tire/PS resulted in a reduction in the yield of methane in the product gas than would be expected from that predicted by addition.

Dewi et al. [202], investigated tire and plastics interaction using a pyroprobe-gas chromatograph, thermogravimetric analysis and a fixed bed reactor system for their experiments. They investigated co-pyrolysis of Tire/LDPE, Tire/PP and Tire/PS. They reported synergistic interaction between tire and plastic which was dependent on the plastic type. For example, mixing tire with LDPE produced a higher yield of oil with enhanced concentration of light hydrocarbons. The co-pyrolysis of Tire/PP and Tire/PS produced negligible change in the total oil yield but a marked change in oil composition.

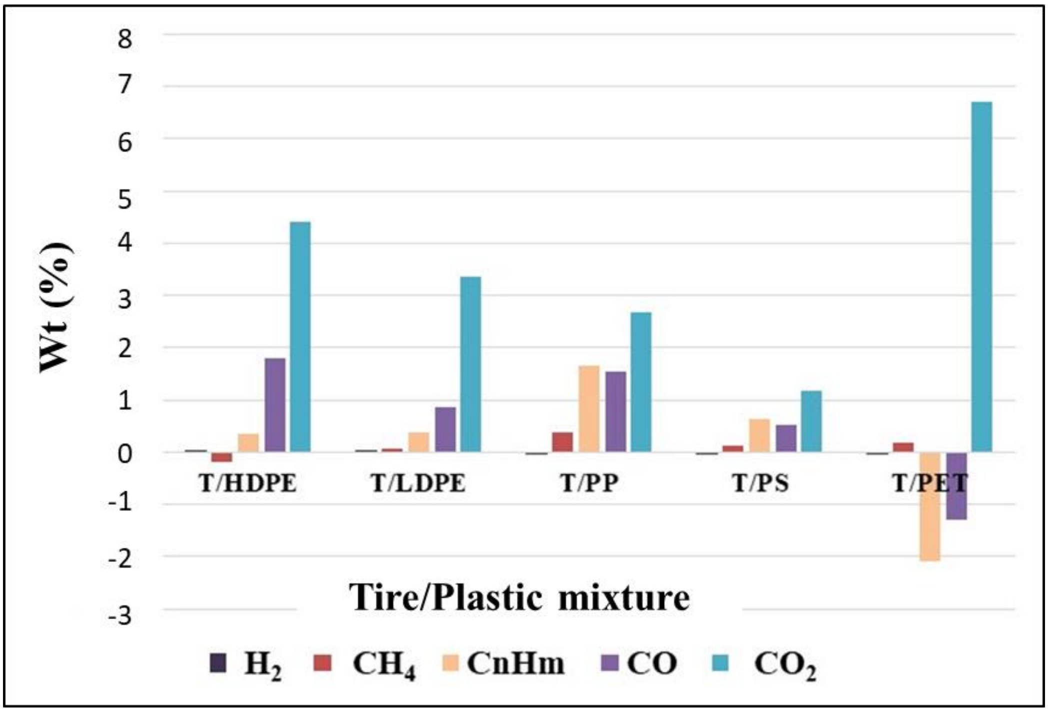


Figure 4.6 Interaction effect of mixing tire/plastic on gas composition from pyrolysis of tire/high density polyethylene (T/HDPE), tire/low density polyethylene (T/LDPE), tire/polypropylene (T/PP), tire/polystyrene (T/PS) and tire/polyethylene terephthalate (T/PET).

The mixtures of Tire/HDPE, Tire/LDPE, and Tire/PP were classified according to the main oil components, and the results are shown in Figure 4.7. BTEX, refers to benzene, toluene, ethylbenzene and xylenes; Aromatic refers to benzene derivatives, biphenyls, limonene, terphenyl, and indene; PAHs refers to for example, naphthalene, anthracene, phenanthrene, pyrene and fluorene and their derivatives; Aliphatic refers to carbon numbers above C_8; Alicyclic compounds refers for example to cyclopentane and cyclohexane etc.,

Aliphatic compounds were increased above that expected from the results obtained from the tire and plastic feedstock pyrolysis data for the co-pyrolysis of Tire/HDPE and Tire/LDPE with lower than expected values for the BTEX, PAHs, alicyclic, and aromatic compounds. Miranda et al. [203], have also reported a strong inter-relationship between aliphatic and aromatic compounds due to interaction between tires and plastics during co-pyrolysis. Dewi et al.[202] , have proposed a reaction mechanism for the interaction of tires and plastics during co-pyrolysis which is dependent on the type of plastic in the co-pyrolysis mixture. HDPE, LDPE have a higher H/C ratio than that of the tire which promotes the large formation of hydrogen radicals during the pyrolysis process, and these promote the breaking of the polymer chains of the tire rubber and the consequent formation of hydrocarbon radicals. These hydrocarbon radicals then bond with the radicals produced from the thermal decomposition of the polyalkene plastics to form alkanes and alkenes and a reduction in the formation of aromatic compounds. This mechanism is supported by the data for Tire/HDPE and Tire/LDPE shown in Figure 4.7, but less so for the Tire/PP where there is a more positive interaction to produce less aliphatic compounds and more aromatic compounds. Figure 4.7 shows that the composition of the oil for the co-pyrolysis of Tire/PP revealed positive values for BTEX, PAHs, and aromatic compounds. For Tire/PP co-pyrolysis the reaction mechanism may be related to the presence of natural rubber in the tire which promotes the pyrolytic decomposition of PP. This increases secondary reactions and recombination to produce light compounds, such as BTEX. Hu et al. [199], undertook co-pyrolysis of tires and different plastics using a thermogravimetric analyser and reported a positive interaction between the Tire/HDPE and Tire/LDPE, at higher temperatures of ~450 °C. For the Tire/PP co-pyrolysis they reported positive interaction at lower temperatures (<445 °C) which they attributed to the decomposition of natural rubber in the tire interacting to decompose the PP. However, at temperatures above 445 °C, once the natural rubber had fully decomposed, there was negative interaction between tire and PP. They have suggested that the synthetic rubber component of tire (e.g. styrene-butadiene-rubber) may also have an influence on plastic polymer thermal degradation at higher temperatures of pyrolysis. Dewi et al.[202] , also proposed that the tire char acts as a catalyst for the cracking of polyalkene plastics since the tire char contains Lewis and Bronsted acid sites which promote the polymer degradation.

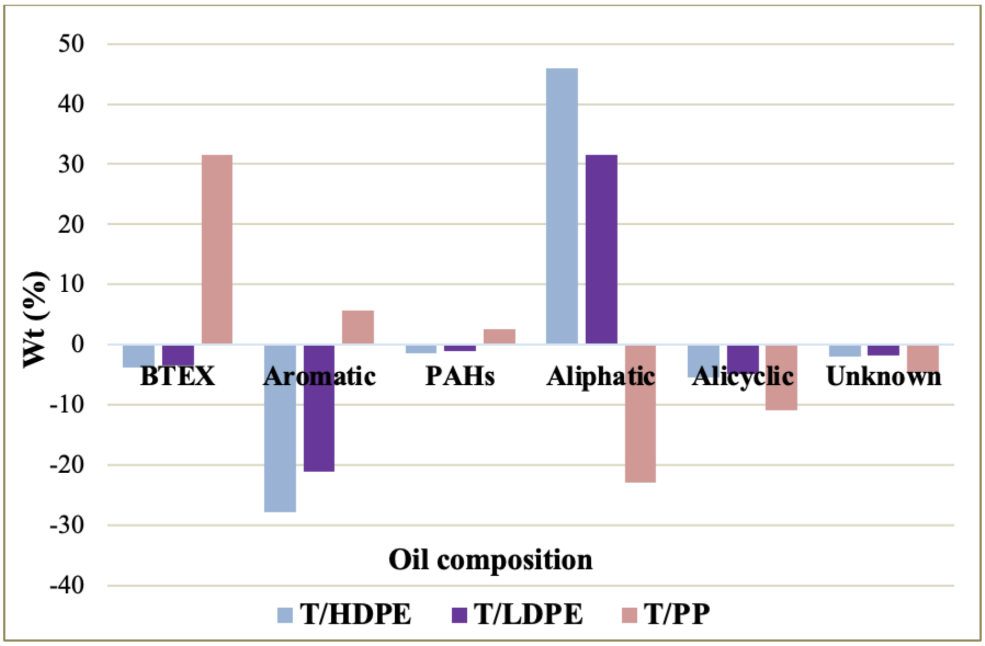


Figure 4.7 Interaction effect of mixing tire/plastic on oil composition from pyrolysis of tire/high density polyethylene (T/HDPE), tire/low density polyethylene (T/LDPE) and tire/polypropylene (T/PP).

Figure 4.8(a) shows the Tire/PS interaction for the product oil produced from co-pyrolysis, and positive interaction values of 3.57 and 4.60 wt.% for BTEX and aromatic compounds, respectively. However, negative values for PAHs at -12.37 wt.%, and alicyclic hydrocarbons at -5.48 wt.% are shown. It has been suggested [202], that the thermal decomposition of the tire produces alkyl radicals which react with the phenyl and benzyl radicals produced from the pyrolysis of the PS to form benzene derivatives and subsequently single ring aromatic compounds. The pyrolysis of tire would also produce more hydrogen radicals than PS so as to promote the hydrogenation reaction of benzene derivative radicals to promote the formation of BTEX. Li et al.[201], have reported that the pyrolysis products of PS can promote the decomposition of natural rubber and butadiene rubber. The co-pyrolysis of Tire/PET produced interaction resulting in changes in oil composition (Figure 4.8(b)) which showed high value for BTEX, while lower values for the oxygenated compounds. The co-pyrolysis of Tire/PET produced more volatile chemicals, which include light hydrocarbons, carbon dioxide, and carbon monoxide.

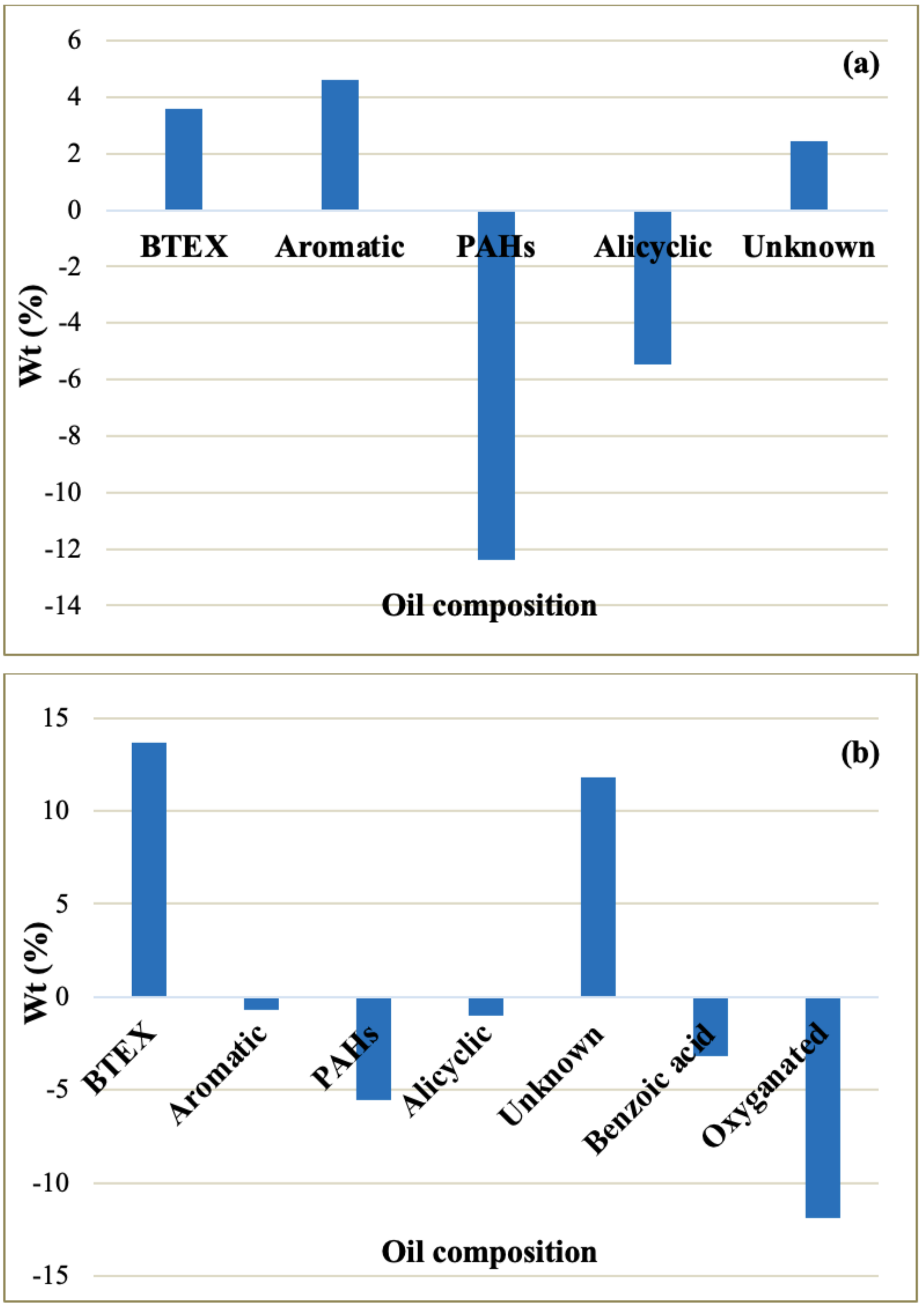


Figure 4.8 Interaction effect of mixing (a) tire/polystyrene and (b) tire/polyethylene terephthalate on pyrolysis oil composition.

A further factor that can influence interaction between the tire and plastics during co-pyrolysis is the different formulations of natural and synthetic rubbers used to manufacture the tire. Also, different tire manufacturers may use different fillers and additives in the manufacturing process which will influence the thermal degradation of the tire. For example, it has been reported that the thermal decomposition of natural rubber using TGA at a heating rate of 20 °C min^{-1}, occurs over the temperature range, 330 - 420 °C, whereas styrene-butadiene rubber decomposes over a temperature range between 370 – 515 °C [155]. On the other hand, the TGA decomposition of polybutadiene rubber occurs in two steps between 370 – 405 °C and 425 - 525 °C. The release of pyrolysis volatiles at these different temperature ranges will influence their availability for interaction with the evolved volatiles from plastics pyrolysis which occur at different temperature (Figure 4.1). Also, Kyari et al.[219], have investigated the pyrolysis of several different brands of tire and showed that distinct differences in gas composition, for carbon dioxide, carbon monoxide, hydrogen, methane, and other hydrocarbon gases. Similarly, the product oil from the different tire brands showed significant differences in composition for several hydrocarbons, for example, limonene, ethylbenzene and ethyltoluene and for PAH, such as, naphthalene, phenanthrene, and pyrene

Overall, the results have shown that co-pyrolysis of tires and waste plastics can generate high yields of pyrolysis oil at ~70 wt.% for Tire/HDPE, Tire/LDPE, Tire/PP and Tire/PS, but only 56 wt.% for the Tire/PET mixture. A key advantage of the co-pyrolysis of tire with HDPE and LDPE, was that the product oil was a liquid oil rather than a waxy product produced by pyrolysis of the HDPE and LDPE alone. Collection and processing of waste plastics and waste tires through co-pyrolysis has been demonstrated as a viable process to produce a liquid oil suitable as a medium grade liquid fuel. Both waste plastics and tires are generated in high tonnages each year and require waste management. Co-pyrolysis as a process for the management of waste plastics and tires has advantages in that in addition to the high yield of oil, gas yields are improved which enable the gas to be considered as a fuel for the heating of the pyrolysis process. In addition, the oil composition can be changed by design, through the selective mixing of different plastics with the tire to manipulate the end product oil composition in terms of the concentrations of aromatic and aliphatic components.

This work has presented results on the yield and composition of the product oils and gases produced from mixing waste tire rubber with waste plastics. In particular, the interaction of tire with the individual plastics, high density and low density polyethylene, polypropylene, polystyrene and polyethylene terephthalate has been investigated and detailed oil and gas yields and compositions presented. However, in practice in an industrial context, the plastics would not be separated and then processed individually with the tires as that would not be commercially viable. Realistically, the process would involve mixed waste plastics and tires co-pyrolysed together. The main aim of this work was to show how the individual plastics interact with the tire to alter the product oil and yield and composition. Thereby, the influence of the different plastics in the mixed plastic feedstock on the final oil and gas product yield and composition can be predicted.

4.6 Summary

In this chapter, pyrolysis of waste plastic, waste tire, and 1:1 mixtures of the tire and plastics has been conducted using a fixed-bed reactor. Pyrolysis of the HDPE and LDPE plastics produced a wax/oil product in high yield, at 85.50 wt.% for HDPE and 90.17 wt.% for LDPE. However, a liquid oil was produced for pyrolysis of PP (89 wt.%), and PS (99.20 wt.%). PET produced only 53.0 wt.% and a high gas yield consisting of mainly CO and CO_2, derived from the oxygenated content of the PET. Pyrolysis of tire produced an oil yield of 54.83 wt.% and a high char content of 37.33 wt.%. The results showed the liquid oil produced from the pyrolysis of tires and PS was mostly composed of aromatic compounds, such as the BTEX, and PAH. The liquid oil formed from the pyrolysis of HDPE and LDPE, on the other hand, was mostly waxes of high molecular weight consisting of aliphatic compound ranging from C_8 - C_{28}, composed of a series of alkanes, alkenes, and alkadienes. Whereas PP produced more alicyclic compounds, such as methyl-cyclohexane. PET pyrolysis oil consisted of compounds, such as xylene, styrene, but was mainly composed of oxygenated compounds, for example, benzoic acid.

Co-pyrolysis of 1:1 mixtures of the tires and individual plastics involved interaction, resulting in significantly higher yields of gas than expected for all the plastic mixtures. The co-pyrolysis of tire with HDPE and LDPE produced a liquid oil product rather than the waxy product produced for pyrolysis of the plastics alone. Gas composition was also influenced by interaction between the tire and plastic, with much higher yields of methane, C_2 – C_4 (C_nH_m) hydrocarbons, carbon monoxide and carbon dioxide, for HDPE, LDPE, PP and PS plastics, but, Tire/PET co-pyrolysis gave higher than expected carbon dioxide, but lower C_2 – C_4 hydrocarbons (C_nH_m) and carbon monoxide yields were found. The oil produced from the co-pyrolysis of the tire with the polyalkene plastics, Tire/HDPE and Tire/LDPE, showed interaction between the polymer pyrolysis products resulting in higher yields of aliphatic compounds and lower yields for the BTEX, PAHs, alicyclic, and aromatic compounds. It was suggested that the increased production of hydrogen radicals from co-pyrolysis promoted alkane and alkene production coupled with de-aromatisation reactions. However, Tire/PP showed negative interaction for aliphatic compounds resulting in lower yield, but higher yields for aromatic compounds, BTEX and PAHs. The mechanism for Tire/PP interaction was linked to the decomposition of natural rubber in the tire which promotes plastic polymer degradation and secondary reactions to form single ring aromatic hydrocarbons. Co-pyrolysis of Tire/PS produced positive interaction for aromatic compounds, since both tire and PS produce aromatic oils, however, the Tire/PS interaction induced reduction in the yield of PAH. Co-pyrolysis of Tire/PET showed positive interaction for BTEX and reduction in the content of oxygenated compounds, which released the oxygen from the PET in the form of increased yields of carbon dioxide.

Chapter 5: The pyrolysis-catalysis of waste tire and waste plastic over ZSM-5 catalyst

5.1 Introduction

The perceived advantage of catalytic pyrolysis is its ability to a produce higher quality product distribution than thermal pyrolysis, thus improving the yield of products with high value [220]. The use of catalysts in waste tire pyrolysis has been discussed in the literature, and several catalysts have been used in the tire pyrolysis process to enhance the quality of the tire pyrolysis oil and gaseous products. Thus, increasing the concentration of high value chemical compounds such as aromatics and light olefins, and also to minimise sulfur-containing compounds[141]. Catalysts such as microporous acid zeolites were the most investigated catalysts[109]. Pyrolysis-catalysis has also been investigated for waste plastics. Catalysts promote cracking processes, increasing the production of gases while decreasing the oil yield[121] compared to the thermal pyrolysis. However, the quality of the oil improves as the long carbon chain molecules are broken down into smaller carbon chain compounds. Catalyst properties such as BET surface area, pore size, pore volume, and acidity are the major parameters affecting the catalytic activity in the process of pyrolysis-catalysis. Zeolites are crystalline alumino-silicate molecular sieves with a three-dimensional structure that includes pores and channels. Zeolite catalysts contain SiO_2/Al_2O_3 in different ratios, which define their reactivity and contribute to the final products of the pyrolysis process. Zeolites catalysts with high acidity such as ZSM-5 and MCM-41 are more active in the process of cracking and promoting the production of light olefins while decreasing the heavy oil portions [96].

5.2 Pyrolysis-catalysis of waste tires and plastics

The process of upgrading the oil to a highly aromatic oil to be used as a potential fuel or chemical feedstock was investigated in this work. The process involved the use of a two-stage reactor system (Chapter 3). The pyrolysis-catalysis of waste tires, plastics, and their mixtures was investigated with pyrolysis in the first stage at a temperature of 650°C. The pyrolysis gases are passed directly to the second stage catalytic reactor which contained ZSM-5 catalyst at a temperature of 550°C. The influence of the pyrolysis -catalysis process on the products composition, particularly, the gas and oil yields were investigated in this chapter. Moreover, the data collected from the co-pyrolysis-catalysis was also investigated to detect any interactions between waste tires and plastics.

