

BINDURA UNIVERSITY OF SCIENCE EDUCATION

FACULTY OF ENVIRONMENTAL SCIENCES

POTENTIAL OF PYROLYSIS AS A PLASTIC WASTE ENERGY SOURCE

IN URBAN AREAS: A CASE STUDY AT CHIWARIDZO PHASE 2

LOCATION IN BINDURA TOWN



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DEDICATION

I dedicate my dissertation work to my family and many friends. A special feeling of gratitude to my loving parents whose words of encouragement and push for tenacity ring in my ears. My siblings have never left my side and are very special.

I also dedicate this dissertation to my many friends and extended family members who have supported me throughout the process.

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ABSTRACT

Traditional recycling and re use methods such as open burning of plastics have proven ineffective and environmentally unsustainable. This study is aimed at examining the potential of pyrolysis as an environmentally friendly energy recovery option for plastic waste in urban areas (Chiwaridzo Phase 2). Three samples of the most abundant different plastic types (LDPE, HDPE and PET) were collected from three different dumpsites (Dumpsite 1, 2, and 3) within Chiwaridzo Phase 2 through waste sorting and each sample was divided into six samples resulting in 18 samples. Three dumpsites for sorting were selected using random sampling (true random number generator). Samples for sorting within each dumpsite and samples for pyrolysis were selected using purposive sampling. All pyrolysis experiments were conducted at a temperature range of 450°C-900°C and a heating rate of 0.1-1°C/s in a stainless steel reactor using a zeolite catalyst at a catalyst feed rate of 1:10. Emitted pyrolysis gases were analysed thermogravimetric software printout. At $p > 0.05$, the statistical package of social science (SPSS) version 20 was utilized to analyse all statistical data. Between the three dumpsites, a One Way Analysis of Variance (ANOVA) was done to see the most abundant plastic type across all dumpsites. The significance of differences in the mean quantities of pyrolysis products (char and oil) recovered from different plastic types, in the mean concentrations of gases emitted during pyrolysis of the three different types of plastic and EMA emission standards were determined using post-hoc analysis. All statistical analyses were performed with a 95% confidence level ($p > 0.05$). The order of abundance of pyrolysis oil was fluctuating depending on plastic type. HDPE plastic had the highest concentration of oil (52%), while PET recorded the least concentration (19%). There was a statistical difference in oil concentration across all plastic types with LDPE recording 29%. LDPE recorded the highest weight in terms of char with an average 42% and there was no statistical difference between weight of char from LDPE and HDPE ($p > 0.05$). All plastic types pyrolysis recorded highest concentrations of CO with LDPE being highest (978.50 mg/cm³) followed by LDPE (938.33 mg/cm³) and HDPE recorded the least among the three (932.67 mg/cm³). LDPE also recorded the

highest concentration of SO₂ (56.167±0.600 mg/cm³) and HDPE had the least with 50.167±1.990. On the other hand, HDPE recorded the highest concentration of NO₂ (136 mg/cm³) with LDPE recording the least with 107.83 mg/cm³. The results concluded that pyrolysis is an environmentally friendly method for plastic waste management since escaped gases were within the SI 72 of 2009 standard limits. Trace elements were found to be present in char obtained from different plastic wastes with Zn across plastic types being statistically significant (p=0.002) with no significant difference on the level of lead (Pb) (p=0.084) and in terms of Cr concentration there was a statistical significant (p=0.008). Modified pyrolysis equipment must be used which can separate and harvest non-combustible volatile gases released during pyrolysis so they can be used for other industrial processes. Process parameters, use of plastic waste and mixture of different wastes during disposal and prior to pyrolysis affect product yields across plastic type and the presence of trace elements in products hence need for waste segregation during disposal and close monitoring of process parameters is needed.

Key words: Plastic waste, waste sorting, dumpsite, pyrolysis oil, char, pyrolysis gas and trace elements.

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ACRONYMS AND ABBREVIATIONS

HDPE: High Density Poly Ethylene

LDPE: Low Density Poly Ethylene

PET: Poly Ethylene Terephthalate

PP: Poly Propylene

PS: Poly Styrene

PVC: Poly Vinyl Chloride

Zn: Zinc

Cr: Chromium

Pb: Lead

SO₂: Sulfur dioxide

NO₂: Nitrogen dioxide

CO: Carbon monoxide

SI: Statutory Instrument

EMA: Environmental Management Act

CHAPTER 1: INTRODUCTION

1.0 Introduction

1.1 Background to the study

Plastic waste generation and improper disposal are growing at an alarming rate due to the increase in human population, rapid economic growth, continued urbanization, and changes in lifestyle (Ali et al., 2021). Additionally, the short lifespan of plastic speeds up the regular manufacturing of plastic waste. Around 6.3 billion tonnes of plastic were produced globally between 1950 and 2018, with 9% and 12% of that being recycled and burned, respectively (Alabi, 2019). Researchers predict that by 2050, seas may weigh more in plastic than fish, indicating that 500 billion plastic bags are used worldwide, of which 13 million tonnes end up in the ocean, killing 100,000 marine creatures (Proshad, 2018).