5.2.1 Pyrolysis product yield distribution and gas composition from the individual tires and plastics

Table 5.1 shows the product yield from the pyrolysis-catalysis of the individual waste tire and plastics. For tire pyrolysis-catalysis, the introduction of the catalyst had an effect on reducing oil yield to 37.30 wt.% compared to the thermal pyrolysis, with a corresponding increase in the gas yield at 24.65 wt.% compared to the thermal pyrolysis of tire that produced a gas yield of at 8.69 wt.% as shown in Figure 5.1. The char yield remained constant at around 38.68 wt.% which was the same for both thermal and catalysis pyrolysis. Shen et al. [174] investigated the catalytic cracking of tires pyrolysis volatiles on HZSM-5 using a two-stage fixed bed batch reactor. They also found an increase in the gas yield with decreasing oil production from 52.0 wt.% achieved without a catalyst to 32.1 wt.% with the ZSM-5 catalyst, while the gas yield increased from 11.9 to 31.8 wt.%. Olazar et al. [114,149] demonstrated that HZSM-5 zeolites resulted in gas yields of 16.7 wt.%. This is due to the various porous structures and acid characteristics of the zeolites. It is important to highlight that the presence of strong acid sites on HZSM-5 is responsible for the increase conversion of liquid products into gases, and the HZSM-5 zeolite facilitates the cracking of heavy fractions. Williams and Brindle [111] carried out the pyrolysis-catalysis in fixed bed reactor using two types of catalysts (ZSM-5 and HY), and they reported the oil yield decreased from 55.8% to 32 wt.%, while the gas yield increased from 6.1 to 20 wt.%. Marcilla et al.[68] investigated the catalytic batch pyrolysis of LDPE and HDPE with HZSM-5 catalyst, and they revealed comparable results to those reported here, with both HDPE and LDPE where the gas production was above 70%. Zhou et al.[113] investigated the pyrolysis of LDPE and PP in a fixed bed reactor using HZSM-5 catalyst at 430°C. The results showed the gas yield of LDPE was 49.0% and 38.2% with PP, while the oil yield was reported as 48.8% and 58.8% for LDPE and PP, respectively. Table 5.1 showed that PS produced the lowest gas yield, while PET produced the highest gas yield. The main gases generated from PET were CO and

CO_2 that formed through decarboxylation of PET, and similar results were also reported by Muhammad et al.[221].

Table 5.1 Product yield from the pyrolysis-catalysis of individual waste tire and plastics.

	Feedstock sample					
	Tire (wt.%)	**HDPE**	**LDPE**	**PP**	**PS**	**PET**
Gas yield	24.65	36.58	39.04	30.85	6.68	40.77
Oil yield	37.30	53.67	51.31	58.70	84.32	43.33
Char yield	38.68	0.34	0.00	1.66	0.34	17.00
Mass balance	100.63	90.59	90.35	91.21	91.34	101.1

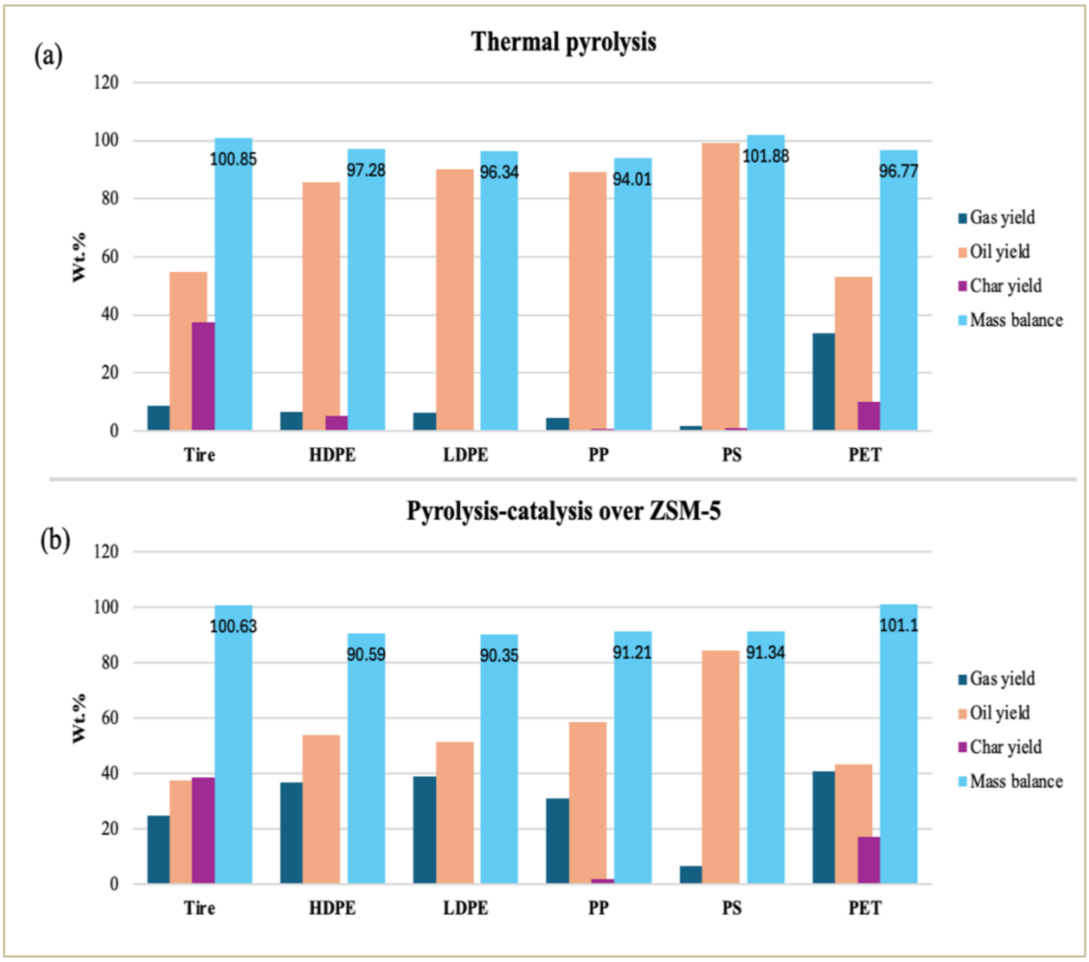


Figure 5.1 Product yield distribution from the thermal (a) and pyrolysis-catalysis over ZSM-5 (b) of the individual waste tire and plastics.

The gas composition (wt.%) from the pyrolysis-catalysis of waste tires and plastics are shown in Figure 5.2. The presence of the ZSM-5 catalyst in the pyrolysis of tire, HDPE, LDPE, PP, PS, and PET provided high gas yields compared to the thermal pyrolysis. For example, Sakata et al.[49] conducted the pyrolysis-catalysis of HDPE over ZSM-5, and they found that lower oil yield at 49.8 wt.%. Furthermore, hydrocarbon gases demonstrated a significant increase in concentration that was produced from tires and plastics (HDPE, LDPE, PP, and PS), resulting in more production of light hydrocarbons (C_1-C_4). On the other hand, PET produced the highest gas yield for all the plastics, with the main gas distribution toward carbon monoxide and carbon dioxide. In relation to pyrolysis/catalysis of waste plastics, several investigations revealed that the ZSM-5 catalyst has been acknowledged as appropriate for the production of C_1-C_4 gases with a significant amount of light olefins [97,222–225]. In relation to pyrolysis/catalysis of waste tires, it has been reported that ZSM-5 enhanced the secondary cracking processes, resulting in more light hydrocarbons at the expense of large molecules in the tire oil [114,149,175,226]. For example, Arabiourrutia et al. [114] reported increased in the yield of ethene, propene, 1,3-butadiene, and 2-butene significantly, and they found that HZSM-5 has a better selectivity for propene and butadiene due to the shape selectivity of this zeolite, which favours monomolecular cracking [175]. Olazar et al.[149,175] found that the presence of HZSM-5 reduces the concentrations of CO and CO_2, due to their poor activity for decarbonylation and decarboxylation processes.

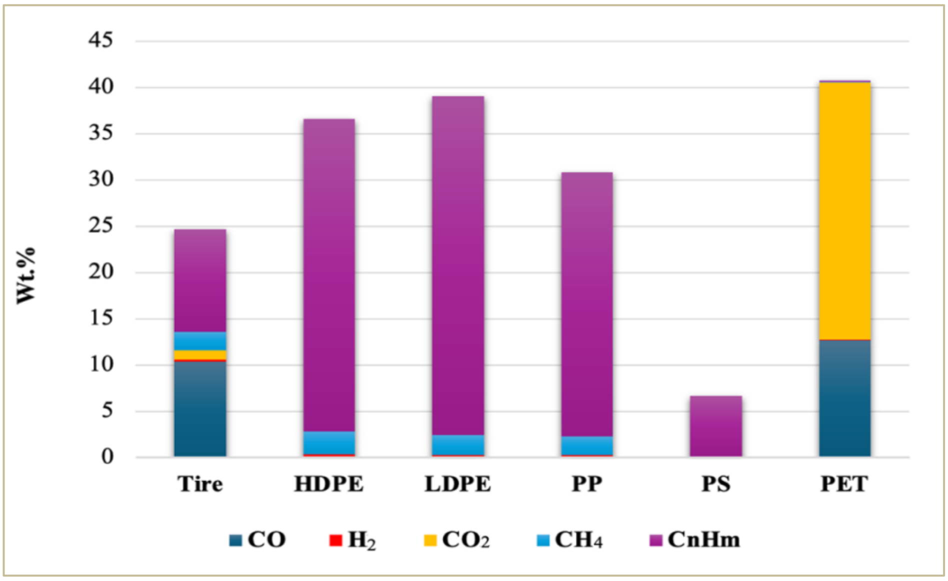


Figure 5.2 Gas composition of the pyrolysis-catalysis of individual tire and plastic (wt.% of the total product yield).

5.2.2 Oil composition from pyrolysis-catalysis of individual waste tires and plastics

The product oil from the pyrolysis of waste tires and plastics determined by GC/MS. The major compounds presented in all the tables consisted of over 95 % of the compounds identified and expressed as wt.% in the pyrolysis-catalysis oil. BTEX, refers to benzene, toluene, ethylbenzene and xylenes; Aromatic refers to benzene derivatives, biphenyls, limonene, terphenyl, and indene; PAHs refers to for example, naphthalene, anthracene, phenanthrene, pyrene and fluorene and their derivatives; Aliphatic refers to carbon numbers above C_8; Alicyclic compounds refers for example to cyclopentane and cyclohexane etc.,

Tire: The GC/MS analysis of the oil produced from the pyrolysis-catalysis of waste tire in relation to the highest concentration compounds revealed 45 main chemical compounds and are presented in Table 5.2. The table represents the main components in tire oil, which contains a significant amount of valuable chemicals such as benzene, toluene, ethyl benzene, xylenes, and styrene. PAH compounds such as naphthalene, naphthalene derivatives, phenanthrene, and pyrene, were also detected in the oil composition at different concentrations. Using ZSM-5 as a catalyst through the pyrolysis-catalysis process has a strong effect in terms of upgrading the oil, and several studies reported that zeolite catalysts, particularly ZSM-5, demonstrated a remarkable selectivity regarding the high production of BTEX [111,149,174].

Table 5.2 Composition of oil obtained from the pyrolysis-catalysis of waste tires.

Tire		
Compound	**RT (min)**	**Mass (wt.%)**
toluene	4.65	16.94
m-xylene	9.01	11.87
o-xylene	8.95	5.02
benzene	2.66	3.74
benzene, 1,2,4,5-tetramethyl-	24.34	3.67
benzene, 2-ethyl-1,3-dimethyl-	22.29	3.42
naphthalene, 1,2-dihydro-	25.86	3.31
1h-indene, 1-methyl-	25.64	3.21
2,4-dimethylstyrene	25.52	3.11
p-methylstyrene	16.67	2.98
benzene, 2-ethyl-1,4-dimethyl-	21.13	2.74
2,6 dimethylnaphthalene	34.52	2.37
naphthalene, 2,3,6-trimethyl-	37.3	2.30
benzene, 1-methyl-4-(1-methylethenyl)-	23.01	1.99
benzene, 1-ethyl-2-methyl-	14.46	1.75
p-xylene	8.93	1.70
ethylbenzene	8.45	1.42
benzene, 2-ethyl-1,4-dimethyl-	22.63	1.24
benzene, 1,2,3-trimethyl-	18.47	1.23
benzene, 1-ethyl-4-methyl-	14.66	1.05
naphthalene, 1,2-dihydro-6-methyl-	29.89	0.95
styrene	10.13	0.81
dibenzyl or dibenzofuran	36.66	0.76
benzothiazole	28.47	0.66
benzo[b]thiophene, 2-ethyl-5,7-dimethyl-	38.56	0.65
benzene, 1,2,4-trimethyl-	15.03	0.60
1h-indene, 1,1,3-trimethyl-	33.27	0.60
1,4,5,8-tetramethylnaphthalene	41.56	0.59
2 methylnaphthalene	30.84	0.58
cyclopentene, 1,2,3-trimethyl-	6.75	0.57
azulene, 7-ethyl-1,4-dimethyl-	40.86	0.57
benzene, 1-methyl-4-(1-methylethyl)-	18.92	0.50
naphthalene, 1-methyl-7-(1-methylethyl)-	39.38	0.50
Total		83.4

In this study, ZSM-5 is also shown to favour the production of a high concentration of the small molecular hydrocarbons, such as BTEX. The concentration of BTEX was increased in the tire oil from 8.38 wt.% in the thermal pyrolysis to 40.69 wt.% in the presence of the ZSM-5. Williams and Brindle [111] reported the oil yields from the pyrolysis-catalysis tires of benzene, toluene and m-, p- and o-xylenes in the oil was 29.6 wt.% with a HZSM-5 catalyst. For tire pyrolysis-catalysis, Olazar et al. [149] also observed that the concentration of single-ring aromatic compounds in the oil increased from 20.17 wt.% in the absence of the catalysts to 32.49 wt.% with the HZSM-5 catalyst. The limonene yield was obtained at a very low concentration (0.04 wt.%) compared to the thermal pyrolysis, in which limonene was the prominent product (39.70 wt.%). That is because ZSM-5 potentially promotes monomolecular cracking, which improves secondary reactions in thermal pyrolysis, particularly the breaking of the oil to C_{10} aromatics and gases[227]. In addition, the selectivity of ZSM-5 plays an important role in cracking the primary product (isoprene dimer limonene) into the monomer isoprene and gasoline [114]. Thus, five catalytic reactions should be considered in the kinetic scheme of the catalytic pyrolysis on a catalyst constructed from a HZSM-5 zeolite, two of these reactions indicate the catalytic cracking of limonene to isoprene and C_5–C_{10} fraction, while another two overlap the secondary reactions for the catalytic cracking of the oil to gases and aromatics. The last catalytic reaction suggests the formation of gases C_1-C_4 through the catalytic cracking of C_5-C_{10} fraction[227]

PAHs were reported in low concentration in the oil produced from the pyrolysis-catalysis of tires. For example, it was found that ZSM-5 significantly reduced the concentration of PAHs, which was (11 wt.%) compared to the uncatalyzed process (14.10 wt.%). Similar results were also reported by Olazar et al. [149] with a low concentration of naphthalene and its derivatives. The efficiency of ZSM-5 is attributed to its structure selectivity regarding the surface micropores, which is approximately equal to 0.56 nm [176]. As a result, the molecules with molecular sizes larger than naphthalene may not fit through the micropores on the surface of ZSM-5. Consequently, ZSM-5 selectively acts as a favourable catalyst to produce BTEX [111,176].

High and low density polyethylene: The identified compounds in the oil obtained from the pyrolysis-catalysis of high density polyethylene and low density polyethylene are presented in Table 5.3 and 5.4. The oil composition is classified into the main compounds, which are BTEX, aromatic, aliphatic (olefins), and PAHs. The produced oil has a very low concentration of the aliphatic content ranging from C_{16}-C_{24} with inconstant set of the aliphatic peaks compared to the thermal pyrolysis with clear and persisted triplet peaks from C_8-C_{28}. ZSM-5 significantly decreased the liquid yield with less wax production compared to the thermal pyrolysis that consisted of more than 90% of heavy wax, compared to an oil was found with the pyrolysis-catalysis. The aliphatic portion in the oil composition was 20.11 wt.% and at 18.29 wt.% for HDPE and LDPE, respectively with no notable production of heavier compounds above C_{24} was observed, and that was also reported by other workers [122,228,229]. Williams and Bagri [70] investigated the catalytic pyrolysis of polyethene over zeolite catalysts, and they found that the aliphatic compounds decreased to low carbon number. The efficiency of ZSM-5 to minimize the heavy aliphatic fraction, which were the main product in the pyrolysis process [230]. Artetxe et al. [230] also reported that HZSM-5 with low deactivation by coke deposition and a high selectivity for the production of light olefins. The PAHs were produced in minor concentrations, and consisted of naphthalene, and its derivatives at 0.39 and 0.77 wt.% for HDPE and LDPE, respectively. The low PAHs content may be due to the selectivity of ZSM-5 through the pore size that allowed only the small molecules to pass through and undergo the catalytic aromatisation reactions [70].

Apart from catalyst properties, the other parameter such as temperature and residence time, which have a significant effect on the yield and composition. As the temperature is increased the cracking reactions are enhanced, resulting in low paraffins, isoparaffins and naphthenes yields. Moreover, a high residence time may increase the secondary reactions to produce more aromatic compounds, when olefin oligomerization and subsequent condensation to produce toluene and xylenes, while the yields of olefins and PAHs become negligible [230].

Table 5.3 Oil composition from the pyrolysis-catalysis of high densitypolyethylene.

High density polyethylene		
Compound	**RT (min)**	**Mass (wt.%)**
o-xylene	8.99	26.02
toluene	4.65	19.67
C20	43.04	4.40
benzene, 1-ethyl-3-methyl-	14.64	4.09
p-xylene	8.92	4.07
C19	41.27	3.77
C18	39.01	3.28
benzene	2.70	2.60
ethylbenzene	8.44	2.57
benzene, 1-ethyl-2-methyl-	14.44	2.19
benzene, 1,2,4-trimethyl-	16.64	1.83
C17	36.59	1.79
m-xylene	10.12	1.76
octane, 3,5-dimethyl	23.72	1.75
C21	45.46	1.48
hexane, 2,4-dimethyl-	10.81	1.21
1h-indene, 2,3-dihydro-1,6-dimethyl-	27.86	1.15
unknown	31.14	1.14
C16	34.01	0.95
C22	47.41	0.93
C23	47.54	0.56
benzene, 1,2-diethyl-	20.99	0.55
Total		87.76

Table 5.4 Oil composition from the pyrolysis-catalysis of low density polyethylene.

Low density polyethylene		
Compound	**RT (min)**	**Mass (wt.%)**
o-xylene	9.02	22.86
toluene	4.67	18.39
benzene	2.66	7.60
p-xylene	8.94	3.66
C20	41.11	3.57
C19	38.83	3.55
C21	43.28	3.24
benzene, 1-ethyl-3-methyl-	14.67	3.05
benzene, 1-ethyl-2-methyl-	14.47	2.22
ethylbenzene	8.46	2.11
benzene, 1,2,3-trimethyl-	16.66	2.04
m-xylene	10.14	1.69
2,3-dimethyldecane	34.01	1.64
unknown	17.48	1.61
hexane, 2,4-dimethyl-	10.83	1.56

Table 5.4 Oil composition from the pyrolysis-catalysis of low density polyethylene (Continued).

Low density polyethylene		
Compound	**RT (min)**	**Mass (wt.%)**
cyclohexane, 1-ethyl-2-methyl-, cis-	23.73	1.53
1h-indene, 2,3-dihydro-1,6-dimethyl-	27.87	1.25
1-undecene, 4-methyl-	31.15	1.21
unknown	7.24	0.80
benzene, 1-methyl-4-(1-methylethyl)-	22.61	0.74
1h-indene, 2,3-dihydro-4-methyl-	25.17	0.65
benzene, 2-ethyl-1,4-dimethyl-	21.01	0.63
1,4-dimethyl-1-cyclohexene	6.84	0.61
benzene, 2-propenyl-	19.32	0.6
Total		86.81

The BTEX compounds were observed in significant concentrations at 56.67 wt.% and 56.30 wt.% for HDPE and LDPE, respectively. That is likely to be related to the catalytic cracking of the polymer chains to penetrate the ZSM-5 pores. It would be expected that high selectively of the ZSM-5 to produce high concentrations of the BTEX compounds, as well as possible transformation through different mechanisms such as beta scission and carbocation occur [231]. Furthermore, the acidity of the ZSM-5 catalyst leads to high aromatic content, and it promotes an effective cracking of the heavier molecular compounds. Toluene, xylene, and benzene are the dominant single ring hydrocarbons that are produced from pyrolysis-catalysis. It is noted that the zeolite behaviour in the degradation of polyethylene produced the aromatic content on the expanse of alkane and alkene yield. Consequently, the small pore size, higher surface acidity, and higher surface area were the main factors that were associated with the production of aromatic compounds [70,232]. Figure 5.3 shows the thermal and catalytic pyrolysis of tire, HDPE, and LDPE, which reveals the influence of ZSM-5 on the oil composition.

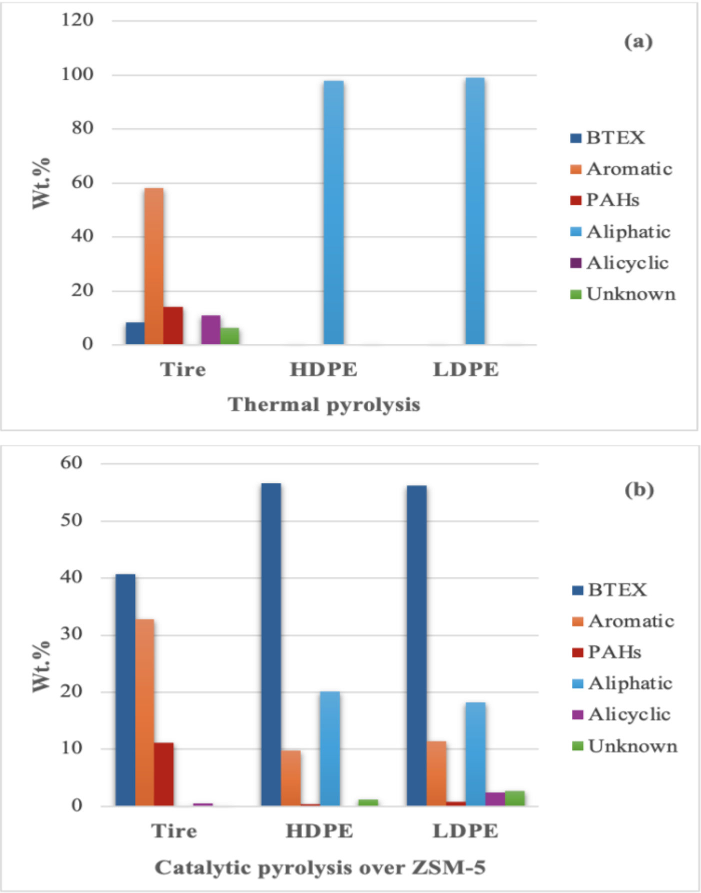


Figure 5.3 Oil composition obtained from the thermal (a) and catalytic pyrolysis (b) of tire, HDPE and LDPE.

Thermal cracking occurs on the catalyst's external surface through the catalytic pyrolysis process. The catalyst porous structure serves as channels for the selective movement and breakdown of the large molecules and allow them to pass through these channels[233]. Because of the tiny pore size, gases are mostly formed inside the pores, whereas wax is created as a consequence of externally cracking on the catalyst's surface[224]. This effect demonstrates that high olefin molecules are degraded on the catalyst's external surface, while additional degradation and product selectivity occur within the catalyst's internal pores[234]. The cracking of hydrocarbons over ZSM-5 involves the formation of a carbonium or carbenium ion at a Brønsted or Lewis acid site, as illustrated in Figure 5.4 [115,235]. Due to the high level of cracking, which produces light hydrocarbons (alkane and alkene) as primary products, this indicates that shape selectivity with small pore size is significantly crucial to produce aromatic compounds.

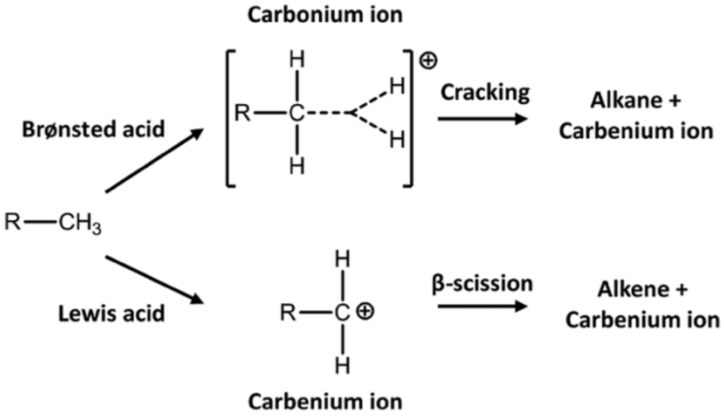


Figure 5.4 Mechanism of acid catalysed cracking of hydrocarbons. Adaptation of [115,235].

Polypropylene: Table 5.5 summarises the main compounds obtained from the pyrolysis-catalysis of polypropylene. In the presence of the ZSM-5, the waxes produced during thermal pyrolysis were converted to mainly aromatics with high concentrations of BTEX at 35.51 wt.%. Toluene was the prominent compound in the product oil at 17.79 wt.% followed by xylene and benzene at 8.45 and 7.33 wt.%, respectively. Whilst the thermal pyrolysis of PP produced mainly unsaturated hydrocarbons in the oil composition. That indicated the high level of the cracking occurred similarly to the PE over ZSM-5; however, polypropylene revealed faster thermal degradation due to its high tertiary carbon content, which is reactive and can undergo both thermal and catalytic cracking reactions [122]. The suggested cracking of PP over the ZSM-5 takes place in the zeolite pores for the lower carbon number, as the most hydrocarbons distribution in the range of C_6-C_{12}. On the other hand, the presence of methyl side groups in the polypropylene chemical structure causes an increase in their molecular cross sections, which limits their access to the pores, and so the external acid sites can contribute to the cracking of PP. PE may also exhibit similar behaviour, as indicated by the product distribution including hydrocarbons < C_{12}that obtained in the conversion of HDPE and LDPE in the absence of activity. These results corresponded with previous studies on the formation of low carbon numbers [73,236,237].

Table 5.5 Oil composition from the pyrolysis-catalysis of polypropylene.

Polypropylene		
Compound	**RT (min)**	**Mass (wt.%)**
toluene	4.67	17.79
benzene	2.67	7.33
cyclopentane, 1,1,3,4-tetramethyl-	7.16	6.16
o-xylene	9.02	6.05
benzene, 1-ethyl-3-methyl-	14.67	3.50
2,4-dimethyl-1-heptene	7.55	3.20
cyclohexane, 1-ethyl-1,3-dimethyl	8.31	3.15
benzene, 1,2,3-trimethyl-	16.67	2.67
benzene, 1-ethyl-2-methyl-	14.47	2.28
3-heptene, 2,6-dimethyl-	7.72	2.25
ethylbenzene	8.47	1.95
hexane, 2,3,4-trimethyl-	17.94	1.57
decane, 4-methyl-	18.25	1.54
m-xylene	10.14	1.39
1,7-octadiene, 2,3,3-trimethyl-	9.68	1.29
2-sec-butyl-3-methyl-1-pentene	6.23	1.27
1,3,5-cycloheptatriene, 3,7,7-trimethyl-	22.63	1.13
1,7-dimethyl-4-(1-methylethyl)cyclodecane	41.86	1.09
cyclododecane	43.39	1.02
p-xylene	8.94	1.01
bicyclo[3.1.1]heptane, 2,6,6-trimethyl-,	6.84	0.96
benzene, 1,3-diethyl-	21.01	0.86
benzene, 1,2,3-trimethyl-	15.04	0.79
octane, 4-methyl-	6.68	0.62
7-tetradecene	36.96	0.59
2-hexyl-1-octene	39.01	0.59
benzene, 1-ethyl-2,3-dimethyl-	24.19	0.57
unknown	47.61	0.57
benzene, 1,2,3,4-tetramethyl-	24.30	0.56
unknown	45.53	0.56
benzene, 1-methyl-4-(1-methylethyl)-	25.66	0.50
Total		74.81

Polystyrene: The polystyrene pyrolysis-catalysis oil was analysed by GC/MS analysis, and above 40 compounds were identified as shown in Table 5.6. The main compounds found in high concentrations were mainly aromatic and single-ring aromatic compounds, which accounted for over 90% of the oil composition. Styrene was the most dominant compound produced in the oils in both thermal and catalytic pyrolysis of PS, which were reported at 70.07 wt.% and 32.40 wt.%, respectively. Moreover, the production of benzene, toluene, ethylbenzene, and xylene was increased in the presence of ZSM-5, with a maximum concentration of 17.91 wt.%

compared to 4.27 wt.% for thermal pyrolysis. The GC/MS analysis also indicated a presence of polycyclic aromatic hydrocarbons, including naphthalene and its derivatives at reduced concentrations of 4.56 wt.%, which may be connected to ZSM-5 selectivity at lower carbon numbers. The high concentration of aromatic compounds in the oil produced by thermal and catalytic degradation of PS was attributed to their excellent stability, which resists further cracking or hydrogenation into paraffin and olefins[238]. Several studies have reported that the high concentration of styrene produced from PS decomposition as the primary product through the thermal cracking and then undergoes further transformation over the acid sites of ZSM-5 in the second stage [239]. As a result, ZSM-5 exhibits the main product distribution through the shape selectivity (micropores), which limits the PS transformation and inner diffusion of bulky products, and that explains the highest concentrations of benzene and toluene that easily migrate from the ZSM-5 pore. Whereas the hydrocarbons >C10+ cannot be derived on the active sites due to diffusion limitations [240].

Table 5.6 Oil composition from the pyrolysis-catalysis of polystyrene.

Polystyrene		
Compound	**RT (min)**	**Mass (wt.%)**
styrene	10.16	32.4
benzene	2.67	9.71
toluene	4.68	6.47
cis-.beta.-methylstyrene	15.87	3.27
benzene, 1-propynyl-	19.98	3.20
benzene, 1,1'-(2-methyl-1-propene-1,3-di	43.37	1.72
bibenzyl	37.02	1.65
ethylbenzene	8.46	1.62
benzene 1,5-hexadiene-1,	40.59	1.62
benzene, 1,1'-(3-methyl-1-propene-1,3-di	41.63	1.38
benzene, 1,1'-(1,3-propanediyl)bis-	40.17	1.18
benzene, 1,1'-(3-methyl-1-propene-1,3-di	40.69	1.05
1,2-diphenylethylene	41.46	1.03
naphthalene, 1,2-dihydro-	25.84	1.01
9,10-dimethylanthracene	45.34	0.74
benzene, 1,1'-(1-methyl-1,2-ethanediyl)	37.75	0.70
1h-indene, 2-phenyl-	42.65	0.69
naphthalene	26.97	0.66
phenylnapthalene	46.83	0.66
indane	19.32	0.58
1h-indene, 2-phenyl-	44.72	0.50
Total		71.84

Polyethylene terephthalate: Table 5.7 summarises the product oil composition from the pyrolysis-catalysis of polyethylene terephthalate. The ZSM-5 catalyst reduced the heavy oil content and hindered wax formation. It was found that PET produced oil with a significant aromatic content for thermal pyrolysis; there was a marked increase when the catalyst was used, particularly BTEX compounds. Benzene is shown to be in high concentrations at 68.72 wt.%, which represents a large production for the pyrolysis-catalysis process compared to tires and other plastics. The main products of PET in the thermal pyrolysis are terephthalic acid and benzoic acid, which may be converted into aromatic hydrocarbons over catalysts with high de-oxygenation capability such as zeolite ZSM-5. However, the presence of oxygen atoms in PET, conversion without a catalyst result in high overall solid residue yields [119]. In the pyrolysis-catalysis of PET, the oxygenated compounds, particularly benzoic acid was not observed. This indicates that benzoic acid may convert to mostly benzene and toluene over ZSM-5, which was also reported by Muhammad et al [221]. Other compounds were also present in negligible concentrations, such as biphenyl, terphenyl, and PAHs such as, naphthalene, fluorene, and phenanthrene. The selectively of ZSM-5 allows only the fraction of carbon number $<C_{12}$, as the pore size of ZSM-5 influences the size of the hydrocarbon molecules that may enter the pore structure and get involved in the catalytic cracking and reformation, which result in more production of aromatic hydrocarbons [221].

Table 5.7 Oil composition from the pyrolysis-catalysis of polyethylene terephthalate.

Polyethylene terephthalate		
Compound	**RT (min)**	**Mass (wt.%)**
benzene	2.67	68.72
toluene	4.67	5.26
xylene	9.01	0.96
biphenyl	33.36	0.80
ethylbenzene	8.46	0.54
Total		76.28

5.3 Co-pyrolysis-catalysis of tire and plastic mixtures

The co-pyrolysis-catalysis of tire and plastic mixtures (Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS and Tire/PET) was undertaken to determine any interaction that may influence the yield and composition of the product oil and gases. The tire and plastic were mixed in a 1:1 ratio and pyrolyzed in the fixed bed reactor system with the addition of the ZSM-5 catalyst in a 1:1 catalyst/feedstock ratio. The product yield, gas and oil composition were analysed and investigated to confirm any synergistic interaction between the waste tires and plastics as well as the influence of ZSM-5 on the gas and oil composition.

5.3.1 Product yield and gas composition from the co-pyrolysis-catalysis of tires and plastics

Table 5.8 shows the product distribution of gas, oil, and char yields from the co-pyrolysis-catalysise experiments for all the tire and plastic mixtures. It also provided the therotical data that was calculated based on the additive data of the individual samples. The experimental gas yields were lower than predicted for all the mixtures and that may be assosiated to the addition of ZSM-5 catayst, which increaed the volatiles content as a result of the high craking of the large moleclular weight compounds in contrast to the co-pyrolysis of all the tire and plastic mixtures that revealed higher gas yields than predicted. The tire/polystyrene co-pyrolysis-catalysis produced the lowest gas yield (9.23 wt.%) than predicted, while the oil yield was slightly higher (64.67 wt.%) than expected, but it produced the highest oil yield of all the other tire/plastic mixtures. Generaly, the oil yields were slightly higher than predicted for all the mixtures, except Tire/HDPE (43.64 wt.%). Also Tire/HDPE produced high char yield than expected, whears the char yields were slightly lower than predicted for the other mixtures,and that attributed to the interaction between tires and plastics during the co-pyrolysis process as well as the possible interaction of the volatiles that undergoes the second stage of the catalysis process over ZSM-5 catalyst. Figure 5.5 shows the product yield distrubtion of all the mixtures in pyrolysis-catalysis over ZSM-5, which revealed high gas yields compared to the thermal pyrolysis.

Table 5.8 Product yield distrubtion from the mixtures of the waste tires and plastics, experimental and theoretical.

	Experimental				
(wt.%)	**Tire/HDPE**	**Tire/LDPE**	**Tire/PP**	**Tire/PS**	**Tire/PET**
Gas yield	29.20	27.70	23.03	9.23	23.22
Oil yield	43.64	46.33	51.00	64.67	42.67
Char yield	21.33	18.33	19.33	17.33	25.67
Mass balance	94.17	92.36	93.36	91.23	91.56
	Additive data (wt.%)				
(wt.%)	**Tire/HDPE**	**Tire/LDPE**	**Tire/PP**	**Tire/PS**	**Tire/PET**
Gas yield	30.62	31.86	27.76	15.67	32.72
Oil yield	45.50	44.33	48.00	60.83	40.33
Char yield	19.50	19.33	20.17	19.50	27.83
Mass balance	95.62	95.52	95.93	96.00	100.88

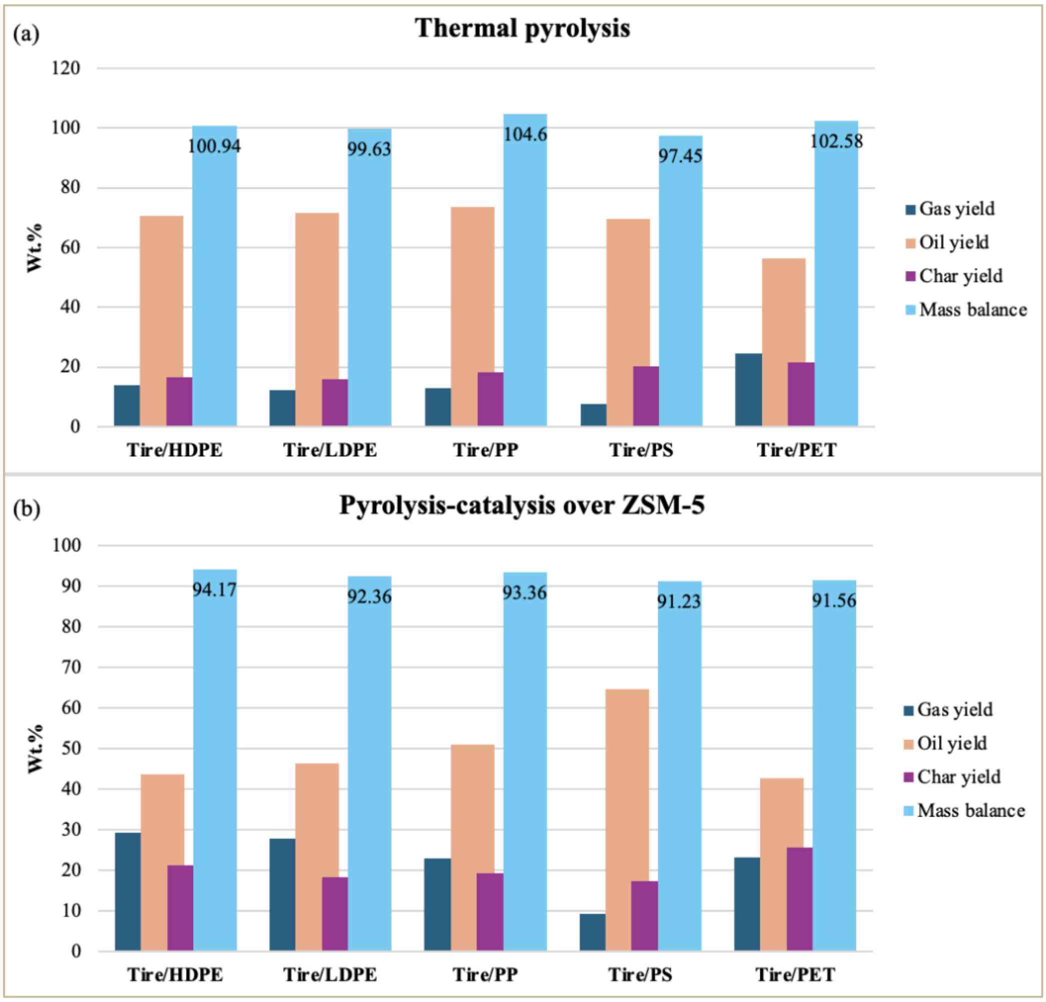


Figure 5.5 Product yield distribution from the thermal (a) and pyrolysis-catalysis over ZSM-5 (b) of tire and plastic mixtures.

Figure 5.6 shows the gas composition obtained from the pyrolysis-catalysis of the tire and plastic mixtures. The gas yields from the pyrolysis-catalysis of the tire and plastic mixtures were lower than the theoretical additive prediction. The gas analysis for the tire/olefinic plastic mixtures, Tire/HDPE, Tire/LDPE, and T/PP revealed higher concentrations of hydrocarbon gases and methane, whereas the hydrogen was observed to be in very low concentration. The Tire/PS mixture showed lower concentrations of these gases from the co-pyrolysis-catalysis process. The Tire/PET mixture gave high gas yields of mainly CO and hydrocarbons. Other researchers have also reported that using a zeolite catalyst increased the production of hydrocarbon gases[221,241–243]. For example, Lopez et al [241] found that adding a zeolite HZSM-5 catalyst to the mixtures of plastics (PE, PP, PS, PET, and PVC) increased the gas yield, particularly hydrocarbon gases compared to the thermal process. This suggested the interaction between these plastics. It has also been reported [67] that mixing different plastics (PE, PP, and PET) with polystyrene enhanced the interaction between the plastics, resulting in an increase in the production of hydrocarbon gases, the pyrolysis products from polystyrene are very aromatic, similar to that produced from waste plastics.

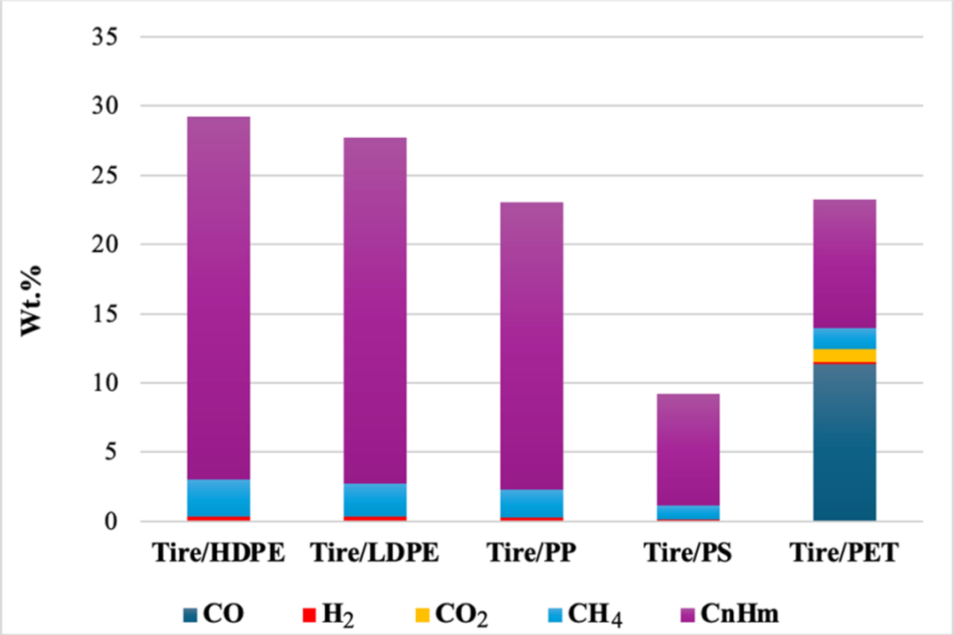


Figure 5.6 Gas composition of the pyrolysis-catalysis of mixture (50:50) tire and plastic.

5.3.2 Composition of oil obtained from the pyrolysis-catalysis of the tire/plastic mixtures

Tire/HDPE and Tire/LDPE: GC/MS analysis of the product oil from the co-pyrolysis/catalysis of Tire/HDPE and Tire/LDPE in the precent of ZSM-5 catalyst, showed that the highest concentration compounds comprised above 40 compounds were identified and presented in Table 5.9 and 5.10. The results showed the distribution of the oil products into BTEX and aromatics as the major compounds, which were produced in much higher concentration compared to the thermal pyrolysis. The influence of mixing tire with PE as well as the presence of ZSM-5 catalyst promoted the high production of the aromatic content, particularly BTEX compounds at 67.45 and 79.96 wt.% for Tire/HDPE and Tire/LDPE product oil, respectively. Toluene was the dominant aromatic compound in the oil products obtained at 26.80 wt.% from Tire/HDPE, while xylene was the highest compound in the oil produced from Tire/LDPE at 32.74 wt.%. The formation of PAHs was increased in the mixtures of tire with PE and that may be associated with the recombination after cracking of the heavy molecular weight compounds, which also corresponded to a reduction of the aliphatic compounds. Moreover, the catalyst improved the production of hydrocarbons from PE compared to the thermal pyrolysis of PE that produced high molecular weight hydrocarbons. Figure 5.7 shows a significant reduction in the aliphatic compounds when it was co-pyrolysed with tire, which was 1.46 and 1.53 wt.% for the co-pyrolysis mixtures of Tire/HDPE, and Tire/LDPE, respectively. Consequently, the aromatic content was increased in the mixtures at the expense of the aliphatic compounds, which revealed higher than the individual pyrolysis of the HDPE and LDPE. The amount of aliphatic compounds shows lower concentration values, and this suggests that the upgrading of the produced oil by the conversion of olefinic intermediates from PE degradation, which was promoted by the presence of aromatic fragments of tire degradation[244].

Table 5.9 Composition of oil obtained from the pyrolysis-catalysis of tire/high density polyethylene.