Sub-Saharan Africa alone produces about 17 million tonnes of plastic garbage per year in Africa (Mayaki, 2020). This massive amount of plastic waste production, fuelled by rapid population growth, increased socio-economic activities, and ever-increasing urbanization, has outstripped the continent's ability to properly dispose of it, leading to plastic disposal in open dumpsites, which end up in nearby water bodies, or open burning, which emits greenhouse gases, hastening global warming and climate change.

According to Ngaza et al. (2018), approximately 1,65 million tons of waste are produced annually, of which 18 percent is plastic, thus approximately 300 thousand tons of plastic, and a significant portion of that waste is dumped in the streets or other open areas instead of being recycled or properly disposed of.

Plastic waste has a significant impact on both aquatic and terrestrial environments. Over 690 species, including sea birds, turtles, and fish, have been reported to ingest micro-plastics, resulting in death by suffocation, starvation, or drowning (Hester & Harrison, 2019). Large plastic debris, such as packaging plastics, can entangle aquatic life and cause suffocation, internal injuries, and infections (Rizzi et al., 2019). Plastic debris can also serve as a vector for the accumulation of hydrophobic organic pollutants, heavy

metals, and metalloids, which can disrupt the endocrine system, cause liver and kidney failure, alter hormone levels, and cause teratogenicity (Hester and Harrison, 2019).

More than half of all plastics' chemical ingredients are hazardous (Wang et al., 2019). These chemicals, when leached from plastic waste or in the form of microscopic debris, can enter the food chain and harm ecologically important species like grass and corals. When mussels and humans consume them, they can build up in the body, causing cell and tissue damage (Luo et al., 2020).

Many attempts have been made to recycle and manage plastic waste, including primary, mechanical, chemical, and energy recovery recycling (Rosano, 2017), with mechanical recycling being the most prominently practiced in Zimbabwe. During mechanical recycling, community-based organizations/individuals collect and sort plastics into various types within their communities before selling them to recycling companies (Feresu, 2017). Recycling companies further shred and melt the various plastic wastes into pellets based on the type of plastic.

In partnership with several producers and distributors of kaylites and plastic bottles, the country established the Polyethylene Terephthalate Recycling Company (PETRECOZIM) (Gwenzi et al., 2020). PET plastic is mechanically recycled into flakes, which are required by fiber manufacturers. PETRECOZIM eliminates 60 tons of PET from the environment each month, accounting for 5% of all PET discarded in the country (Feresu, 2017). Because this is such a small percentage of total waste reduction in the country, alternative chemical recycling, such as pyrolysis, is required.

Plastic pyrolysis is a method of chemical recycling that entails transforming waste plastic into energy in the form of solid, liquid, and gaseous fuels in the absence of oxygen at varying temperatures (300–900°C) (Rehan et al., 2017). Pyrolysis can be thermal or catalytic, and it can be done in a number of different methods, including rapid or slow flash pyrolysis. These variables influence the kind and amount of fuel produced by the pyrolysis process.

Thermal pyrolysis requires high temperatures, resulting in fuels of low quality, making the process unfeasible (Almeida et al., 2016). Different kinds of catalysts are used to improve the pyrolysis process, to enhance process efficiency, to reduce the temperature and reaction time and allow the production of hydrocarbons with a higher added value

(Gandidi et al., 2018). The major advantage of pyrolysis is that it is a cost-effective technology and helps curb environmental pollution.

1.2 Problem statement

Plastic manufacture, usage, and improper disposal have increased as a result of continuous urbanization, economic growth, and an increase in the human population, with changes in lifestyle boosting the applicability of plastic for various household functions. Plastic production and recycling require a significant amount of energy, part of which comes from fossil fuels, resulting in the emission of greenhouse gases into the atmosphere, hastening global warming and climate change. Furthermore, land-filling of plastics has caused chemical components of the plastic to leak into the soil, impacting soil biota and underground water. Locally, there is a significant prevalence of illegal dumpsites in Chiwaridzo Phase 2, most likely because the generation of waste outstrips municipal authorities' ability to collect and dispose of the created waste. Mosquitoes and other disease-causing viruses, such as the Zika virus, have found new breeding grounds as a result of this. Open burning and illegal dumping have been used to minimize plastic waste levels, but they have caused more harm than gain. The goal of this research is to show that pyrolysis is an environmentally and economically effective plastic waste recycling process that can be used to manage plastic waste in urban areas. During the research, several fuel kinds and air quality during pyrolysis will be revealed.

1.3 Aim

To reduce the volumes of plastic wastes being incinerated/introduced to landfills in an economically beneficial way through plastic pyrolysis (energy production).

1.4 Specific objectives

- a. To identify the three most abundant types of plastics within Chiwaridzo Phase 2 location waste streams.
- b. To determine energy quantities to be produced by each type through pyrolysis.
- c. Determination of air quality during plastic pyrolysis

1.5 Justification

Plastic waste is piling up in the environment at an alarming rate, and our knowledge of its persistence is limited. This study will assist individuals in comprehending the detrimental consequences of plastic on the environment, as well as the many recycling options that will be provided.