Tire/high density polyethylene		
Compound	**RT (min)**	**Mass (wt.%)**
toluene	4.73	26.80
benzene	2.71	16.51
o-xylene	9.10	11.88
m-xylene	10.22	5.01
ethylbenzene	8.54	4.69
benzene, 1,2,3-trimethyl-	16.76	3.60
p-xylene	9.02	2.57
benzene, 1-ethyl-3-methyl-	14.56	2.34
2,4-dimethylstyrene	25.59	1.12
benzene, 1,2,4,5-tetramethyl-	24.41	1.01
benzene, 1,2,4-trimethyl-	18.56	0.99
naphthalene, 1,2-dihydro-	25.70	0.90
1H-indene, 2,3-dihydro-4-methyl-	25.24	0.87
benzene, 2-ethyl-1,4-dimethyl-	21.22	0.81
benzene, 1,2,4-trimethyl-	15.13	0.75
naphthalene, 1,4-dimethyl-	34.46	0.73
naphthalene, 1,7-dimethyl-	34.10	0.72
indane	19.42	0.71
pentane, 2,2,3,4-tetramethyl-	10.91	0.68
benzene, (1-methyl-2-cyclopropen-1-yl)-	25.93	0.66
1h-indene, 1-ethylidene-	31.35	0.59
benzene, 1-propynyl-	20.08	0.54
Total		84.48

Table 5.10 Composition of oil obtained from the pyrolysis-catalysis of tire/low density polyethylene.

Tire/low density polyethylene		
Compound	**RT (min)**	**Mass (wt.%)**
benzene	2.72	14.15
p-xylene	9.04	13.86
o-xylene	9.12	13.4
m-xylene	10.24	5.48
ethylbenzene	8.56	5.12
benzene, 1,2,3-trimethyl-	16.78	4.60
benzene, 1-ethyl-4-methyl-	14.58	2.73
benzene, (1-methylethyl)-	14.78	1.59
benzene, 1,2,3-trimethyl-	18.58	1.25
benzene, 1-methyl-4-(1-methylethyl)-	22.38	1.24
benzene, 1,2,3,4-tetramethyl-	24.42	1.22
2,4-dimethylstyrene	25.6	1.21
benzene, 2-ethyl-1,4-dimethyl-	21.23	1.12
1h-indene, 3-methyl-	25.71	1.07
indane	19.44	0.82
1,4-pentadiene, 2,3,4-trimethyl-	6.17	0.79
1,4-cyclohexadiene, 3-ethenyl-1,2-dimeth	23.63	0.71
benzene, 1-ethyl-2-methyl-	15.68	0.68
naphthalene, 1,7-dimethyl-	34.46	0.64
benzene, 1-propynyl-	20.1	0.60
9h-fluorene	41.34	0.53
naphthalene, 2,3,6-trimethyl-	37.35	0.50
1h-indene, 1-ethylidene-	31.36	0.50
Total		101.76

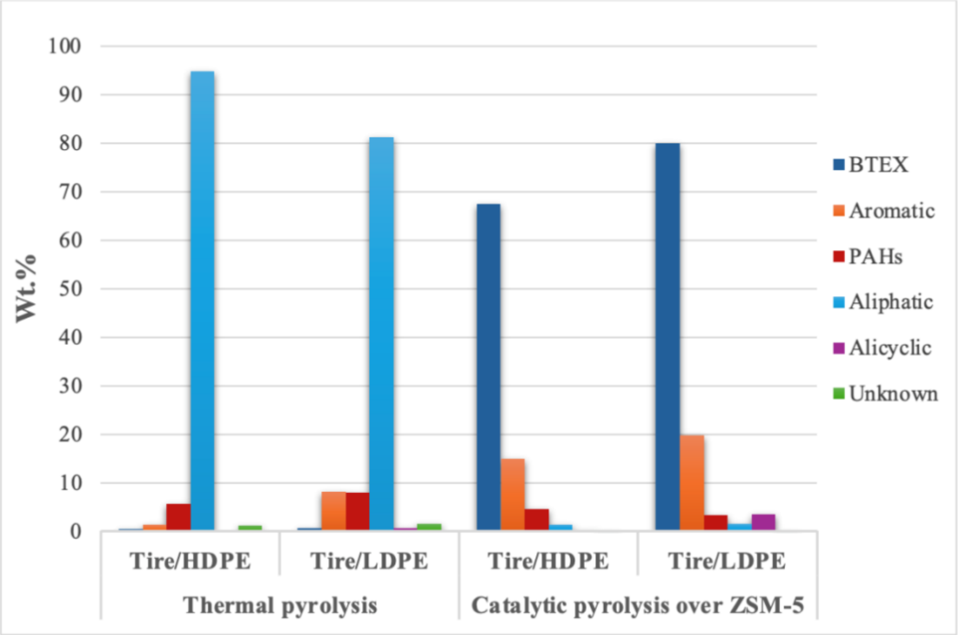


Figure 5.7 Oil composition obtained from the thermal and catalytic co-pyrolysis of Tire/HDPE and Tire/LDPE.

Tire/polypropylene: Table 5.11 represents the GC/MS analysis results obtained from the pyrolysis-catalytic processing of Tire/PP. The identified compounds were distributed to high aromatics production and relatively low aliphatic compounds. Mixing tire with PP during co-pyrolysis and the use of catalyst improves the production of the valuable chemicals. According to the results the thermal pyrolysis of PP produced unsaturated hydrocarbons without any aromatic products, whilst the co-pyrolysis of PP with tire enhanced the oil composition and produced more aromatic compounds. Thus, the oil composition of the Tire/PP mixture with ZSM-5 catalyst revealed a significant decrease in the heavy molecular weight compounds in the product oil, and the catalytic degradation of this mixture consisted of mainly BTEX compounds. Toluene was the dominant compound, and it observed in high concentration at 23.78 wt.%, benzene, xylene, and ethylbenzene were also shown to be in significant concentrations at 9.80, 15.14 and 1.90 wt.%, respectively. It was found that the thermal pyrolysis of Tire/PP produced the concentrations of BTEX at 35.80 wt.%, which was lower than that produced by the pyrolysis-catalysis of Tire/PP at 50.58 wt.%. The main influence of mixing tire with PP was the production of high aromatic content which would be expected as the degradation of PP promoted by the presence of the aromatic fragments of tire degradation. Additionally, it has been suggested that the strong acid sites of the ZSM-5 catalyst involves the cracking of the

Tire/PP mixture, resulting in carbenium ions which can undergo b-scission followed by a hydrogen transfer to produce the aromatic compounds. Polystyrene produces a similar aromatic product slate compared to tire pyrolysis. For example, similar results have been reported by Kim et al.[244] in relation to the mixing of PS with PP on the catalytic degradation, which comes from the intermolecular transfer of carbenium ion between the degraded fragments of PP and PS. This may suggest that the carbenium ion from PS degradation may offer hydrogen to olefinic fragments of PP.

Table 5.11 Composition of oil obtained from the pyrolysis-catalysis of tire/polypropylene.

Tire/polypropylene		
Compound	**RT (min)**	**Mass (wt.%)**
toluene	4.76	23.78
benzene, 1,3-dimethyl-	9.05	10.48
o-xylene	9.13	10.13
benzene	2.72	9.80
m-xylene	10.25	4.14
benzene, 1,3,5-trimethyl-	16.79	4.14
cyclohexane, 1,1,3-trimethyl-	7.26	2.67
benzene, 1-ethyl-3-methyl-	14.59	2.04
ethylbenzene	8.42	1.90
decane, 4-methyl-	18.07	1.36
benzene, 4-ethyl-1,2-dimethyl-	22.72	1.36
decane, 4-methyl-	18.37	1.32
benzene, 1-ethyl-4-methyl-	14.79	1.30
benzene, 1,2,4-trimethyl-	18.59	1.25
benzene, 1,2,4,5-tetramethyl-	24.42	1.25
2,4-dimethyl-1-heptene	7.65	1.17
benzene, 1,3,5-trimethyl-	15.16	1.17
benzene, 2-ethyl-1,4-dimethyl-	21.24	1.09
2,4-dimethylstyrene	25.6	0.95
cyclopentane, 1,1,3,4-tetramethyl-, cis-	6.33	0.92
benzene, 1,2,4,5-tetramethyl-	25.74	0.91
p-xylene	8.57	0.88
1h-indene, 2,3-dihydro-4-methyl-	25.25	0.69
benzene, 1,2-diethyl-	23.64	0.68
indane	19.45	0.61
1,4-pentadiene, 2,3,4-trimethyl-	6.18	0.52
benzene, 1-ethyl-4-methyl-	15.69	0.50
benzene, 1-methyl-2-(1-methyl-2-propenyl	27.23	0.50
Total		87.43

Tire/polystyrene: Table 5.12 shows most of the compounds identified by GC/MS in the product oil obtained from the pyrolysis-catalysis of Tire/PS. The oil composition contains aromatic compounds without any aliphatic content than would be expected, as the thermal pyrolysis of tire and polystyrene mixture mainly produced aromatic compounds. Moreover, the addition of the ZSM-5 catalyst promotes the cracking of the hydrocarbons chain as well as the interaction between tire and PS to produce more aromatics at the expense of styrene. As a result, the BTEX compounds were identified in high concentration at 46.84 wt.%. Whereas, in the co-pyrolysis of Tire/PS the BTEX content was produced in low concentration at 9.90 wt.%. This suggests that the influence of ZSM-5 increased the cracking reaction of the polycyclic aromatic hydrocarbons as it showed a reduction in concentration due to the small pore size that sterically hindered these large compounds to pass through the pore cavities. This will increase the selectivity toward the light compounds [96]. Consequently, ZSM-5 favored the production of C_1-C_4 gases and the high content of the BTEX in the oil.

Table 5.12 Composition of oil obtained from the pyrolysis-catalysis of tire/polystyrene.

Tire/polystyrene		
Compound	**RT (min)**	**Mass (wt.%)**
benzene	2.72	25.09
styrene	10.29	19.20
toluene	4.77	14.09
benzene, 1-propynyl-	20.15	6.55
p-xylene	8.60	4.76
alpha-methylstyrene	16.01	4.18
benzene, 1,3-dimethyl-	9.06	3.67
o-xylene	9.13	2.91
indane	19.47	2.73
benzene, 1-butynyl-	25.93	1.58
benzene, 1,2,3-trimethyl-	16.80	1.37
benzene, 1,1'-(1,3-propanediyl)bis-	40.25	1.07
benzene, 1-ethyl-3-methyl-	14.60	1.00
naphthalene	27.06	0.85
2,4-dimethylstyrene	22.44	0.76
benzene, (1-methylethyl)-	12.17	0.75
naphthalene, 1,2-dihydro-	25.71	0.62
2 methylnaphthalene	30.92	0.58
beta-methylstyrene	19.12	0.55
2,4-dimethylstyrene	22.67	0.50
Total		92.78

Tire/polyethylene terephthalate: Table 5.13 represents the highest concentration of identified compounds that were obtained from the pyrolysis-catalysis of the tire/polyethylene terephthalate mixture. The oil composition of the Tire/PET mixture consists mainly of BTEX, aromatic and PAH compounds at 55.08, 19.75 and 2.51 wt.%, respectively. Benzene is the dominate compound produced from the pyrolysis-catalysis of Tire/PET, which was expected as the pyrolysis of individual tire and PET produced a significant amount of benzene in the oil. Furthermore, the selectively of ZSM-5 can promote the decarboxylation of the oxygenated compounds, particularly benzoic acid to produce benzene[245]. The PAHs content was in low concentration, and this has been suggested that inside the small pores of the catalyst where is the cavities may act as an inverse template for the formation of the accumulated aromatics such as PAHs, and ultimately that can control the activity, selectivity and deactivation of the catalysts[246].

Table 5.13 Composition of oil obtained from the pyrolysis-catalysis of tire/polyethylene terephthalate.

Tire/polyethylene terephthalate		
Compound	**RT (min)**	**Mass (wt.%)**
benzene	2.72	29.27
toluene	4.76	12.06
benzene, 1,3-dimethyl-	9.05	8.99
o-xylene	9.13	7.07
m-xylene	10.25	4.41
benzene, 1,3,5-trimethyl-	16.8	2.34
p-xylene	8.57	2.26
benzene, 1-ethyl-2-methyl-	14.60	1.56
indane	19.47	1.15
benzene, 1,2,3-trimethyl-	18.6	1.10
biphenyl	33.4	1.06
benzene, 1,2,4-trimethyl-	15.17	0.70
naphthalene, 1,4-dimethyl-	34.59	0.47
Total		72.44

5.4 Tire-plastic co-pyrolysis-catalysis interaction effects

The synergistic impact of mixing waste tire with different plastics may be seen by comparing the co-pyrolysis product yields to the theoretical value predicted using the additive rule from the yields of the separate components. The synergistic effect occurs during co-pyrolysis when the experimental value exceeds (positive) or is less than (negative) the theoretical value[199]. The synergistic results indicated that the influence of the tire and ZSM-5 catalyst resulted in an increase in the cracking of the high molecular weight compounds which leads to the production of high concentrations of BTEX compounds that were around 70% of the oil composition, particularly for Tire/HDPE and Tire/LDPE.

The main investigated gases in the co-pyrolysis-catalysis of tires and plastics were. H_2, CH_4, C_nH_m, CO, and CO_2. Figure 5.8 shows the synergetic interaction results, which observed negative values of the CO and CO_2 for all the mixtures. The C_nH_m gases showed a positive synergetic effect for Tire/HDPE, Tire/LDPE, Tire/PP, and Tire/PET, while Tire/PS showed a negative effect compared to the other mixtures. The synergistic interaction in relation to H_2 and CH_4 showed very low values which make it difficult to assess their synergetic effects. Overall, the gas composition shows high yields of hydrocarbons values that were generated by the pyrolysis- catalysis of individual tires and plastics. Increasing the volatile compounds during the pyrolysis-catalysis should be addressed as the main influence of the high gas yields regarding the high level of cracking compared to the thermal pyrolysis with low gas yields for all the mixtures.

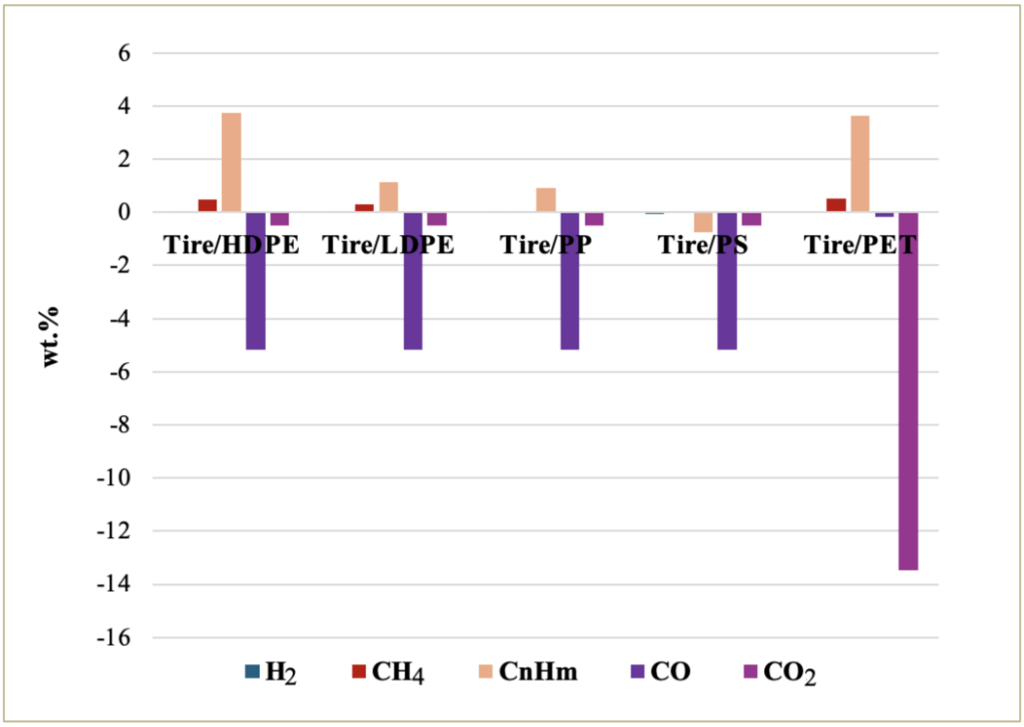


Figure 5.8 Synergistic effect of mixing tire/plastic on gas composition from pyrolysis-catalysis of Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS, and Tire/PET.

The mixtures of Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS, and Tire/PET were classified according to the main oil components, as shown in Figure 5.9. BTEX, refers to benzene, toluene, ethylbenzene and xylenes; Aromatic refers to benzene derivatives, biphenyls, limonene, terphenyl, and indene; PAHs refers to for example, naphthalene, anthracene, phenanthrene, pyrene and fluorene and their derivatives; Aliphatic refers to carbon numbers above C_8; Alicyclic compounds refers for example to cyclopentane and cyclohexane etc.,

BTEX compounds obtained positive synergistic values for the co-pyrolysis-catalysis of all the mixtures at 18.80, 31.50, 12.71, and 17.55 wt.% for Tire/HDPE, Tire/LDPE, Tire/PP, and Tire/PS, respectively. However, for Tire/PET revealed a slight negative value at -3 wt.% due to the low concentration. The positive values indicate that positive interaction may occur between tire and plastics according to the reaction mechanism of the hydrocarbon radicals produced from the tire rubber with the radicals produced from the thermal decomposition of the polyalkene plastics to form the aliphatic portion as the principal products. Then the catalytic process promotes the cracking of the aliphatic content of the pyrolysis products to produce more aromatic compounds such as BTEX. As a result, the negative values of the aliphatic portion were reported for Tire/HDPE, Tire/LDPE, and Tire/PP at -8.60, -7.61, and -2.18 wt.%, respectively. Figure 5.9 also shows that the composition of the oil for the co-pyrolysis-catalysis of Tire/PP, Tire/PS, and Tire/PET revealed positive values for aromatic compounds compared to the Tire/HDPE and Tire/LDPE mixtures. It may be suggested that and the pyrolysis-catalysis of the individual PP, PS, and PET produced high aromatic content compared to HDPE and LDPE. For example, the interaction between tire and PP as a part of the reaction mechanism of natural rubber in the tire, which increased the decomposition of PP [50]. For Tire/PS co-pyrolysis-catalysis obtained positive interaction as PS can promote the decomposition of natural rubber and butadiene rubber, as reported by Li et al. [201], resulting in positive values for both aromatic and BTEX contents. Furthermore, the influence of the catalyst indicated high selectivity toward the production of the light aromatic compounds, such as BTEX. The negative values for PAHs were observed for all the mixtures and that would be expected due to the high level of cracking, which are mainly based on the secondary reactions for the formation of hydrocarbons in the range of (C_4-C_{10}) [247].

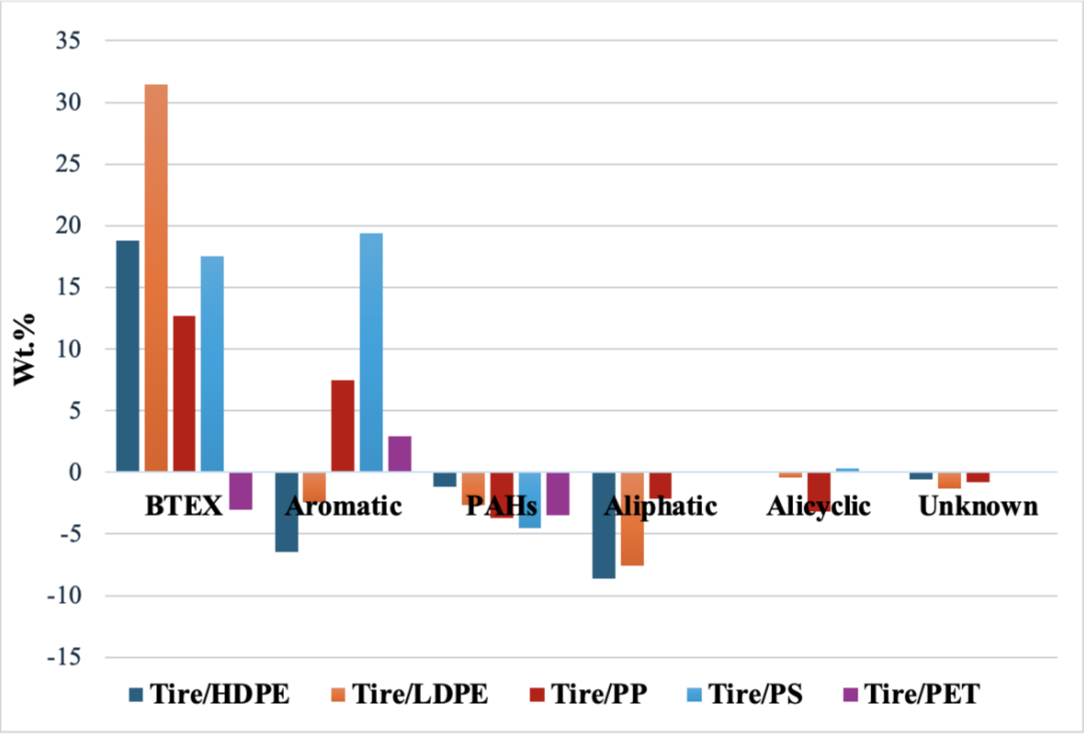


Figure 5. 9 Synergistic effect of mixing tire/plastic on oil composition from pyrolysis-catalysis of Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS, and Tire/PET.

5.5 Summary

In this chapter, pyrolysis-catalysis of waste plastic, waste tire, and mixtures of the tire and plastics has been conducted using a two-stage fixed-bed reactor. ZSM-5 was used as a catalyst to investigate the influence on the products distribution and the composition of the produced gases and oils. Pyrolysis-catalysis of tire over ZSM-5 had an effect on reducing oil yield form 54.83 wt.% in the non-catalysis pyrolysis to 37.30 wt.% in pyrolysis-catalysis over ZSM-5, with a corresponding increase in the gas yield at 24.65 wt.%. Pyrolysis-catalysis of HDPE, LDPE, PP, and PS showed also an increase in the gas yields that consisted mainly of hydrocarbons (C_1-C_4), while decreasing in oil production at 53.67, 51.31, 58.70, and 84.32 wt.% respectively. PS produced the lowest gas yield, while PET produced the highest gas yield, and the main gases generated from PET were CO and CO_2. Pyrolysis-catalysis of individual tire and plastic over ZSM-5 produced a significant amount of valuable chemicals such as benzene, toluene, ethyl benzene, xylenes, and styrene. The efficiency of ZSM-5 to minimize the heavy aliphatic fraction, which were the main product in the pyrolysis of HDPE and LDPE, on the other hand, the ZSM-5 with low deactivation by coke deposition and a high selectivity for the production of light olefins. The pyrolysis of PP over the ZSM-5 produced hydrocarbons distribution in the range of C_6-C_{12}. PET produced oil with a significant aromatic content for thermal pyrolysis; there was a marked increase when the catalyst was used, particularly the BTEX compounds.

Pyrolysis-catalysis of the tire and plastic mixtures over ZSM-5 revealed higher gas yields. Tire/HDPE, Tire/LDPE, and T/PP produced higher concentrations of hydrocarbon gases and methane, while the Tire/PS mixture showed lower concentrations of these gases. The Tire/PET mixture gave high gas yields of mainly CO and hydrocarbons. The mixtures of Tire/HDPE and Tire/LDPE observed a significant reduction in the aliphatic compounds when it was co-pyrolysed with tire and the presence of ZSM-5 catalyst promoted the high production of the aromatic content, particularly BTEX compounds on expense of aliphatic content. The oil composition of the Tire/PP mixture with ZSM-5 catalyst showed a significant reduction in the heavy molecular weight compounds and oil obtained from the catalytic pyrolysis of this mixture consisted of mainly BTEX compounds. The mixture of Tire/PS mainly produced aromatic compounds, and the addition of the ZSM-5 catalyst promotes the cracking of the hydrocarbons chain as well as the interaction between tire and PS to produce more aromatics at the expense of styrene. The oil composition of the Tire/PET mixture produced BTEX and aromatic compounds due to the selectively of ZSM-5 that promotes the decarboxylation of the oxygenated compounds. The positive interaction may occur between tire and plastics, and that promotes the cracking of the long chain hydrocarbons to produce more aromatic, and the addition of catalyst indicated high selectivity toward the production of the light aromatic.

Chapter 6: Pyrolysis-catalysis of waste tire and plastic over MCM-41/ZSM-5 catalyst

6.1 Introduction

Improving the product quality, particularly the oil yield is the main objective of this chapter. In this work, pyrolysis-catalysis of tire, HPDE, LDPE, PP, PS, and PET was carried out in the fixed bed, two stage reactor for the production of upgraded pyrolysis oils, using MCM-41 and ZSM-5 catalysts used in two layers in series of MCM-41 followed by Zeolite ZSM-5. Ratnasari et al. [103] reported that applying MCM-41 catalyst alone in two-stage pyrolysis-catalysis of high density polyethylene led to high molecular weight hydrocarbons $>C_{13}$, and the oil produced was mainly aliphatic. The purpose of using two catalysts staged one after the other in layers was firstly, to enhance the pre-cracking of the large molecules of produced from the pyrolysis of the plastic/tire into smaller molecules via the larger mesopores of the MCM-41 catalyst; secondly, the smaller fractions produced from the MCM-41 catalyst layer then enter the smaller micropores of the ZSM-5 catalyst for further cracking[103]. It should also be mentioned that the acidity of the catalyst has a significant impact on its activity in converting plastic pyrolysis gases, with higher catalyst acidity contributing to higher catalytic activity. Zeolite ZSM-5 and MCM-41 are aluminosilicates that have a silica:alumina ratio that can be modified to produce Si:Al ratios in which different amounts of Al replace the Si in the structure of the crystals, resulting in lower Si:Al ratios with higher surface acidity and thus increased catalyst activity [103].

6.2 Pyrolysis-catalysis of waste tires and plastics

The pyrolysis-catalysis of individual tire, plastics and mixtures of tire/plastic over a staged catalyst of MCM-41 followed by ZSM-5 catalysts was investigated in the two-stage fixed bed reactor (Chapter 3), with ratio of feedstock (tire/plastic):catalyst, and the ratio of MCM-41/ZSM-5 was 1:1. The process involved the use of a two-stage reactor system (Chapter 3). The influence of the pyrolysis -catalysis (zeolite catalysts in a staged layered) process on the products composition, particularly, the gas and oil yields were investigated in this chapter. Furthermore, the data collected from the co-pyrolysis-catalysis was also investigated to detect any interactions between waste tires and plastics.

6.2.1 Product yield and gas composition from the pyrolysis-catalysis of waste tires and plastics

The product yield from the pyrolysis-catalysis of individual waste plastics and tire over the MCM-41/ZSM-5 catalyst layer in series is presented in Table 6.1. The results show that as the oil yield decreased the gas yield increased. The oil yields were produced over a staged catalyst (MCM-41/ZSM-5) for tire, HDPE and LDPE at 39.50, 57.25, 53.50 wt.%, respectively. Table 6.1 shows an increase in the gas yield produced from the PS pyrolysis-catalysis over MCM-41/ZSM-5 at 11 wt.% compared to the thermal pyrolysis. That may be attributed to the combining of MCM-41 with ZSM-5, which increased the cracking and maximised the conversion of plastics to produce the lower molecular weight hydrocarbons. Furthermore, the gas yield produced from the pyrolysis-catalysis of PET at 42 wt.%, while the oil yield was lower over MCM-41/ZSM-5 at 36.75 wt.%. It can be concluded that for the most catalytic process, the impact of catalyst favours the gas yield while reducing the amount of oil yield as shown in Figure 6.1, thus increasing the light oil fraction with no significant change in char yield[17,114,248,249]. Using two catalysts in series has also been investigated by several researchers, for example, Escola et al. [250], Serrano et al. [105], and Ratnasari et al. [103] proposed combining the microporous and mesoporous of catalysts to optimise the conversion of plastic pyrolysis products to low molecular weight hydrocarbon fuels and chemicals. Aguado et al.[122] found that the oil yield was the main product produced from the pyrolysis-catalysis of HDPE over MCM-41 at 52.6 wt.%; however, cracking of HDPE over ZSM-5 resulted in a low oil yield at 46.3 wt.%, while the gas yield was above 50 wt.%. Ratnasari et al.[103] reported that oil and gas yields produced by catalytic pyrolysis of HDPE depends on the MCM-41:ZSM-5 catalyst ratios, which demonstrated only minor changes in gas and oil yields.

Table 6.1 Product yield from the pyrolysis-catalysis of individual waste plastics and tires over MCM-41/ZSM-5.

	Feedstock sample					
	Tire (wt.%)	**HDPE**	**LDPE**	**PP**	**PS**	**PET**
Gas yield	17.48	26.60	31.70	29.29	11.03	42.12
Oil yield	39.50	57.25	53.50	58.50	77.00	36.75
Char yield	37.75	3.75	0.00	0.50	0.25	13.00
Mass balance	94.73	87.60	85.20	88.29	88.03	91.87

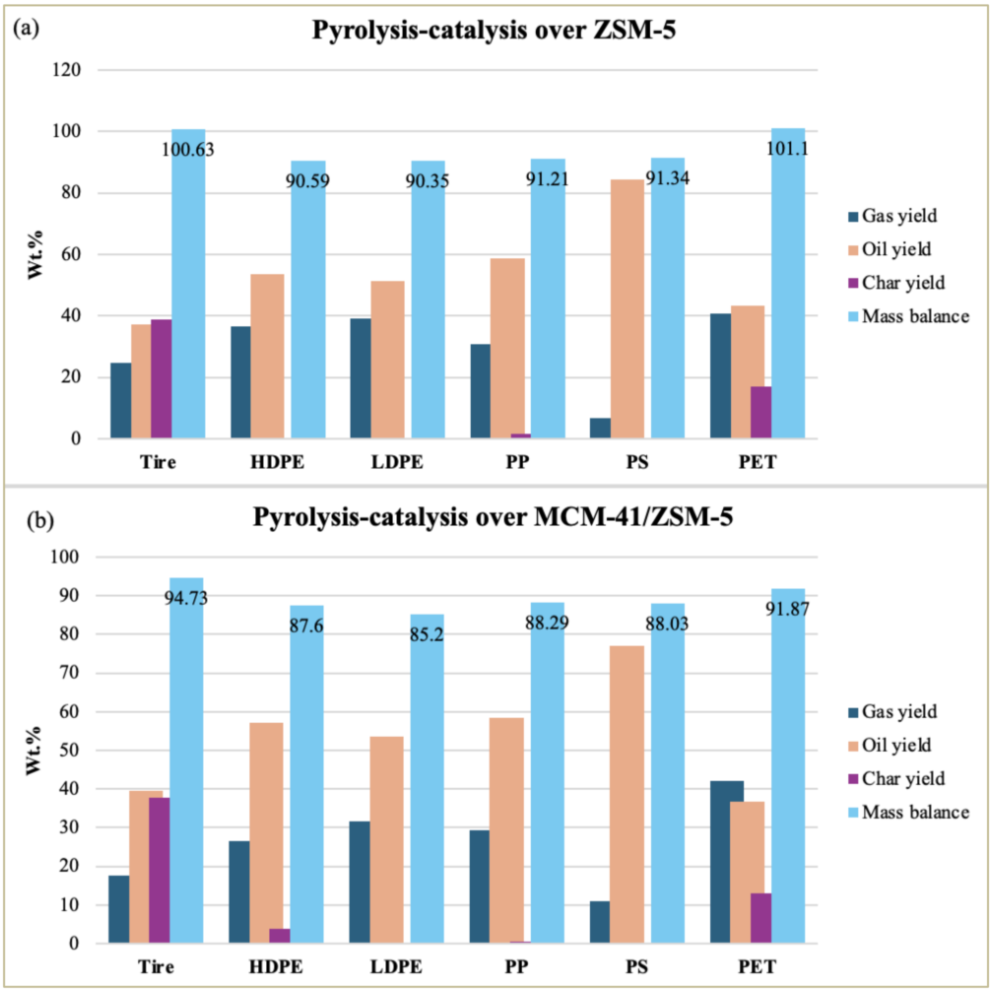


Figure 6.1 Product yield distrbution from the pyrolysis-catalysis of individual waste plastics and waste tire over ZSM-5 (a) and over a staged catalyst (MCM-41/ZSM-5)(b).

Figure 6.2 shows the gas composition (wt.% of the mass of gases (Table 6.1)) produced from the pyrolysis-catalysis of the individual tire and plastics over MCM41/ZSM-5 catalyst layer. The main gases produced were hydrogen, methane,

ethane, ethene, propane, propene, butane, butene, butadiene, and for PET, carbon dioxide, and carbon monoxide. PET produced the highest gas yield over all the other plastics, which due to its structure that tends to produce more CO and CO_2. Tire, HDPE, LDPE, PP, and PS produced the highest quantity of hydrocarbon gases compared to PET. Ratnasari et al. [103] found that the main gases obtained from the staged pyrolysis- catalysis process of HDPE over MCM-41/ZSM-5 were ethene, propene, butene and butadiene. An increase in the production of gases during catalytic pyrolysis, particularly with acid catalysts. Furthermore, it has been demonstrated that using a zeolite catalyst reduces the concentrations of carbon monoxide and carbon dioxide, while hydrogen, ethane, ethene, and butane increased significantly [182].

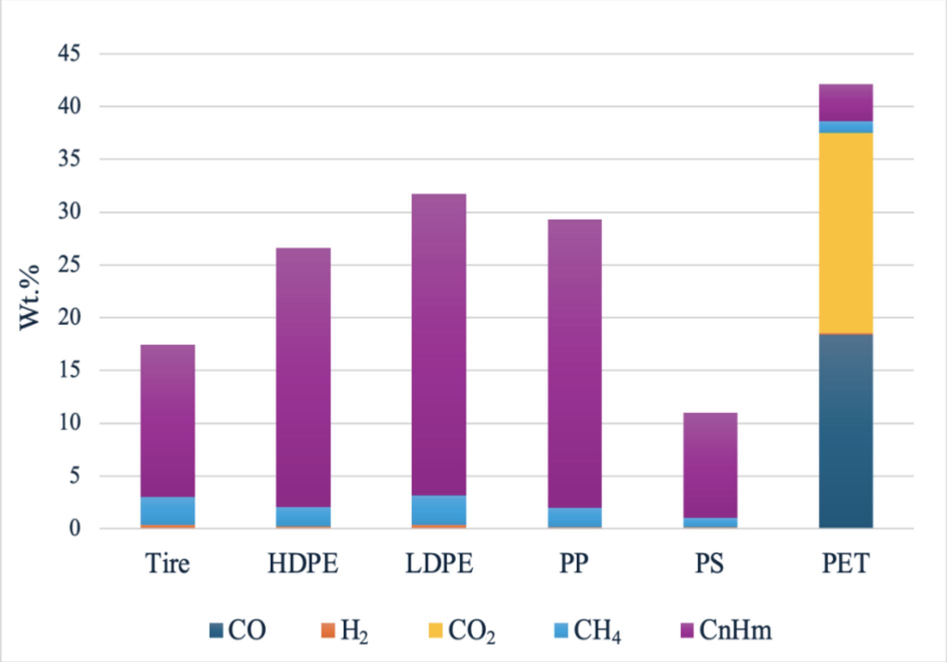


Figure 6.2 Gas composition of the pyrolysis-catalysis of individual tire and plastics over MCM-41/ZSM-5.

6.2.2 Composition of oil obtained from the pyrolysis-catalysis of waste tires and plastics over MCM-41/ZSM-5

The product oil from the pyrolysis-catalysis of waste tires and plastics determined by GC/MS. The major compounds presented in all the tables consisted of over 95 % of the compounds identified and expressed as wt.% in the pyrolysis-catalysis oil. BTEX, refers to benzene, toluene, ethylbenzene and xylenes; Aromatic refers to benzene derivatives, biphenyls, limonene, terphenyl, and indene; PAHs refers to for example, naphthalene, anthracene, phenanthrene, pyrene and fluorene and their derivatives; Aliphatic refers to carbon numbers above C_8; Alicyclic compounds refers for example to cyclopentane and cyclohexane etc.,

Tire: The main advantage of applying the MCM-41/ZSM-5 in the two staged pyrolysis-catalysis of waste tire is to control the product distribution, which promotes the production of lower molecular weight hydrocarbons compared to thermal pyrolysis. Figure 6.3 demonstrates the main oil composition obtained from the pyrolysis-catalysis of tire over MCM-41/ZSM-5 and ZSM-5 alone (results from Chapter 5), which were mainly BTEX, aromatic compounds, PAH, and alicyclic compounds. For example, BTEX, and aromatic compounds were 46.13 wt.% and 40.36 wt.%, respectively. The pyrolysis-catalysis of tire over MCM-41/ZSM-5 revealed more selectively toward producing lower molecular weight compounds. In comparison to the pyrolysis-catalysis of tire over ZSM-5 alone which was 40.69 wt.%, and 32.86, wt.% for BTEX and aromatic compounds, respectively. This indicated a variation between MCM-41/ZSM-5 and ZSM-5 alone, and that may be associated with the hydrogenation reaction and cracking of higher hydrocarbons, which increases the formation of lighter aromatic hydrocarbons; however, the cracking activity also leads to the reduction of the oil yields while increasing the gas yield [172] .Similarly, Olazar et al.[149] also investigated the influence of HY and HZSM-5 zeolite catalysts on oil composition, and they reported that the catalysts increased the concentration of single-ring aromatic compounds from 20.17 wt.% in the absent of catalyst to 32.49 wt.% and 40.49 wt.% for HZSM-5 and HY, respectively. Consequently, using the MCM-41/ZSM-5 promoted the aromatisation reactions, as the primary cracking occurred in the first layer of MCM-41 catalyst and then passing into ZSM-5 pores for further cracking and rearrangement [103].

MCM-41 has high surface area at 734 m^2 g^{-1}, and large pore volume. These characteristics can improve hydrogen transfer, which leads to the formation of more aromatic hydrocarbons. PAH such as naphthalene, and its derivatives (methyl and trimethyl naphthalene) increased from 11.11wt.% with ZSM-5 to 13.23 wt.% over MCM-41/ZSM-5 due to the Diels-Alder dehydrogenation of alkenes to form the polyaromatic hydrocarbon content by cyclisation and aromatisation, which is enhanced by the catalysts' steric and acidic capabilities [251]. Moreover, MCM-41 has large pores that would allow the large molecular hydrocarbons to pass into their pores, some of these large molecular get involved through the cracking to form the lighter aromatic hydrocarbons [143].

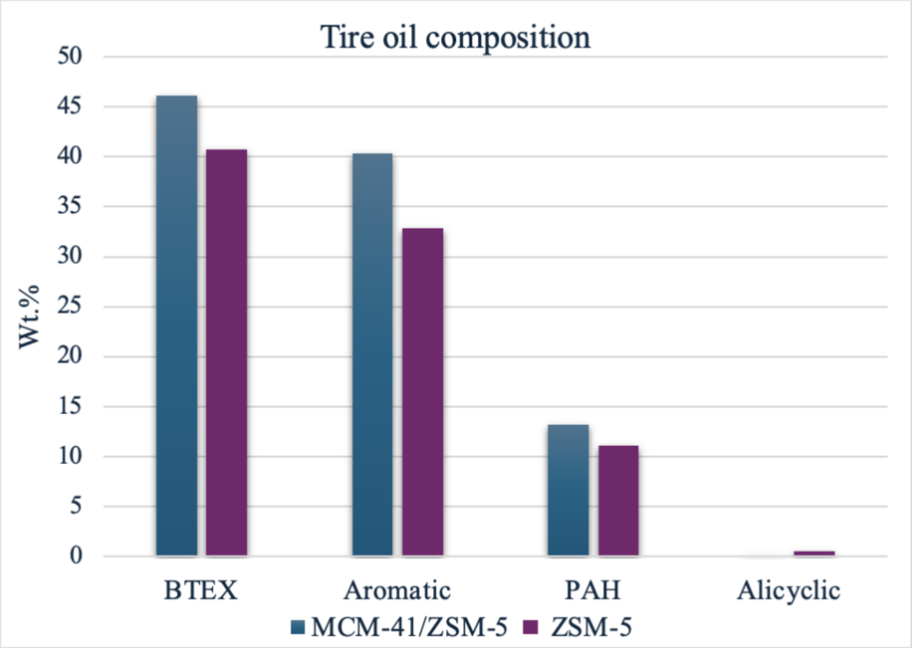


Figure 6.3 Oil composition obtained from the pyrolysis-catalysis of tire over MCM-41/ZSM-5 and ZSM-5.

High and low density polyethylene: The pyrolysis-catalysis of HDPE and LDPE over MCM-41/ZSM-5 produced high yields of BTEX at 62.39 wt.% and 67.27 wt.%, respectively as shown in Figure 6.4a and 6.4b. Toluene was the dominant compound in the oil composition of both HDPE and LDPE. The high BTEX content was increased by a significant decreased in the aliphatic and PAH contents. This behaviour was noticed as the fact of the second cracking of the MCM-41/ZSM-5 through the pyrolysis-catalysis process. These highly valuable chemicals are produced as a result of the primary cracking of the larger compounds through the wider MCM-41pores and then followed by the smaller pores of ZSM-5 for further cracking. In comparison to the results of the pyrolysis-catalysis of HDPE and LDPE over ZSM-5 alone (Figure 6.4a and 6.4b (data from Chapter 5)), the highest yields of the BTEX and aromatic were achieved over MCM-41/ZSM-5. Ratnasari et al. [103]reported the yield of gasoline in the range of C_8-C_{12}, which was the highest yield produced from the pyrolysis-catalysis of HDPE over the MCM-41/ZSM-5 catalyst instead of applying each catalyst individually. This particularly supports the main objective of this chapter in terms of upgrading the produced oil and reducing the heavier molecular weight compounds.

For example, Tian et al.[125] found that for pyrolysis-catalysis of LDPE with MCM-41the BTEX content was low, and the high BTEX content was reported over ZSM-5. Chen et al. [252] researched the pyrolysis of LDPE over MCM-41and produced compounds such as, methyl pentene and hexene through the end-chain scission as the primary products. These primary products can pass through the large pores of MCM-41 as well as the low concentration of acid sites that limited the cracking process. As a result, it produced alkenes (pentene and hexene), which are less likely to undergo the secondary reactions such as oligomerization and aromatization[253,254]. In contrast, the use of ZSM-5 generated BTEX compounds, which can be assigned to its strong acidic sites that promote the light aromatic formation and its small pores that allow entrance to single-ring aromatics[125].

Liu et al. [255]conducted the pyrolysis-catalysis of LDPE over ZSM-5 and MCM-41catalysts. They reported that the pyrolysis-catalysis of LDPE over MCM-41 improves macromolecule accessibility and inhibits the secondary reactions [256]. The mesoporous structure of MCM-41 with a large pore size allows for unlimited movement of larger LDPE pyrolysis hydrocarbons. Consequently, MCM-41-promoted oil fractions that were less favourable for cracking and aromatisation processes, leading to a higher C_{12}-C_{18} concentration[116]. For the pyrolysis-catalysis of LDPE with ZSM-5, they reported high aromatic content due to ZSM-5 high acidity and shape selectivity. The suggested mechanism, suggested that the acid sites favour the hydrogen transfer reactions and Diels-Alder reactions, leading to the synthesis of aromatics [257]. Aromatic compounds are mostly produced by hydrogen transfer reactions. Dehydrogenation active sites can facilitate Diels-Alder reactions and cyclisation intermediates. Heavy aromatic hydrocarbons were more easily converted into light aromatic hydrocarbons by hydrogenation.