Electricity is an important service in the economy and severe interruptions in electricity supply in Zimbabwe have attracted a great deal of attention to the country's under-recovery after a decade of loss (Kaseke, 2013). This study will divulge plastic pyrolysis as a source of fuels, an energy source for the country's different economic sectors. This is going to handle the severe interruptions in energy supply enabling economic recovery. According to the ZPC annual report (2017), Zimbabwe imports about 50% of its electricity needs, with total current demand of over 2100MW compared to available capacity from internal sources of 1850MW. Kaseke (2013) confirmed that the country has a staggering electricity debt to regional power utilities; Southern African Power Pool (SAPP) with other members cutting power supply. The generation of fuels through pyrolysis to supplement the existing internal sources will help meet the current demands of power by the nation.

According to Rosano (2014), chemical recycling methods require expertise, knowledge, and manpower, and planning. When successful the findings of this study will create employment for youths within Chiwaridzo Phase 2. This will also solve societal problems within the community like theft and drug abuse by youths.

The pyrolysis method creates little pollution, with carbon, hydrogen, and nitrogen levels of 3.06 percent, 0.43 percent, and 1.80 percent, respectively (Jamradloedluk et al., 2014). In comparison to other power generating technologies such as thermal power stations, which employ greenhouse gas-producing fossil fuels, pyrolysis is an environmentally favorable process. As an outcome of the conclusions of this study, greenhouse gas emissions will be reduced, decreasing the rate of climate change.

Many academic writers, including Francis (2014), have commented on plastic waste recycling choices, their pros, and their limitations, which are also encompassed in this

study resulting in information development for readers and residents of Chiwaridzo phase 2.

CHAPTER 2: LITERATURE REVIEW

2.0 Introduction

This chapter reviews the existing frame of literature on methods used to analyze waste streams, on types and quantities of fuels derived from the pyrolysis of plastics as well as on the release of volatile gases during pyrolysis process. The first part will scrutinize plastic waste (in its different forms) as one of the most abundant, hazardous and pervasive forms of solid waste in the environment. A review on national existing legal framework on air quality will mark the end of the literature review.

2.1 Plastic waste in the environment

2.1.1 Plastics

Plastics, according to Geyer et al. (2017) plastics are high molecular mass synthetic organic polymers manufactured mostly from hydrocarbons obtained from crude oil and natural gas and used for a wide range of applications. Evode et al. (2021) also define plastics as, or "long chains of monomers," that are joined to other identical sub-units to create a polymer by the biochemical process of polymerization or poly-condensation. Plastic becomes garbage when it is mishandled and ends up in the environment. Hammer et al. (2017) describe plastic pollution/waste as the accumulation of plastic items and particles such as bottles and bags.

Rhodes (2018) highlighted that global primary production of plastics since 1967 amounted to around 23 million tons which rose to 407 million tons in 2015. He further specified that between 1950 and 2015, a total of 6.3 billion tonnes of primary and secondary (recycled) plastic waste was generated globally, of which around 9% has been recycled, 12% incinerated, with the remaining 79% either being stored in landfills or having been released directly into the natural environment.

2.1.2 Classification of plastics

Thermosets and thermoplastics are two types of plastic materials (Rosano, 2017). According to Yang et al. (2012), thermoset polymers are those that have undergone

irreversible polymerization through chemical reaction or heat curing, resulting in an infusible and insoluble material that cannot be heated and re-molded once formed, such as polyurethane (PUR) and epoxy resins or coatings. He went on to explain thermoplastics as a polymer made up of linear molecular chains that softens when heated and hardens when cooled and is represented by a wide range of plastic materials, including crystalline thermoplastics (e.g. polypropylene (PP), low-density polyethylene (LDPE), and high-density polyethylene (HDPE)) (Hart et al., 2020).

Other examples of thermoplastics are amorphous thermoplastics (e.g. poly vinyl chloride (PVC), polymethylmethacrylate (PMMA), polycarbonate (PC), polystyrene (PS), and acrylonitrile butadiene styrene (ABS) (Nicholson, 2017) and semi-crystalline polymers which are both amorphous and crystalline in nature (e.g. polyester polybutylene terephthalate (PBT) (Nokhostin & Hopmann, 2021). Crystalline, amorphous and semi-crystalline thermoplastics find their uses in households, optical products (due to their translucence) and as industrial plastics used for fabrication of fibers, films, blends, and composites respectively (Matyjaszewski & Moller, 2012).

Plastics have a high specific strength, similar thermal stability with great chemical resistance, cheap cost, electrical insulating properties, and are highly light-weight when compared to metal components, allowing them to be used in a variety of applications (Hogue et al., 2021). These same traits that make them useful for the creation of a wide range of items also make them a significant environmental danger.

2.2 Methods of analyzing a waste stream

Ferronato and Torretta (2019) describe a waste stream as the whole flow of trash from its residential or industrial source to recovery, recycling, or final disposal. A waste stream analysis, according to Agbavitor (2018), is the process of determining the composition of elements in a local waste stream. It might be as easy as analysing data that a local government already has on hand, or it can entail a thorough waste sort to estimate the proportions of various items in the waste stream.

2.2.1 Waste sorting

Stričík and Čonková (2021) define a waste sort as the manual separation of waste into its elements or by type to facilitate its recyclability. A waste sort is an effective method

of waste stream analysis as it can clearly characterise a local dumpsite when conducted correctly, however, costs of conducting of waste sort may outweigh the benefits (Wang et al., 2020). In a study of plastic waste discarded by families in Watamu district in Kenya, Gwada et al. (2019) found that LDPE was discarded at a substantially greater rate than other forms of plastic waste, accounting for 55 percent of all plastic waste disposed, followed by PET mixed LDPE at 40.7 percent. HDPE and PP were found in modest amounts in home plastics, with just 2.9 percent and 1%, respectively (Merkel, 2016). Lahtela et al. (2019) conducted another waste sort on a residential dumpsite in an urban region, with 57.74 kg of mechanically sorted plastic indicating the most frequent plastic grades as LDPE and PET in order of dominance.

2.3 Plastic types most common in residential waste streams

2.3.1 PET

PET is a clear, strong, and lightweight plastic that is widely used for food and beverage packaging, particularly convenience-sized soft drinks, juices, and water (Ügdüler et al., 2020). PET contains no bisphenol-A (BPA) or phthalates (plasticizers), and it can be recycled commercially by thorough washing and re-melting, or by chemically breaking it down to its component materials to make new PET resin (Das et al., 2021). Because the polymer is inert, it is resistant to microorganism attack and will not degrade biologically.

According to Jablonska et al. (2019), its chemical formula is $(C_{10}H_8O_4)_n$, and its density, melting point, molar mass, and thermal conductivity are 1,38g/cm³, 260°C, 10-50kg/mol (varies with type of PET), and 0.15-0.24 W/(Mk). In an experiment of PET pyrolysis by Jia et al. (2020) with the fixed-bed reactor at 500°C at heating rates of 10 and 6°C/min, the liquid product yields were 23.1 wt. and 39.89 wt. percent, the gas yields were 76.9 wt. and 52.13 wt. percent, and the char yields were 0 and 8.98 wt. percent.

2.3.2 HDPE

High Density Poly Ethylene, also known as polyethylene high-density (PEHD), is a thermoplastic polymer derived from the monomer ethylene. HDPE is used to make plastic bottles, toys, oil containers, corrosion-resistant piping, geo-membranes, and plastic lumber due to its high strength-to-density ratio (Mejia et al., 2019). It has the chemical formula $(C_2H_4)_n$, a density of 940kg/m^3 , a melting point of 130.8°C , and a thermal conductivity of $0.44\text{W/m}^\circ\text{C}$ (Constantinescu et al., 2019). In an experimental study, HDPE was used as a raw material in a semi-batch reactor pyrolysis process at 350°C . The yield of liquid product was 80.88 wt. percent (Anene et al., 2018).

2.3.3 LDPE

Because low-density polyethylene (LDPE) plastics have excellent water resistance, they are widely used for plastic bags, garbage bags and wrapping foils for packaging. The density range of LDPE is $917\text{--}930\text{ kg/m}^3$ and except for strong oxidizers, it is not reactive at room temperature; some solvents cause it to swell (Fotopoulou & Karapanagioti, (2017)). According to Fotopoulou and Karapanagioti (2017), it can withstand temperatures of up to 65°C continuously and up to 90°C for a short period of time. It is quite flexible and tough, and comes in translucent and opaque variations with a chemical formula $(C_2H_4)_n$ (Crawford & Martin, 2020). In some experimental studies in a fixed-bed reactor at 500°C with a heating rate of 10°C/min , and in a batch reactor at 550°C with a heating rate of 5°C/min , the liquid yields are found at 95 and 93.1 percent (Sogancioglu et al., 2017).

2.3.4 Other plastic types

PVC

Depending on the heat treatment, polyvinyl chloride (PVC) can be transparent or semi-crystalline. Because of the chlorine content in PVC, it becomes an excellent fire-resistant material and is thus ideal for electrical insulation (Janajreh et al., 2015).

PP

Polypropylene (PP) is a chemical, heat, and fatigue resistant material. It is a plastic with a medium hardness and gloss. PP has a lower density than HDPE but greater hardness and rigidity, making it preferred in the plastics industry (Jonbi et al., 2019).

PS

Polystyrene (PS) is a multipurpose plastic that is very hard, brittle, glossy, and foam-shaped. It's a low-cost resin with a relatively low melting point. PS offers reasonable durability, strength, and lightness. For this reason, it is used in a variety of sectors such as construction, electronics, medical appliances, food packaging, and toys (Alabi et al., 2019).