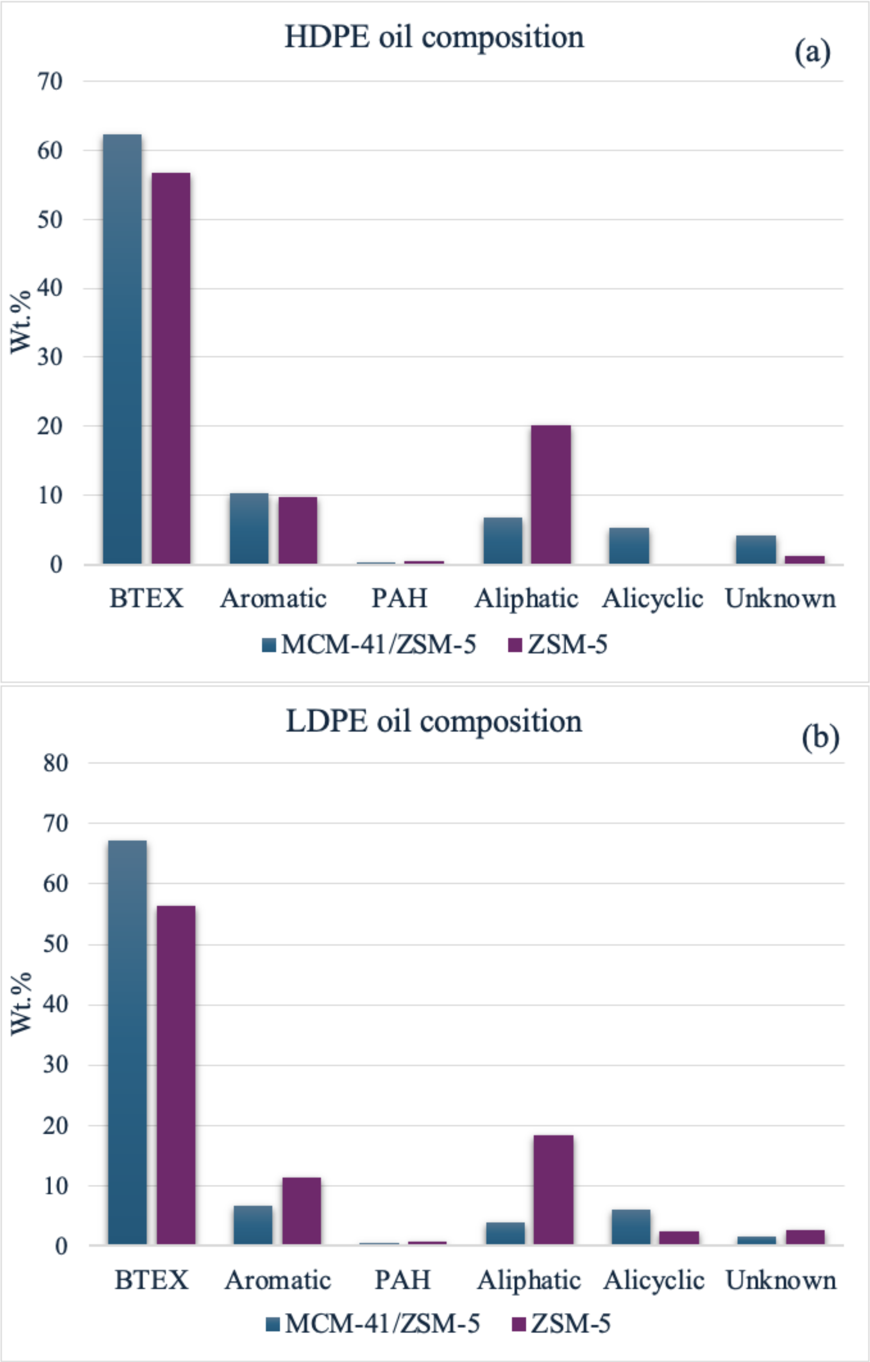


Figure 6.4 Oil composition obtained from the pyrolysis-catalysis of (a) HDPE and (b) LDPE over MCM-41/ZSM-5 and ZSM-5.

Polypropylene: Figure 6.5 shows the oil composition obtained from the pyrolysis-catalysis of PP with the MCM-41/ZSM-5 catalyst layers compared with using ZSM-5 catalyst alone (Chapter 5). The product oil consisted of BTEX, aromatic compounds, PAH, aliphatic compounds and alicyclic compounds, which were the main identified compounds. The highest yields of BTEX and aromatic were reported over MCM-41/ZSM-5 at 44 wt.% and at 27wt.%, respectively. That was expected as a result of the MCM-41 and ZSM-5 combination, with acidic sites that enhanced the oligomerization, aromatization and deoxygenation mechanism that increased the production of aromatic content [258] . However, PAH showed a negligible amount which can be explained through the two layers of MCM-41/ZSM-5 that promotes more single-ring compounds and can limit the secondary reactions for PAH production [259]. The acid sites on the catalyst surface initiate the carbocationic process, leading to the decomposition of polypropylene [258,260,261]. The accessibility of bulky polymeric molecules to the solids' internal catalytic acid sites is largely determined by porosity, and surface area properties. Applying the two stages MCM-41/ZSM-5 has the advantage as the ZSM-5 presents higher reactivity than MCM-41 in the cracking of HDPE, LDPE, and PP at the decomposition of the large molecules, and the transformation is almost the same as that of thermal cracking, due to the cross-section of the polymer which is very large enabling entry to the catalysts' micropores [262]. Furthermore, the high BET surface area of MCM-41 increased the contact between reactants and the catalyst surface, which maximizes the rate of cracking for more formation of small compounds[121] .

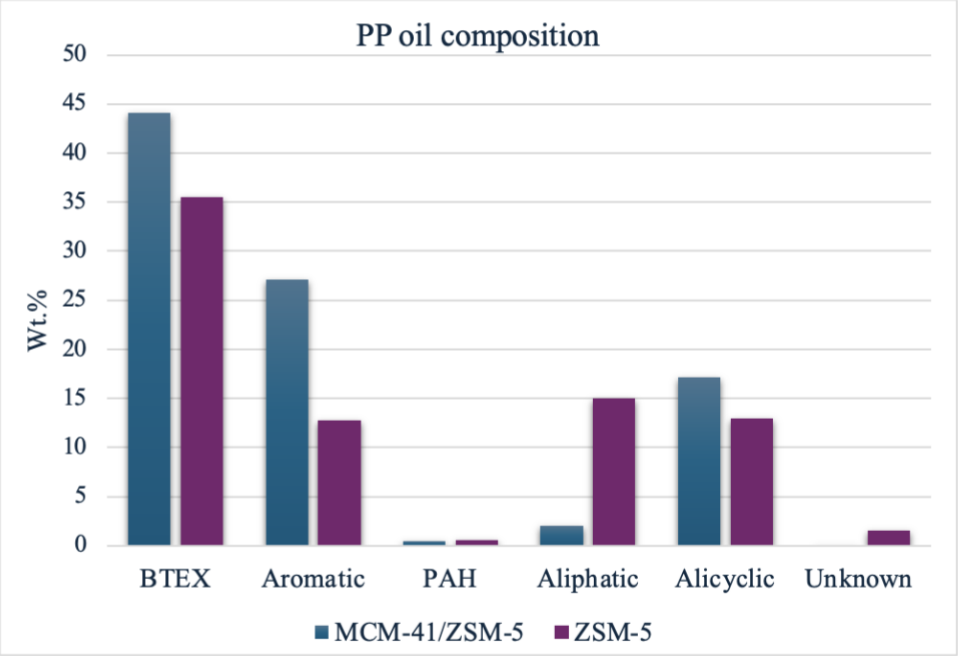


Figure 6.5 Oil composition obtained from the pyrolysis-catalysis of PP over MCM-41/ZSM-5 and ZSM-5.

Polystyrene: The pyrolysis-catalysis of polystyrene with the layered MCM-41/ZSM-5 catalyst system produced an oil rich in aromatic content as shown in Figure 6.6. The process produced a high BTEX content at 48.54 wt.% compared to the thermal pyrolysis and pyrolysis -catalysis of PS over ZSM-5 alone, which were reported at 4.27 wt.% and 17.91 wt.%, respectively. The content of the aromatic compounds, consisting of styrene, methyl styrene, indene, and benzene derivatives was reported at 52.09 wt.% with ZSM-5 (Chapter 5), while with MCM-41/ZSM-5 these aromatic compounds was observed at 30.50 wt.%. The low aromatic compound content may be attributed to the further cracking that occurred when both MCM-41 and ZSM-5 catalysts were used. For example, the styrene content decreased from 32.40 wt.% with ZSM-5 to 23.02 with MCM-41/ZSM-5. As it was reported that BTEX was increased at the expense of styrene[263], and that would be explained via the degradation mechanism of polystyrene. For example, thermal pyrolysis of polystyrene occurred by a free-radical chain reaction through the random-scission and end-chain β-scission for styrene as the primary product, which include the monomers, dimers, and trimers. [264] However, when catalysts were applied, the production of styrene significantly decreased whereas the formation of benzene, toluene, xylene, and ethylbenzene increased. Figure 6.7 shows the reaction pathways to produce monoaromatics (benzene, toluene, and ethylbenzene), and styrene dimers [263]. It demonstrates that the formation of these compounds depends on the availability and accessibility of protons as well as the active acid sites that control the product distribution. The results show notable levels of PAH over the MCM-41/ZSM-5 catalysts at 10.61 wt.%, which can be attributed to the high Brønsted and Lewis acid sites as well as the high external surface area which tends to produce high BTEX and PAH compounds through the free proton exchange on surface active sites [79]. On the other hand, PAH was predominantly produced on the external catalyst surface area rather than within pores. [263] ZSM-5 with its small pore size can limit the PAH production, and that may explain the low amount of PAH produced over ZSM-5 (Chapter 5) at 4.56 wt.% (Figure 6.5).

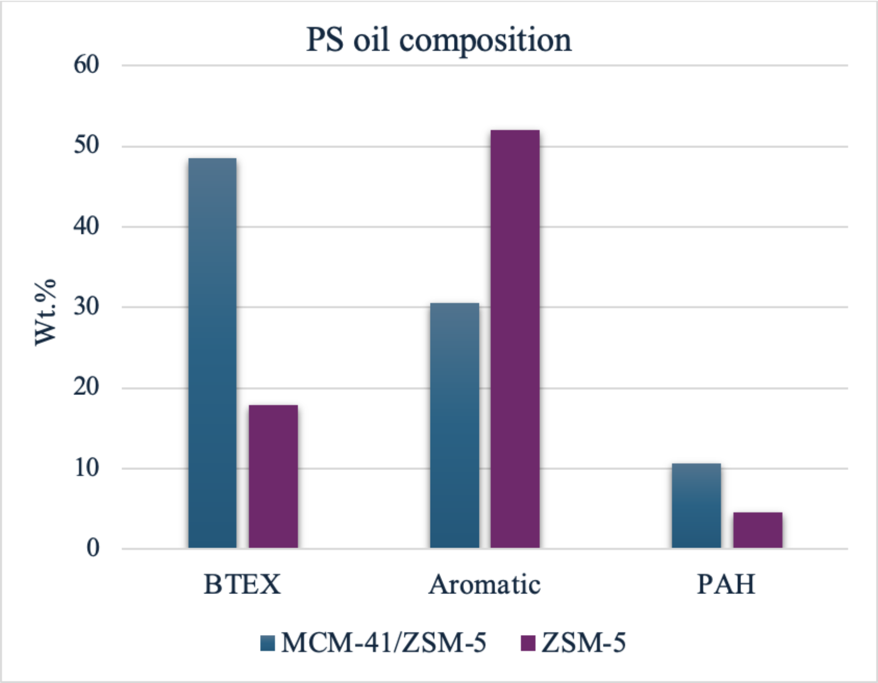


Figure 6.6 Oil composition obtained from the pyrolysis-catalysis of PS over MCM-41/ZSM-5 and ZSM-5.

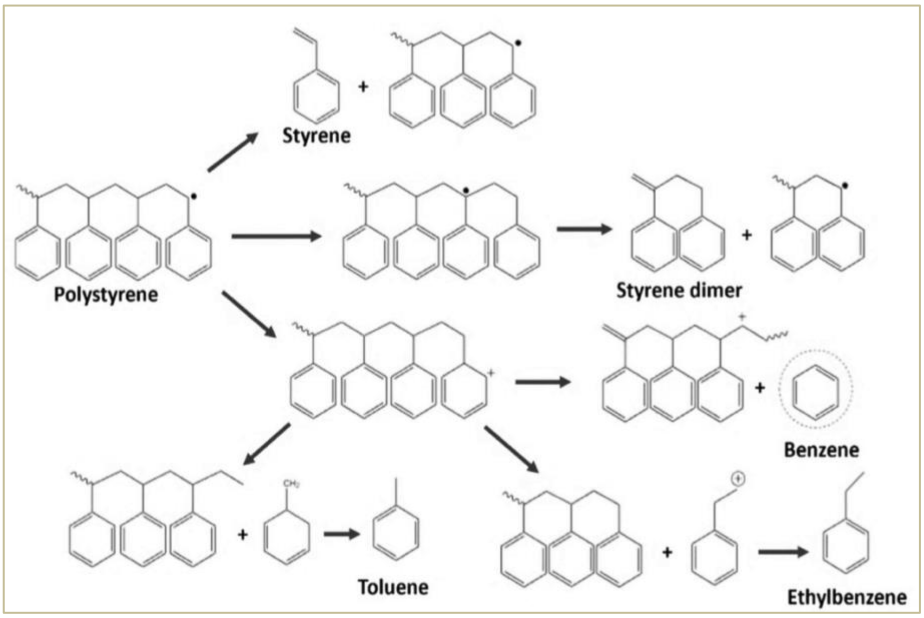


Figure 6.7 Reaction pathway for the production of high value compounds (benzene, toluene, and ethylbenzene over catalysts during the pyrolysis of polystyrene [79].

Polyethylene terephthalate: Figure 6.8 shows the oil obtained from the pyrolysis-catalysis of PET over the layered MCM-41/ZSM-5 catalysts showing that the oil contains high BTEX yield at 44.06 wt.%. The selectivity of the zeolite catalysts for upgrading the oil to high BTEX content was achieved compared to the thermal pyrolysis of PET that produced a waxy liquid with a high content of oxygenated compounds. Both pyrolysis-catalysis of PET over MCM-41/ZSM-5 and ZSM-5 (alone) produced less quantities of oxygenated compounds, and benzene was the dominant product. These results demonstrate that the zeolite catalyst may enhance the degradation of ether bonds in the pyrolysis vapours produced from the pyrolysis of PET. As a result, it can be concluded that zeolite could promote the pyrolysis of the oxygen-compounds, which includes carbonyl (C=O), aliphatic C-O, and aromatic C-O in the pyrolytic volatile products [245]. The low content of oxygenated compounds was reported for the pyrolysis-catalysis of PET over MCM-41/ZSM-5 at 5.15 wt.%, which indicates that some oxygenated compounds remain after the deoxidation of the volatile products. Similarly, Du et al. [245], reported high yields of benzene and benzene derivatives over ZSM-5, while low oxygen content was observed in the oil obtained from the catalytic pyrolysis of PET with ZSM-5. PAH content increased in the presence of MCM-41/ZSM-5 at 29.43 wt.% compared to ZSM-5 at 0.89 wt.%. This suggested that the external protons can attack C=O bonds at Bronsted acid sites, resulting in the production of benzene free radicals and carbon oxides. Thilakaratne et al.[134] proposed that benzene free radicals can react with olefins to form naphthalenes.

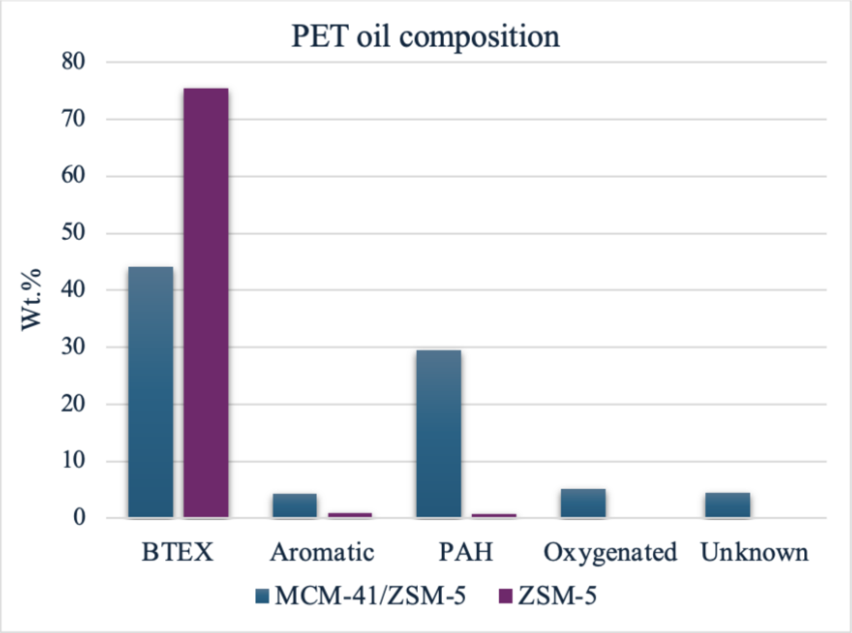


Figure 6.8 Oil composition obtained from the pyrolysis-catalysis of PET over MCM-41/ZSM-5 and ZSM-5.

6.3 Co-pyrolysis-catalysis of tire and plastic mixtures over MCM-41/ZSM-5

The co-pyrolysis-catalysis of tire and plastic mixtures (Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS and Tire/PET) was undertaken to determine any interaction that may influence the yield and composition of the product oil and gases. The tire and plastic were mixed in a 1:1 ratio and pyrolyzed in the fixed bed reactor system with the addition of the MCM-41/ZSM-5 catalyst (staged layered system). The product yield, gas and oil composition were analysed and evaluated to confirm any synergistic interaction between the waste tires and plastics as well as the influence of MCM-41/ZSM-5 on the gas and oil composition.

6.3.1 Products yield and gas analysis of the pyrolysis-catalysis of waste tires and plastics over MCM-41/ZSM-5

The co-pyrolysis of the tire sample with each of the plastics in a 1:1 mixture were processes in the two stage pyrolysis-catalysis reactor with the layered MCM-41/ZSM-5 catalyst system. Table 6.2 shows results of the co-pyrolysis-catalysis of tire and plastics over MCM-41/ZSM-5, which reveals high gas yields for all the mixtures (Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS, and Tire/PET) compared to the expected yields based on the additive values from the previous section. This indicates the interaction between tire and plastics was responsible for the production of high gas yields at the expense of the oil yields. The highest gas yield was reported for Tire/PET at 39 wt.%, while Tire/PS produced the lowest gas yield at 14.31 wt.%. On the other hand, Tire/PS produced the highest oil yield at 58.75 wt.%, whereas the other mixtures observed less oil yields than would be expected, particularly Tire/PET which produced the lowest oil yield at 36.50 wt.%. The char yields produced from the co-pyrolysis of the mixtures did not show much difference as the experimental and predicted values were quite close, as would be expected. Figure 6.9 indicated that gas yields were high for all the mixtures over MCM-41/ZSM-5 at the expense of the oil yields compared to the pyrolysis catalysis over ZSM-5. For example, the pyrolysis-catalysis of Tire/PET over MCM-41/ZSM-5 produced high gas yield at 39.05 wt.% which is attrbutied to the high amount of CO and CO_2 that produced in gas. The oxygenated compounds in the oil were reduced compared to the pyrolysis-catalysis over ZSM-5.

Table 6.2 Product yield from the pyrolysis-catalysis of mixtures of the tire and waste plastics over MCM-41/ZSM-4, experimental and additive data (results calculated based on the additivity data of the individual samples).

	Experimental (wt.%)				
	Tire/HDPE	**Tire/LDPE**	**Tire/PP**	**Tire/PS**	**Tire/PET**
Gas yield	30.04	35.40	25.40	14.31	39.05
Oil yield	40.25	41.00	45.50	58.75	36.50
Char yield	20.75	18.50	20.25	19.75	26.75
Mass balance	91.04	94.90	91.15	92.81	102.3
	Additive data (wt.%)				
	Tire/HDPE	**Tire/LDPE**	**Tire/PP**	**Tire/PS**	**Tire/PET**
Gas yield	22.04	24.59	23.39	14.26	29.80
Oil yield	48.38	46.50	49.00	58.25	38.13
Char yield	20.75	18.88	19.13	19.00	25.38
Mass balance	91.17	89.97	91.52	91.51	93.31

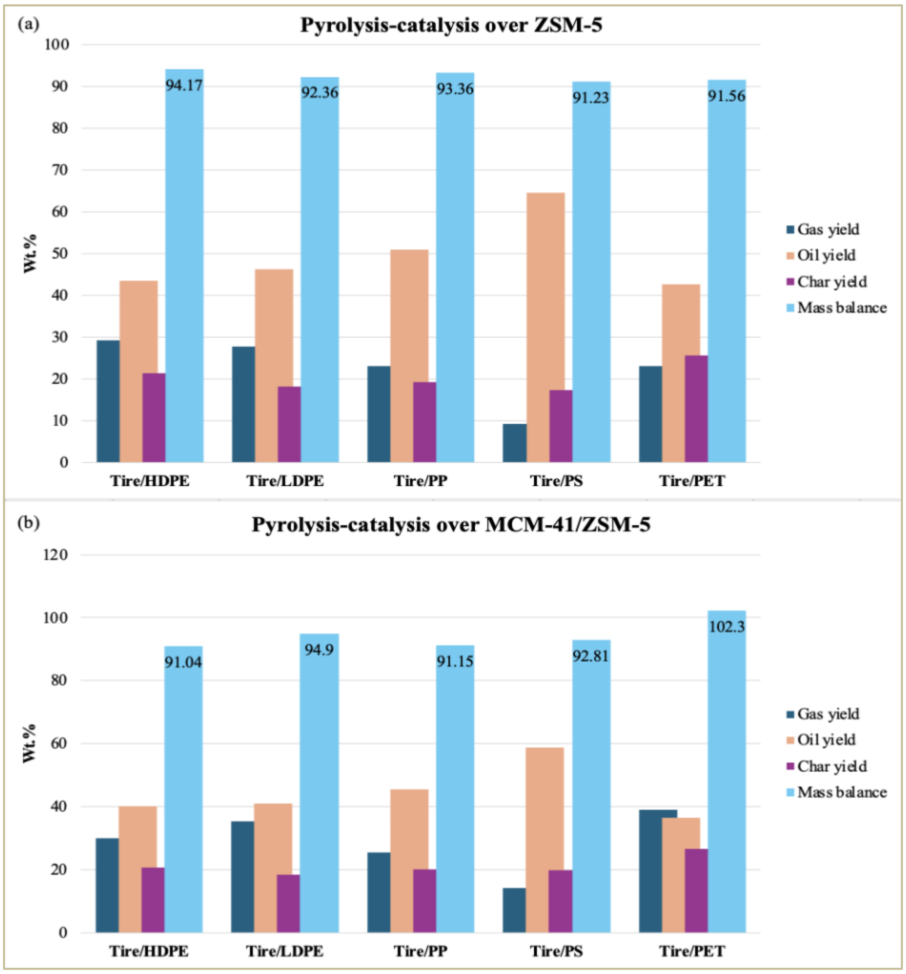


Figure 6.9 Product yield distribution from the pyrolysis-catalysis over ZSM-5 (a) and pyrolysis-catalysis over MCM-41/ZSM-5 (b) of tire and plastic mixtures.