2.4 Existing recycling methods

Recently, the use of plastic products, has significantly increased, which has led to many environmental issues discussed earlier. However many attempts have been made towards the reduction of plastic waste volumes including recycling. According to Rosano (2017) plastic recycling can be grouped into primary, secondary/mechanical, chemical and quaternary recycling.

2.4.1 Primary recycling

Francis (2016) define primary recycling as to the reuse of plastic products in their original structure. Primary recycling is simple and cost effective. However, according to Singh et al. (2017), the existence of a limit on the number of cycles for each material is the disadvantage of this recycling process. This technique of recycling is mostly practiced within households considering its simplicity and cost effectiveness.

2.4.2 Secondary/ mechanical recycling

Merrington (2017) define secondary recycling as the re-melting and reprocessing of plastic waste into end products without altering the polymer during the process (applicable to thermoplastics only) and this form of recycling is mostly practiced at the industrial level. In Zimbabwe, this is a commonly practiced recycling method as mentioned by Feresu (2014).

This method is cost-efficient and well known compared to other advanced techniques, however, the deterioration of the product's properties due to pre-treatment is a disadvantage (Rosano, 2017). It also require a substantial initial investment (Kumagai et al., 2016)

2.4.3 Chemical recycling/ feedstock recycling

Chemical recycling, according to Thiounn and Smith (2020), is the process of chemically converting polymers to monomers or partly depolymerizing polymers to oligomers. Chemical recycling and its methodologies, according to George and Kurian (2014) are an acknowledged recycling approach that adheres to the ideals of sustainable development by using waste as a precursor in the generation of pure value-added products for diverse industrial and commercial purposes. Most practiced chemical recycling methods are chemolysis, pyrolysis, and gasification. Pyrolysis will be reviewed in the coming section in the context of this study, as an alternative for all chemical and other recycling methods.

2.4.3.1 Chemolysis

Under chemolysis, there are different de-polymerization routes such as methanolysis, glycolysis, and hydrolysis used depending on the chemical agent used for the chain scission for the complete de-polymerization of plastic (Barnard et al., 2017)

Hydrolysis is a recycling method that involves a reaction of plastic waste with water in an acid, alkaline, or neutral environment at high temperatures (between 200 and 250°C), high pressures (between 1.4 and 2 MPa), and a long period of time, resulting in total de-polymerization into monomers (Ügdüler et al., 2020). The primary drawback is that the result is less pure than that produced by other processes, and the procedure is expensive (Yan et al., 2015)

Glycolysis is the process of inserting glycol into plastic chains to produce a plastic and other oligomer substrate. For example, ethylene glycol is inserted into PET chains to produce bis(hydroxyethyl) terephthalate (BHET), which is a PET synthesis substrate (Rudolph et al., 2017). The downside of this method is that it can only be used when the incoming PET feed is of excellent quality (Wang et al., 2020).

Methanolysis is a process that involves treating plastic with methanol at quite high temperatures (180–280 C) and pressures (20–40 atm) to produce DMT and EG as the major products (Ragaert et al., 2017).

2.4.3.2 Gasification

It uses partial oxidation to turn solid starting materials, such as plastics, into a gaseous mixture including CO₂, CO, H₂, CH₄, and other light hydrocarbons (Heidenreich & Foscolo, 2015). Impurities in the syngas generated include NH₃, H₂S, NO_x, alkali metals, and tars (Dudyn' ski et al., 2015), which are recognized toxins for downstream processes, particularly catalytically converted processes.

2.4.4 Energy Recovery or Quaternary Recycling

This approach, such as incineration, refers to recovering the energy component of the plastic (Rosano, 2017). It's an excellent solution since it creates a lot of energy from polymers, but it's not environmentally friendly because it exposes people to dangerous compounds in the air, such as dioxins in heavy metals, chlorine-containing polymers, poisonous carbon, and oxygen-based free radicals (Alabi et al., 2019).

2.5 Plastic pyrolysis types and fuel products of pyrolysis

Pyrolysis, according to Ragaert et al. (2017), Rehan et al. (2017), Rosano (2017), Bridgwater (2012), and Verma et al. (2019), is the thermo-chemical decomposition of plastic wastes at elevated temperatures (200-13000C) in the absence of oxygen to produce solid products, a variety of volatile liquids, and gases. Due to heat and/or pressure applied during the breakdown process, the complex molecules of plastic trash decompose into organic compounds with lower molecular weight, short chain, and less complicated molecules, according to Maqsood et al. (2021).

The pyrolysis of plastic wastes to hydrocarbon mixtures has gotten a lot of interest since it provides for waste reduction, chemical recovery, and the substitution of alternative fuels with less environmental contamination (Harussani et al., 2020).

2.5.1 Methods of plastic waste pyrolysis

Table 1 below shows the categories and types of pyrolysis as explained by (Maqsood et al., 2021).