The gas composition produced from the co-pyrolysis of the tire/plastic mixtures over the MCM-41/ZSM-5 catalysts showed an increase in the gas yield compared to the individual tire and plastics as shown in Figure 6.10. The main gases produced were, methane, hydrocarbons, and hydrogen, while PET produced more carbon monoxide and carbon dioxide.

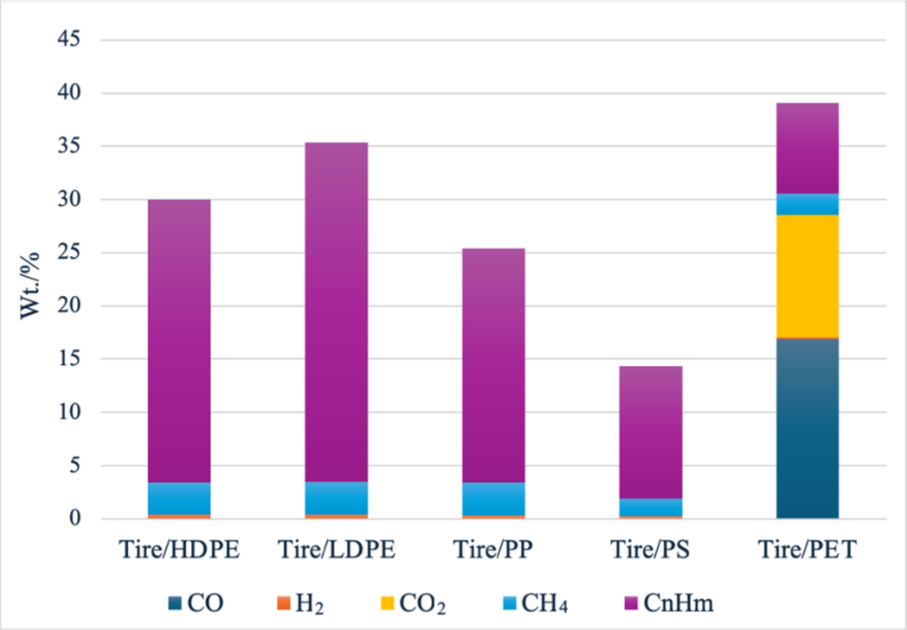


Figure 6.10 Gas composition derived from the pyrolysis-catalysis of tire/high density polyethylene (T/HDPE), tire/low density polyethylene (T/LDPE), tire/polypropylene (T/PP), tire/polystyrene (T/PS) and tire/polyethylene terephthalate (T/PET) over MCM-41/ZSM-5.

6.3.2 Composition of oil obtained from the co-pyrolysis-catalysis of the tire/plastic mixtures over MCM-41/ZSM-5

Tire/HDPE and Tire/LDPE: Table 6.3 shows the oil compound groups identified using GC/MS from the co-pyrolysis-catalysis of HDPE and LDPE using the layered MCM-41/ZSM-5 catalyst. The highest BTEX contents were reported for Tire/HDPE and Tire/LDPE during the catalytic pyrolysis compared to the thermal pyrolysis. The major influence of the co-pyrolysis (tire and PE) was the reduction of the paraffin and olefin compounds, which were found in the product oil for both thermal and catalytic pyrolysis of tire/PE compared to the individual polyethylene produced long chain hydrocarbons. The oil compositional results revealed the influence of mixing tire with HDPE and LDPE that eliminated the aliphatic compounds when the MCM-41/ZSM-5 catalyst was used.

Table 6.3 Oil composition of the co-pyrolysis-catalysis of the tire/PE mixtures over MCM-41/ZSM-5.

Oil composition	Tire/HDPE	Tire/LDPE
BTEX	43.35	39.82
Aromatic	22.95	27.62
PAH	19.89	17.68
Aliphatic	0.00	0.00
Alicyclic	0.00	0.00
Unknown	0.41	4.72
Total	86.60	89.84

Figure 6.11 compares the composition of the product oil from the thermal pyrolysis (no catalyst) of HDPE, LDPE and the co-pyrolysis of Tire/HDPE and Tire LDPE (no catalyst, data from chapter 4, Figure 6.11(a)) and also the pyrolysis-catalysis of the plastics using ZSM-5 catalyst (alone, data from chapter 5, Figure 6.11(b)), and the layered MCM-41/ZSM-5 catalyst (Figure 6.11 (c)).

Figure 6.11(a) shows the thermal pyrolysis of HDPE, LDPE, Tire/HDPE, and Tire/LDPE where high amounts of wax were produced from both HDPE and LDPE, which were over 95 wt.% of the oil. The mixtures of Tire/plastic showed a slight reduction of the aliphatic content and slight increase of the BTEX, aromatic, and PAH compounds. Figure 6.11(b) represents the significant changes in the oil composition using ZSM-5 compared to the thermal pyrolysis where it can be seen that a reduction of the aliphatic content was produced over the ZSM-5 catalyst. This would be linked to the high cracking of the C-C bond in HDPE and LDPE that formed free radical fragments, and then produced more aromatic compounds at the expense of alkenes[116] .The mixtures of Tire/HDPE and Tire/LDPE enhanced the oil composition as the BTEX and aromatic were the major compounds reported, and that interpreted the influence of mixing tire with PE. The pyrolysis of tire would also produce more hydrogen radicals that can promote the hydrogenation reaction of benzene derivative radicals to promote the formation of BTEX [202]. Furthermore, the high abundance of alkenes that were produced during the thermal pyrolysis of HDPE and LDPE, followed by aromatization via dehydrogenation, was promoted by the catalysts and delocalization stability of the aromatic rings[265] .

Figure 6.11(c) shows that pyrolysis-catalysis over MCM-4/ZSM-5 of individual HDPE and LDPE produced an oil with a composition of aliphatic content in low concentration. Using MCM-4/ZSM-5 enhanced the oil composition and facilitated the further carking of HDPE and LDPE, which demonstrated the selectivity to produce more BTEX. On the other hand, the mixtures (Tire/HDPE and Tire/LDPE) over MCM-41/ZSM-5 catalysts produced a rich aromatic oil. The size of the pores plays an essential factor in the selection of which products and reactants can reach the catalyst's active sites[70] . Thermal cracking occurs on the solid catalyst's outer surface, while interior pores serve as conduits for the selective compounds that pass and then breakdown of larger hydrocarbons[266]. As a result, gases are mostly produced in the microscopic pores, whereas waxes are formed on the catalyst's outer surface. Above the catalyst surface, low-molecular-weight hydrocarbons are formed, which are volatile at the reaction temperature and can permeate through the molten polymer layer as the end products or react further inside the pores[266]. Microporous catalysts increase the catalytic process by producing gases and minimising the liquid yield while providing higher quality than catalytic pyrolysis with macropores[267]. The secondary reactions depend primarily on cracking, ring rupture, and aromatisation, which result in the synthesis of hydrocarbons ranging from (C_4-C_{10}) and low molecular-weight aromatic compounds [247]. The literature demonstrates that pyrolysis of polyolefins can produce oils with high aromatic concentrations, and several researchers have hypothesised a production process based on the Diels-Alder reaction of alkenes[87,268,269]. The Diels-Alder reactions involve dehydrogenation and unimolecular cyclisation, which is favoured as the high concentration of alkene in polyolefin catalytic pyrolysis products [270,271].

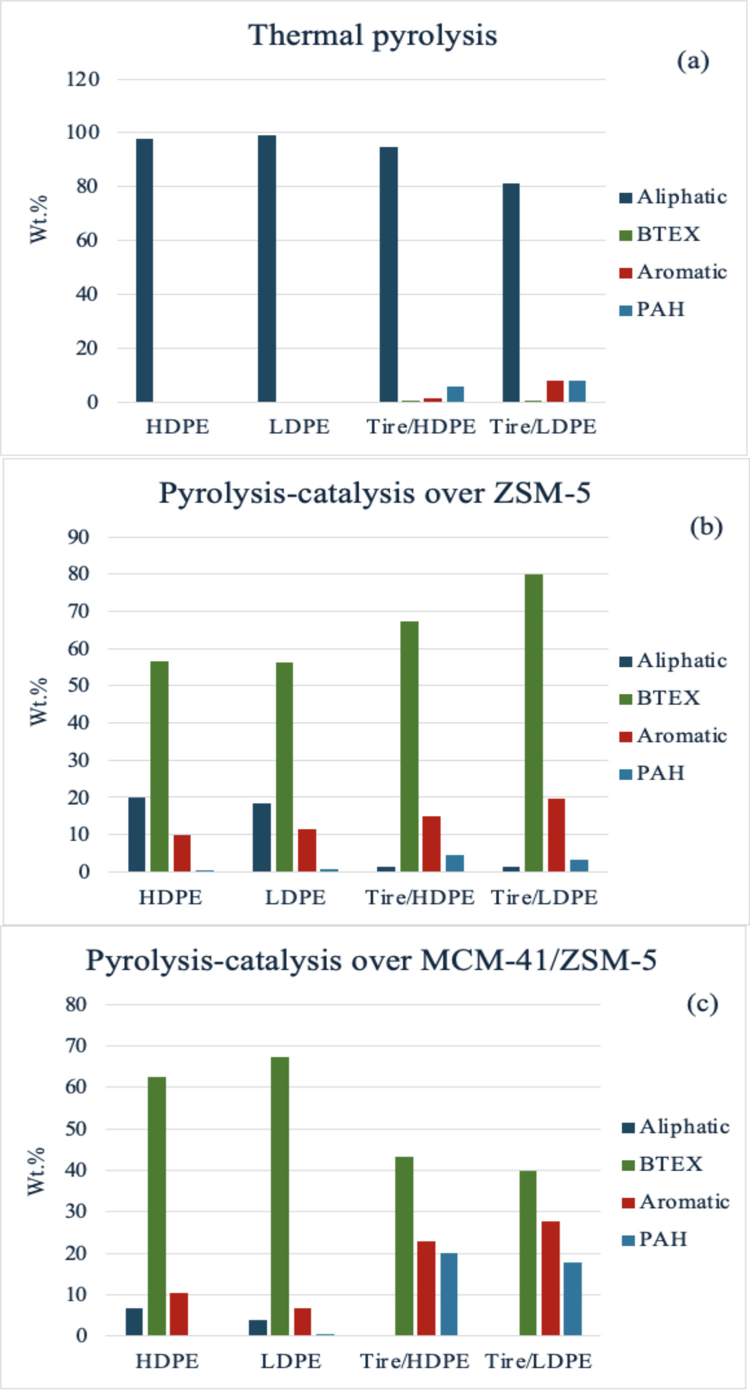


Figure 6.11 The oil composition of the individual polyethylene (HDPE, and LDPE), and mixtures of (Tire/HDPE and Tire/LDPE): (a) thermal pyrolysis, (b) catalytic pyrolysis over ZSM-5, and (c) catalytic pyrolysis over MCM-41/ZSM-5.

Tire/polypropylene: The oil composition from the co-pyrolysis-catalysis of the Tire/PP mixture over MCM-41/ZSM-5 catalyst produced an aromatic oil as shown in Figure 6.12. BTEX and aromatic contents were the major produced yield in the oil at 44. 28 wt.% and 32.78 wt.%, respectively. The low yield of alicyclic compounds was at 0.70 wt.%, and no aliphatic content was produced over the layered MCM-41/ZSM-5 catalyst. In comparison to the pyrolysis-catalysis of Tire/PP over ZSM-5, which is also shown in Figure 6.12, showed oil composition concentrations of 50.58 wt.%, 30.54 wt.%, 3.60 wt.% and 5.34 for BTEX, aromatic, alicyclic, and aliphatic contents, respectively. Although, Tire/PP produced a considerable aromatic portion through the thermal pyrolysis, [62], the thermal decomposition of the natural rubber in tire [199], and that may allow more interaction to take a place between tire and PP. Dewi et al. [202] considered that tire char behaves as a catalyst for the cracking of polyalkene polymers due to the presence of Lewis and Bronsted acid sites that facilitate polymer degradation. The BTEX for Tire/PP was high, suggesting that utilising high acidity and shape selectivity catalysts (MCM-41or ZSM-5) improved the cracking and aromatisation processes, resulted in oil with a high aromatic content [64,272].

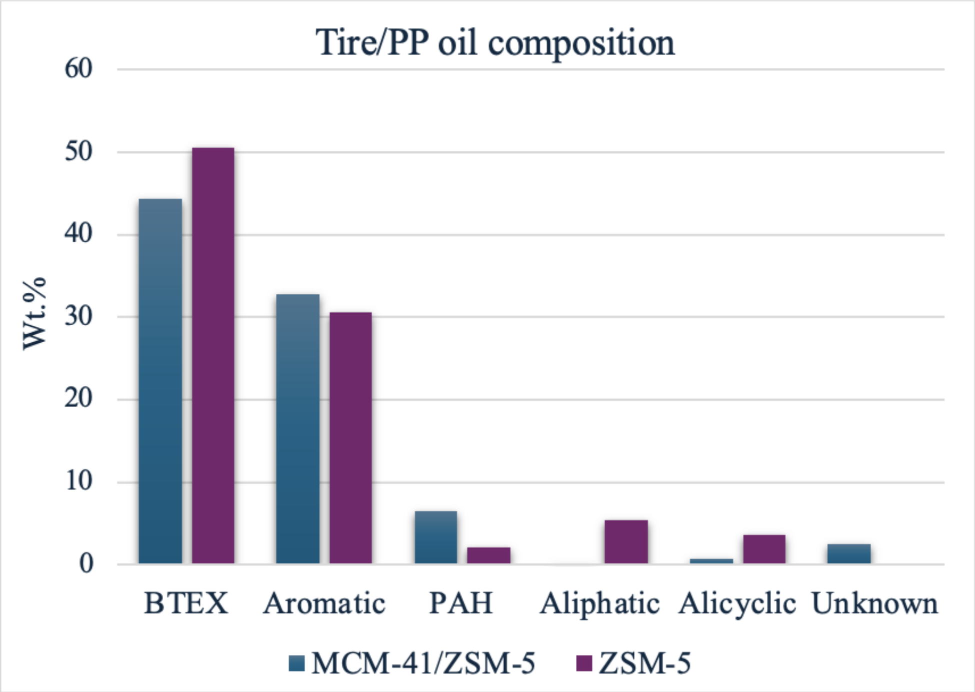


Figure 6.12 Oil composition obtained from the pyrolysis-catalysis of Tire/PP over MCM-41/ZSM-5 and ZSM-5.

Tire/polystyrene: The oil composition obtained from the pyrolysis-catalysis of Tire/PS over MCM-41/ZSM-5 is characterized by a high aromatic compound content as shown in Figure 6.13. That is due to the tire and polystyrene chemical structures, which produced more aromatic compounds in both thermal and catalytic pyrolysis. Tire/PS produced the highest BTEX yield at 56.50 wt.% compared to the other mixtures. Ethylbenzene was the dominant compound at 28.03 wt.%, while the amount of styrene showed a reduction at 17.54 wt.% compared to the styrene produced from the individual PS at 23.02 wt.%. The interaction between tire and PS caused the production of the high aromatic contents. The fragments of the thermal decomposition of the tire produced alkyl radicals, while PS produced phenyl and benzyl radicals, which then can react and form the single ring aromatic compounds[202]. This reduction would be linked to the production of benzene, toluene, xylene, and ethylbenzene, which were mainly formed by styrene reactions. The reaction pathway through the styrene monomers and the presence of protons via active acid sites of catalysts showed that styrene initially produced by the tire and PS is converted to BTEX (as shown in Figure 6.7). It was found that benzene production increased, whereas that of styrene, -methyl styrene, and dimers decreased through the surface acidity of the zeolites[79]. Furthermore, naphthalene derivatives are the condensed fragments that are mainly formed on the Zeolites' surface-active centres. The production of PAH is controlled by the surface area and the pore volume of the Zeolite catalyst, and the low yield of PAH might be attributable to these reasons[79].

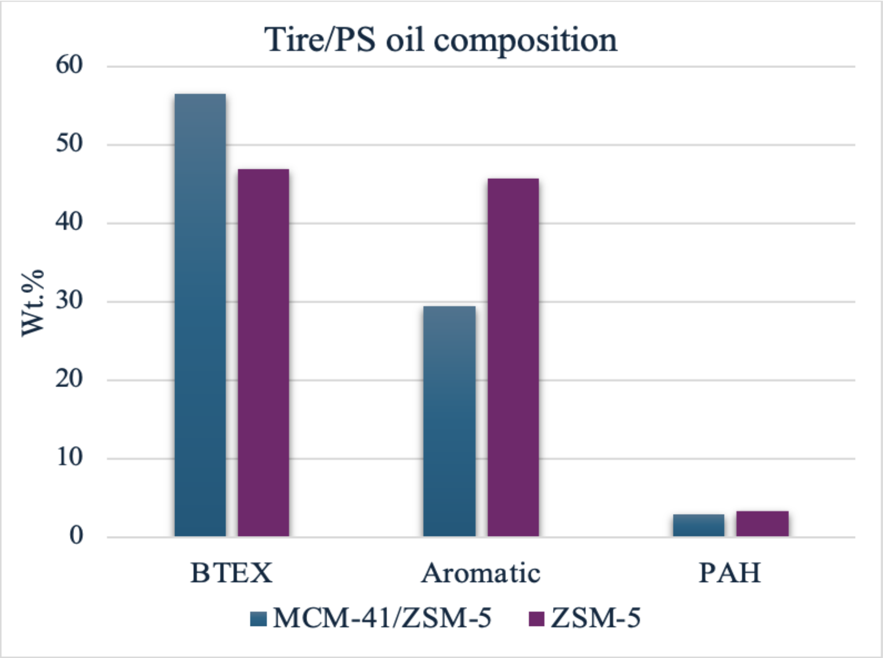


Figure 6.13 Oil composition obtained from the pyrolysis-catalysis of Tire/PS over MCM-41/ZSM-5 and ZSM-5.

Tire/Polyethylene terephthalate: Figure 6.14 shows the oil composition of the Tire/PET co-pyrolysis in relation to the MCM-41/ZSM-5 catalyst and ZSM-5 catalyst alone (Chapter 5). The results show the oil obtained over MCM-41/ZSM-5, that revealed the BTEX content produced at 43.85 wt.%, which was lower than with ZSM-5. The pyrolysis-catalysis of Tire/PET over ZSM-5 showed more selectively to produce more BTEX at 55 wt.% at the expense of the oxygenated compounds. That may be attributed to the differences in the pore size between ZSM-5 and MCM-41. As mentioned previously, the high selectively of ZSM-5 catalyst was associated to its small pore size, while MCM-41 has larger pores that allow the formation of compounds such as, naphthalene and benzoic acid to be present in the oil at 5.85 and 1.36 wt.%, respectively. However, benzoic acid showed a low amount compared to the thermal pyrolysis of PET, and the production of benzene increased over ZSM-5 and MCM-41/ZSM-4 at 29.30, and 14.43 wt.% respectively. Du et al.[245] examined the ZSM-5 zeolite and found that pyrolysis of PET produced aromatic hydrocarbons, particularly benzene at higher temperatures and slow heating rates. They also observed that ZSM-5 was an efficient catalyst for deoxygenating the PET products. Xu et al.[133] reported that the production of aromatic hydrocarbons was enhanced over H-ZSM-5 more than the pyrolysis without a catalyst. As a result, the decomposition of individual tire and PET produced BTEX and aromatic compounds, and combining tire with PET maximized the production of aromatic compounds and reduced the oxygenated compounds.

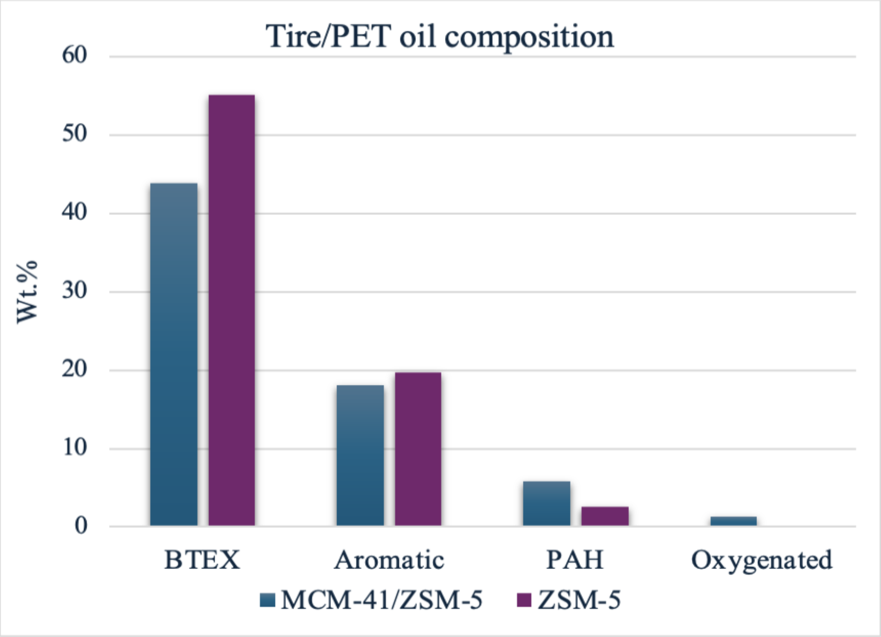


Figure 6.14 Oil composition obtained from the pyrolysis-catalysis of Tire/PET over MCM-41/ZSM-5 and ZSM-5.

6.4 Tire-plastic co-pyrolysis-catalysis interaction effects

Any synergistic interaction between the pyrolysis compounds produced from co-pyrolysis of tire/plastic over the layered MCM-41 and ZSM-5 catalyst was investigated, and the results are shown in Figure 6.15 and Figure 6.16. Figure 6.15 shows the results for pyrolysis-catalysis of tire/high density polyethylene (T/HDPE), tire/low density polyethylene (T/LDPE) and tire/polypropylene (T/PP) over MCM-41/ZSM-5. Figure 6.16 (a and b) shows the results for tire/polystyrene (Tire/PS) and tire/polyethylene terephthalate (Tire/PET) on the oil composition through the pyrolysis-catalysis over MCM-41/ZSM-5.