Pyrolysis category	Temperature, heating rate and volatile residence time,	Environment used	Heating method
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Type under category	Slow, fast and flash	Hydro, oxidative, catalytic, steam and vacuum	Microwave, plasma and electrical

Table 1: Categories and types of pyrolysis (Maqsood et al., 2021)

This study is going to look at thermal slow, fast and flash pyrolysis in detail as these are the major types of pyrolysis processes in plastic waste. Benefits of adding catalyst to thermal pyrolysis (catalytic pyrolysis) will also be reviewed.

2.5.1.1 Slow pyrolysis

According to Harussani et al. (2020), slow pyrolysis is characterized by lower heating rates (0.1 to 1°C/s), longer solid and vapor residence periods (minutes to hours) and low temperatures. The temperatures of slow pyrolysis range from 550 to 900°C with solid residence of 300 to 3600 seconds and a required particle size ranging from 5-50mm (Li et al., 2013). Matayewa et al. (2019) reported fixed bed and vacuum reactors as two of the most relevant technologies used to conduct slow pyrolysis. Main products of slow pyrolysis are char, oil and gas (Harussani et al., 2020). However, in a study conducted by Santaweek and Janyalertadun (2018) reviewed that slow pyrolysis of LDPE, HDPE, PP and mixed plastic from municipal landfill resulted in 73 %, 70 %, 80 % and 46 % liquid fuel, respectively. Das and Tiwari (2018) also reported that pyrolysis of LDPE and HDPE in a lab scale semi batch reactor at a very slow dynamic condition (1 °C min⁻¹) produced gaseous and liquid products at a maximum temperature of 400degrees Celsius.

The main components of the resulting oil were paraldehyde (54.7 wt. percent) and ethylene glycol (23.7 wt. percent) in another study conducted by Straka et al. (2022) on PET plastic waste, in which PET was completely pyrolyzed at 25 °C min⁻¹ to a final temperature of 400 °C; further, benzoic acid and benzoates were obtained. Furthermore, the pyrolysis produced a solid carbonaceous residue (char), which is particularly useful as a low-ash and low-sulphur smokeless fuel with a greater heating value of 31.3 MJ kg⁻¹ and a lower heating value of 30.4 MJ kg⁻¹.

2.5.1.2 Fast pyrolysis

Harussani et al. (2020) define fast pyrolysis as a rapid thermal decomposition characterized by higher heating rates as compared with slow pyrolysis. During fast pyrolysis, the initial heating time of the precursors is smaller than the final retention time at pyrolysis peak temperature (Maqsood et al., 2021). This approach necessitates a small particles size feed stock of less than 1mm and specially built equipment to collect rapidly released vapors (Alcazar-Ruiz et al., 2021). The main products of fast pyrolysis are liquid and gas fuels.

Sharuddin et al. (2016) conducted fast pyrolysis of plastic waste at temperature range of 500 ~ 700 °C, and the commodity yields were gas yield of 9.79 % ~ 88.76 % and liquid oil yield of 18.44 % ~ 57.1 %. Xue et al (2015) used a temperature range of 525 ~ 675 °C to conduct co-pyrolysis of red oak and HDPE. It was observed that, rise in pyrolysis temperature facilitated the production of liquid oil with a yield of 57.6 wt % which crack releasing lighter gases when temperatures are raised (Singh et al., 2019).

2.5.1.3 Flash pyrolysis

Flash pyrolysis involves rapid heating rates (>1000 °C/s) and extremely high reaction temperature (900 ~ 1300 °C) (Klaimy et al., 2021). Flash pyrolysis best occurs at high temperature (over 700 °C), very quick reaction time (less than 500 milliseconds), and higher heating rate (greater than 1000 °C/s) (Harussani et al., 2020). Flash pyrolysis normally uses less than 0.5 s of residence time and the particles size of the feed stock should be as small as possible that is 0.2 mm (Li et al., 2013).

In a flash pyrolysis study of polystyrene waste, the effect of temperature in the range of 700 - 875 °C yields liquid output distribution of benzene, styrene, toluene, naphthalene and gaseous output C1- C4 contents were measured (Maqsood et al., 2021). At 750 °C, the maximum liquid oil yield achieved, while the maximum styrene yield was achieved at 825 °C.

2.5.1.4 Catalytic pyrolysis

As we have observed earlier in this section, thermal pyrolysis requires high temperatures which often results in fuels with low quality, making this process unfeasible (Rehan et al., 2017). According to Chatopadhyay et al. (2016) most plastic

pyrolysis plants utilize high temperature (700 °C) which reduces to moderate temperatures of approximately 500 °C in the presence of a suitable catalyst denoting that catalyst play an important role in reducing the high temperatures needed for thermal pyrolysis.

Different kinds of catalysts can be used to improve the pyrolysis process of plastic waste overall, to enhance process efficiency, to reduce the temperature and reaction time and allow the production of hydrocarbons with a higher added value (Fadillah et al., 2021). This is crucial since the pyrolysis process requires high energy that hinders its commercial application.

According to Wang et al. (2014) the catalytic pyrolysis of LDPE and cellulose in the presence of HZSM-5(catalyst) enhanced the aromatic yield and reduce coke formation. Zhang et al. (2015) accomplished a catalytic pyrolysis of plastic and pine sawdust and due to the presence of acid catalysts including LOSA-1, spent FCC and γ -Al₂O₃, problems reported previously with slow thermal plastic pyrolysis in fluidized bed reactor did not happen in this study.

Pyrolysis methods	Residence time	Heating rate	Final temp(°C)	Major product
Slow	5-30min	Low-100C/s	500	Char, oil, gas
Fast	<2s	High-1000C/s	650	Oil
Flash	<1s	Very high-5000C/sec	>650	Oil, gas

Table 2: Types of plastic waste pyrolysis (Harussani et al., 2020)

2.6 Volatile gases produced during pyrolysis

According to Laskar and Kumar (2019) plastics are materials composed of various elements such as carbon, hydrogen, oxygen, nitrogen, chlorine, and sulphur. Hence when plastics undergo any form of thermal degradation, a significant amount of these elements are emitted as gases. Das and Tiwari (2017), conducted slow pyrolysis of PET at temperature ranging from 350°C-500°C and trace amount of hydrogen, carbon monoxide and carbon dioxide were present in the gaseous product along with various hydrocarbon gases ranging from C₁-C₅. In another study conducted by Dhahak et al. (2019) in a pyrolysis experiment of PET plastic at laboratory scale, CO₂ was emitted

before CO, C₂H₄ and C₆H₆. During pyrolysis, nitrogen is continuously supplies as an oxidizing agent hence considerable amounts of nitrogen dioxide will be released during pyrolysis. Alsaleh et al. 2014 reported components of gases produced during pyrolysis to be methane (CH₄), Hydrogen (H₂), Carbon monoxide (CO), sulphur oxides (SO_x) and nitrogen oxides (NO_x including NO₂). Gas yield is believed to be affected by the type of plastic, temperature ranges and residence time (Williams, 2013).

CHAPTER 3: METHODOLOGY

3.0 Introduction

This chapter gives a brief outline of the study area. The chapter discusses the research design and sampling techniques used. Research instruments used to gather data and the analytical framework used will also be discussed in this chapter.

3.1 Description of the study area

Bindura is a town in the province of Mashonaland Central, Zimbabwe. It is located in the Mazowe Valley about 88 km northeast of Harare on the main road to Mount Darwin. According to the world population review, 2022, Bindura has a population of 37,423. Within Bindura town is Chiwaridzo Phase 2, a high-density location south of the Shamva- Harare road, west of Brockdale, and northeast of Antherstone (two other locations close-by). Chiwaridzo Phase 2 is situated four and a half kilometers northwest of Bindura town and its co-ordinates are latitude- 17° 19' 41" south and longitude 31° 21' 40" east. The population of Chiwaridzo consists of 3680 households. Fig 1 below shows the location of Chiwaridzo within Bindura.