Figure 6.15 shows the mixtures of Tire/HDPE, Tire/LDPE, and Tire/PP obtained negative values of the BTEX contents at -10.91, -16.88, and -0.83 wt.%, respectively and that due to the high volatile compounds of the catalytic cracking over two layers of MCM-41/ZSM-5, even though the high amount of BTEX was produced according to the experimental values. However, the predicted values indicated more concentrations of BTEX should be observed, which was related to the individual values of HDPE, LDPE, and PP that showed relatively low values than would be expected. The aromatic contents observed negative values for Tire/HDPE and Tire/PP at -2.43, and - 0.96 wt.%, respectively. In the case of tire/LDPE, the aromatic content was positive at 4.11 wt.%. This may indicate a significant interaction between tires and LDPE, considering the branched structure of LDPE that facilitates the decomposition under degradation temperatures close to tires compared to HDPE. The PAH content revealed positive values at 13.12 wt.% and 10.81wt.% for Tire/HDPE, and Tire/LDPE, and that could be attributed to the production of light hydrocarbons (C_1-C_4). The main PAH compound such as naphthalene and its derivatives that are primarily produced from the thermal degradation of tire compared to HDPE and LDPE that produced more alkenes. Although, the Tire/PE produced a significant amount of PAH as the result of the addition of catalyst with the high Bronsted and Lewis acid sites as well as the high external surface area of the MCM-41catalyst in particular, which predominantly tends to produce PAH compounds on external area rather than pores. Aliphatic and alicyclic compound interaction revealed negative values at -3.37, -1.98, and -1 wt.% for Tire/HDPE, Tire/LDPE, and Tire/PP and that would be expected of the high cracking of the long chain polyolefins, and the interaction between hydrocarbon radicals produced from the tire rubber and the radicals produced from the thermal decomposition of PE and PP, which caused the reduction of both aliphatic and alicyclic contents.

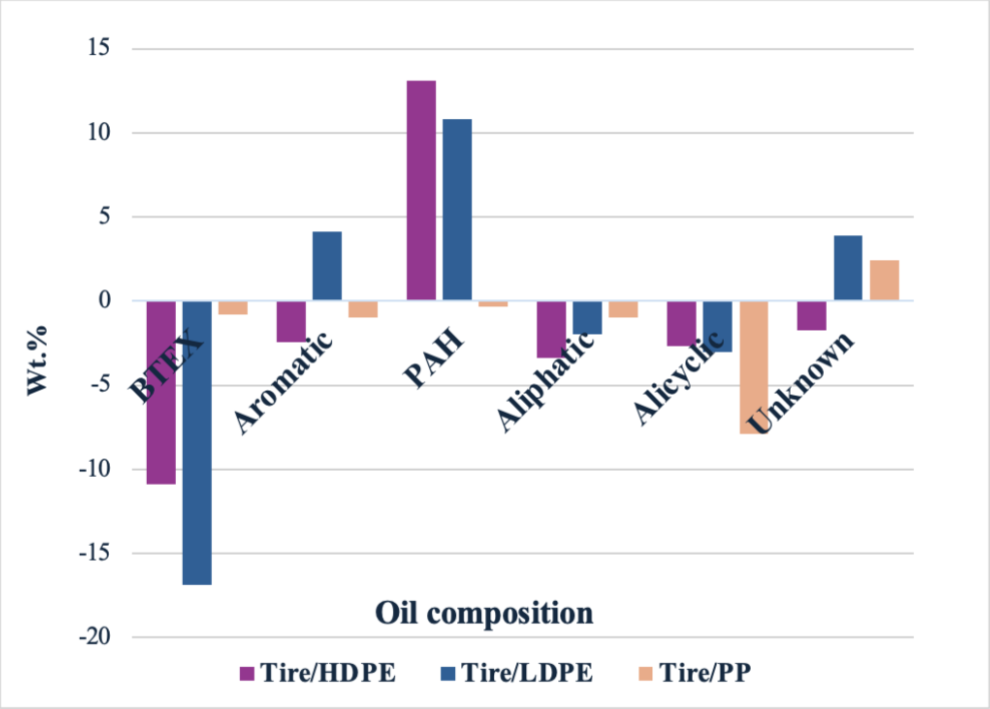


Figure 6.15 Interaction effect of mixing tire/plastic on oil composition from pyrolysis-catalysis of tire/high density polyethylene (T/HDPE), tire/low density polyethylene (T/LDPE) and tire/polypropylene (T/PP) over MCM-41/ZSM-5.

Figure 6.16(a) shows the Tire/PS interaction for the product oil produced from co-pyrolysis-catalysis over MCM-41/ZSM-5, which revealed a positive interaction value of 9.16 wt.% for the BTEX compounds. However, Tire/PET obtained a negative value of -1.25 for BTEX as shown in Figure 6.16(b). The negative values were reported for the aromatic contents than would be expected for both mixtures at -5.97 and -4.34 wt.%, respectively. PAH also obtained negative values for Tire/PS at -9.02 wt.% and for Tire/PET at -15.47 wt.%, which indicated a significant reduction in PAH production. This suggested that mixing tire with PS and PET promote the production of more BTEX than PAH as the experimental values of PAH were less than the predicted values. Thus, tire enhanced the degradation of PS through the hydrogenation reaction of benzene derivative radicals to produce BTEX. Furthermore, the influence of using two stage catalysts of layered MCM-41/ZSM-5, which increased the selectively for BTEX production. Tire/PET reported negative values of interaction for the oxygenated compounds as the individual PET produced negligible amount of the oxygenated compounds through the catalytic pyrolysis, and the conversion of the primary products (phthalic and benzoic acid) to benzene with CO_2 release[82].

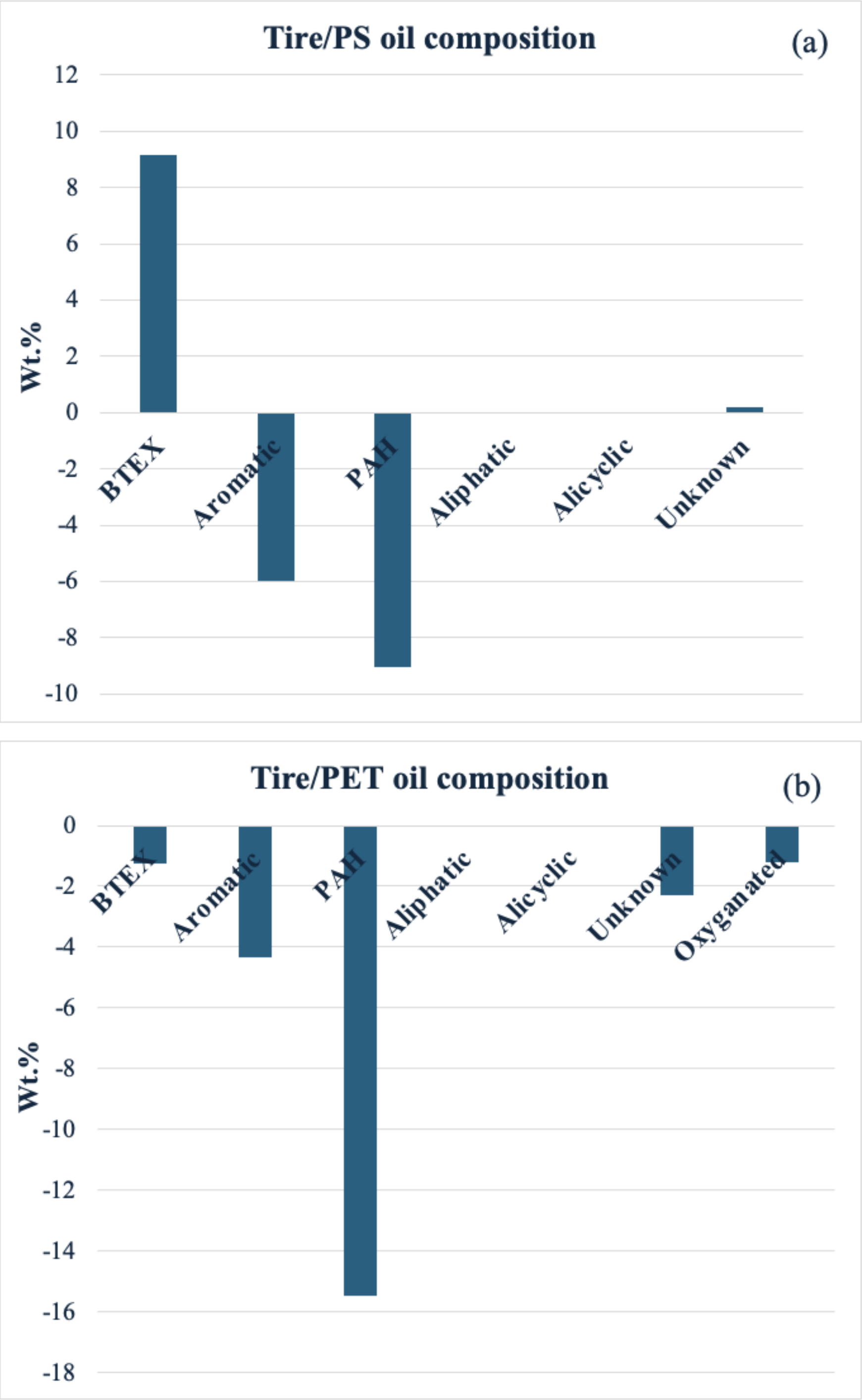


Figure 6.16 Interaction effect of mixing (a) tire/polystyrene (Tire/PS) and (b) tire/polyethylene terephthalate (Tire/PET) on the oil composition through the pyrolysis-catalysis over MCM-41/ZSM-5.

6.5 Summary

In this chapter, pyrolysis-catalysis of waste plastic, waste tire, and 1:1mixtures of the tire and plastics has been conducted over the MCM-41/ZSM-5 catalyst layer. The influence of the pyrolysis -catalysis (zeolite catalysts in a staged layered) process on the products composition, particularly, the gas and oil yields were also investigated in this chapter. It was found that combining the microporous and mesoporous of catalysts to optimise the conversion of plastic pyrolysis products to low molecular weight hydrocarbon fuels and chemicals. The production of gases during catalytic pyrolysis, increased on expense of oil yields. The oil yields were at 39.50, 57.25, 53.50, 58.50, 77.00, and 36.75 wt.% for Tire, HDPE, LDPE, PP, PS, and PET respectively. Moreover, tire and plastics produced hydrocarbon gases, while PET produced the highest gas yield of all the other plastics, due to its chemical structure, which produces more CO and CO_2. Applying the two stages MCM-41/ZSM-5 has the advantage as the ZSM-5 presents higher reactivity than MCM-41 in the cracking of HDPE, LDPE, and PP. The primary products can pass through the large pores of MCM-41 as well as the low concentration of acid sites that limited the cracking process. The use of ZSM-5 with (strong acidic sites and small pores) that promote the light aromatic formation. The pyrolysis-catalysis of PS produced BTEX which was increased at the expense of styrene. While PET over MCM-41/ZSM-5 produced less quantities of oxygenated compounds, and benzene was the dominant product.

The co-pyrolysis of the tire/plastic mixtures over MCM-41/ZSM-5 catalyst layer showed an increase in the gas yields compared to the individual tire and plastics. The major influence of the co-pyrolysis (tire and PE) was the reduction of the paraffin and olefin compounds, which were found in the product oil for both thermal and catalytic pyrolysis of tire/PE compared to the individual polyethylene produced long chain hydrocarbons. The BTEX content obtained from Tire/PP was high, suggesting that utilising MCM-41/ZSM-5 improved the cracking and aromatisation processes, resulted in oil with a high aromatic content. Tire/PS gave the high production of the aromatic content, and combining tire with PET maximized the production of aromatic compounds and reduced the oxygenated compounds. The high cracking of the long chain polyolefins, and the interaction between hydrocarbon radicals produced from the tire rubber and the radicals produced from the thermal decomposition of PE and PP caused the reduction (negative values) of both aliphatic and alicyclic contents in the mixtures of Tire/HDPE, Tire/LDPE, and Tire/PP. Tire/PET resulted in negative values of interaction for the oxygenated compounds as the individual PET produced negligible amount of the oxygenated compounds through the catalytic pyrolysis.

Chapter 7: Conclusion and future work

Pyrolysis and co-pyrolysis of waste tire and plastic

- Pyrolysis of waste plastic, waste tire, and 1:1 mixtures of the tire and plastics has been conducted using a fixed-bed reactor. Pyrolysis of the HDPE, LDPE, and PP plastics produced a wax/oil product in high yield at 85.50, 90.17, 89.00 wt.%, respectively. PET produced a high gas yield (33.60 wt.%) consisting of mainly CO and CO_2, derived from the oxygen content of the PET. The results showed the liquid oil produced from the pyrolysis of tires and PS at 54.83 and 99.20 wt.%. was mostly composed of aromatic compounds, such as the BTEX, and PAH. The liquid oil formed from the pyrolysis of HDPE and LDPE, on the other hand, was mostly waxes of high molecular weight consisting of aliphatic compound ranging from C_8 - C_{28}, composed of a series of alkanes, alkenes, and alkadienes. Whereas PP produced more alicyclic compounds, such as methyl-cyclohexane. PET pyrolysis oil consisted of compounds, such as xylene, styrene, but was mainly composed of oxygenated compounds, for example, benzoic acid.

- Co-pyrolysis of 1:1 mixtures of the tires and individual plastics involved interaction, resulting in significantly higher yields of gas at 13.94, 12.13, 12.77, 7.61, 24.58 wt.% than expected for all the plastic mixtures Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS, and Tire/PET. The co-pyrolysis of tire with HDPE and LDPE produced a liquid oil product rather than the waxy product produced for pyrolysis of the plastics alone. Gas composition was also influenced by interaction between the tire and plastic, with much higher yields of methane, C_2 – C_4 (C_nH_m) hydrocarbons, carbon monoxide and carbon dioxide, for HDPE, LDPE, PP and PS plastics, but Tire/PET co-pyrolysis gave higher than expected carbon dioxide, but lower C_2 – C_4 hydrocarbons (C_nH_m) and carbon monoxide yields were found.

- The oil produced from the co-pyrolysis of the tire with the polyalkene plastics, Tire/HDPE and Tire/LDPE, showed interaction between the polymer pyrolysis products resulting in higher yields of aliphatic compounds and lower yields for the BTEX, PAHs, alicyclic, and aromatic compounds. It was suggested that the increased production of hydrogen radicals from co-pyrolysis promoted alkane and alkene production coupled with de-aromatisation reactions. However, the co-pyrolysis of the tire with the PP polyalkene Tire/PP showed negative interaction for aliphatic compounds resulting in lower yield, but higher yields for aromatic compounds, BTEX and PAHs. The mechanism for Tire/PP interaction was linked to the decomposition of natural rubber in the tire which promotes plastic polymer degradation and secondary reactions to form single ring aromatic hydrocarbons. Co-pyrolysis of Tire/PS produced positive interaction for aromatic compounds, since both tire and PS produce aromatic oils, however, the Tire/PS interaction induced reduction in the yield of PAH. Co-pyrolysis of Tire/PET showed positive interaction for BTEX and reduction in the content of oxygenated compounds, which released the oxygen from the PET in the form of increased yields of carbon dioxide.

Pyrolysis-catalysis and co-pyrolysis-catalysis of waste tire and plastic over ZSM-5 catalyst

- Pyrolysis-catalysis of waste plastic, waste tire, and 1:1 mixture of the tire and plastics has been conducted using a two-stage fixed-bed reactor. ZSM-5 was used as a catalyst to investigate the influence on the products distribution and the composition of the produced gases and oils. Pyrolysis-catalysis of tire over ZSM-5 had an effect on reducing oil yield to 37.30 wt.% compared to the non-catalysis pyrolysis , with a corresponding increase in the gas yield at 24.65 wt.%. Pyrolysis-catalysis of HDPE, LDPE, PP, and PS showed also an increase in the gas yields at 36.58, 39.04, 30.85, and 6.68 wt.% respectively, that consisted mainly of hydrocarbons (C_1-C_4), while decreasing in oil production at 53.67, 51.31, 58.70, and 84.32 wt.% respectively. PS produced the lowest gas yield, while PET produced the highest gas yield at 40.77 wt.%, and the main gases generated from PET were CO and CO_2.

- Pyrolysis-catalysis of individual tire and plastic over ZSM-5 produced a significant amount of valuable chemicals such as benzene, toluene, ethyl benzene, xylenes, and styrene. The ZSM-5 also minimized the heavy aliphatic fraction, which were the main product in the pyrolysis of HDPE and LDPE had a high selectivity to produce light olefins. The pyrolysis of PP over the ZSM-5 produced a hydrocarbon distribution in the range of C_6-C_{12}. PET produced oil with a significant aromatic content from thermal pyrolysis at 5.40 wt.%, but there was a marked increase when the catalyst was used, particularly the BTEX compounds at 75.48 wt.%.

- Co-pyrolysis of the tire and plastic mixtures over ZSM-5 revealed higher gas yields at 29.20, 27.70, and 23.03 wt.% for Tire/HDPE, Tire/LDPE, Tire/PP, and Tire/PS, compared with co-pyrolysis in the absence of a catalyst. Tire/HDPE, Tire/LDPE, and T/PP produced higher concentrations of hydrocarbon gases and methane, while the Tire/PS mixture showed lower concentrations of these gases. The Tire/PET mixture gave high gas yields at 23.22 wt.% of mainly CO and hydrocarbons. Plastics co-pyrolysed with tire and the presence of ZSM-5 catalyst promoted the high production of the aromatic content, particularly BTEX compounds on expense of aliphatic content. This suggests that the upgrading of the produced oil by the conversion of olefinic intermediates from PE degradation, which was promoted by the presence of aromatic fragments of tire degradation

- The mixtures of Tire/HDPE and Tire/LDPE observed a significant reduction in the aliphatic compounds. The oil composition of the Tire/PP mixture with ZSM-5 catalyst showed a significant reduction in the heavy molecular weight compounds, and oil obtained from the catalytic pyrolysis of this mixture consisted of mainly BTEX compounds. The mixture of Tire/PS mainly produced aromatic compounds, and the addition of the ZSM-5 catalyst promotes the cracking of the hydrocarbons chain as well as the interaction between tire and PS to produce more aromatics at the expense of styrene. The oil composition of the Tire/PET mixture produced BTEX and aromatic compounds due to the selectively of ZSM-5 that promotes the decarboxylation of the oxygenated compounds.

Pyrolysis-catalysis and co-pyrolysis-catalysis of waste tire and plastic over MCM-41/ZSM-5 catalyst layer

- The pyrolysis-catalysis of waste plastic, waste tire, and 1:1mixtures of the tire and plastics has been conducted over the MCM-41/ZSM-5 catalyst layer. The influence of the pyrolysis -catalysis (zeolite catalysts in a staged layered) process on the products composition, particularly, the gas and oil yields. It was found that combining the microporous and mesoporous catalysts optimised the conversion of plastic pyrolysis products to low molecular weight hydrocarbons. The production of gases during catalytic pyrolysis, increased at the expense of oil yields at 17.48, 26.60, 31.70, 29.29, 11.03, and 42.12 wt.%, while the oil yields were 39.50, 57.25, 53.50, 58.50, 77.00, and 36.75 wt.% for Tire, HDPE, LDPE, PP, PS, and PET respectively. Moreover, the hydrocarbon gases were produced from the tire and plastics compared to PET produced the highest gas yield over all the other plastics and produced more CO and CO_2.

- Applying the two stages of catalyst MCM-41/ZSM-5 has the advantage in the cracking of HDPE, LDPE, and PP. The primary products can pass through the large pores of MCM-41 as well as the low concentration of acid sites that limited the cracking process. The use of ZSM-5 with (strong acidic sites and small pores) promote the light aromatic formation, catalysing the reaction of products emitting from the MCM-41 layer of catalyst. The pyrolysis-catalysis of PS produced BTEX which was increased at the expense of styrene. While PET over MCM-41/ZSM-5 produced less quantities of oxygenated compounds, and benzene was the dominant product.

- The co-pyrolysis of the tire/plastic mixtures over MCM-41/ZSM-5 catalyst layer showed an increase in the gas yields at 30.04, 35.40, 25.40, 14.31, 39.05 wt.% for Tire/HDPE, Tire/LDPE, Tire/PP, Tire/PS, and Tire/PET. While the oil yields were reported at 40.25, 41.00, 45.50, 58.75, and 36.50 wt.% respectively. The major influence of the co-pyrolysis (tire and PE) was the reduction of the paraffin and olefin compounds. The BTEX content obtained from Tire/PP was high, suggesting that utilising MCM-41/ZSM-5 catalysts in series improved the cracking and aromatisation processes, resulted in oil with a high aromatic content. Tire/PS gave the highest aromatic content, and combining tire with PET reduced the oxygenated compounds.

- The high cracking of the long chain polyolefins, and the interaction between hydrocarbon radicals produced from the tire rubber and the radicals produced from the thermal decomposition of PE and PP, which caused the reduction (negative values) of both aliphatic and alicyclic contents in the mixtures of Tire/HDPE, Tire/LDPE, and Tire/PP. Tire/PET reported negative values of interaction for the oxygenated compounds.

Future work

- This research investigated the pyrolysis and the co-pyrolysis of waste tire and plastic regarding to the essential changes in the product yield distribution as well as oil and gas compositions. It is worth to investigate any changes that may occur during the pyrolysis or co-pyrolysis process at different parameters and conditions such as temperature, heating rate, and tire/plastic ratio.

- It has been investigated the impact of pyrolysis-catalysis and co-pyrolysis-catalysis of waste tire and plastic. It would be significant to examine the effect of different catalysts and metal supports such as Ni-ZSM-5 catalysts on the product yield distribution and oil composition. Furthermore, there was limited work in co-pyrolysis-catalysis of waste tire and plastic using metal impregnated ZSM-5 catalysts. It would be worth to examine the effect of applying metal-impregnated ZSM-5 catalysts on the product yield and oil composition.

- Pyrolysis and the co-pyrolysis of waste tire and biomass in first stage fixed-bed reactor may be of value to expand this research to involve the catalytic pyrolysis and co-pyrolysis using a two-stage fixed-bed reactor. Different parameters and conditions such as temperature, heating rate, and tire/biomass ratio, catalysts can be examined to determine any interactions between tire and biomass and how that effect the products particularly, oil composition.

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