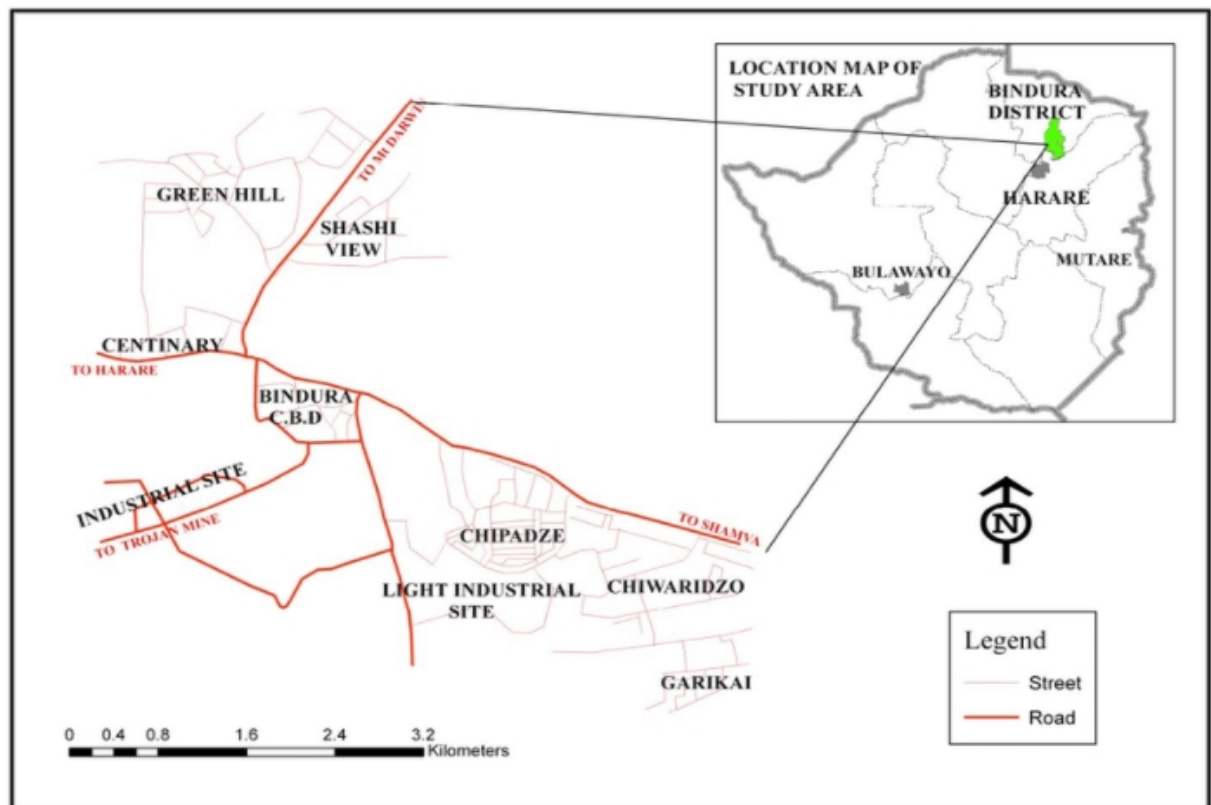


Figure 1: Map of study area

3.2 Research Design

In this research, both qualitative and quantitative methods of data collection were used. The researcher adapted a waste sorting technique to analyze the waste stream for the most abundant plastic types within Chiwaridzo Phase 2. During the process, the researcher will identify three suitable illegal dumpsites among the five within the study area, and conduct a waste sort on a 60kg sample of waste on each dump to come up with the waste composition at each dumpsite. Another 1.5kg sample of each of the most three abundant plastic types at each dumpsite will be collected for pyrolysis at the laboratory. A 100kg hanging digital weighing scale will be used to weigh the waste sample and a 50kg hanging handheld weighing scale will be used to determine the weight of the sorted and segregated wastes. A quantitative approach will also be used to determine fuels types and quantities which will be derived from the pyrolysis of selected plastic waste types. Gas emissions during pyrolysis of each plastic-type will also be measured through experiments. The study is going to be cross-sectional that is at a certain point in time, thus not retrospective or prospective.

3.3. Study Population

The population of Chiwaridzo consists of 3680 households. This population under study consists of both house owners and lodgers of Chiwaridzo Phase 2. The data will be gathered from three of the five illegal dumpsites within the location.

3.3.1. Sample

The researcher used simple random sampling in selecting three dumpsites among the five within the study area. The dumpsites were numbered from 1 to 5 and a true random number generator was used to select three dumpsites that were used (Schreier, 2018). For the selection of a sample to sort, the researcher used purposive sampling in which she used her own expertise to select a sample that was more useful to her research (Campell et al., 2020), thus 60kg of waste was selected for sorting. From the observed and weighed plastic types, the researcher collected a 2kg sample of each of the three abundant plastic types based on purposive sampling which she used for the pyrolysis experiment.

3.4. Data Collection

To determine the most abundant plastic types the researcher conducted a waste sort. The researcher came up with a waste sort plan for sorting garbage (Appendix 1). Within the sort plan is a sort team with four participants whose roles and responsibilities were outlined. The selected waste sample was segregated according plastic type and other forms of waste which are not related to plastic. After sorting, each pile of separated waste was visually inspected, weighed and recorded in the waste sort plan form (Appendix 1). The data was aggregated and analyzed using a bar graph to obtain a snapshot of the waste stream. After the waste sort, a 2kg sample of each plastic type was collected. The 2kg samples were washed and cleaned using running water to remove all foreign non-plastic matter. Paper stickers and labels on LDPE and PET plastics were also removed during the process. The clean plastics (now 1.5kg) were reweighed before being crushed down to particle size of 5-50mm. 6 samples of 0.025kg (25g) were measured and weighed for each plastic type. Samples were labelled according to plastic type as *PET1, PET2, PET3, PET4, PET5, PET6; LDPE7, LDPE8, LDPE9, LDPE10, LDPE11, LDPE12 ;HDPE13, HDPE14, HDPE15, HDPE16*,

HDPE17, *HDPE18*. Samples were packed as 25g and labelled as above for easy identification before stored inside a glove box where there are inert conditions.

3.4.1 Experimental data gathering

The researcher conducted experiments using the selected 6* 0.025kg samples of each plastic type to determine the types of fuels derived from the pyrolysis of every 25g sample and air pollutants released during the process for comparison.

3.4.4.1 Pyrolysis process

Materials used

Three different types of plastic, a zeolite type catalyst, a Mettler Toledo weighing balance, Retsch shredder, liquid nitrogen, pestle and mortar, stainless steel reactor with fitted lid, nitrogen inflow and product outflow pipe and pressure gauge, a muffle furnace with a programmable temperature controller for heating reactor, glove box, product collection bottles, handheld thermometer, distilled water, ice bath, spirit for cleaning pyrolysis equipment..

Methods

The thermo gravimetric analysis (TGA) of the samples was performed prior to the pyrolysis experiment to identify the rate of deterioration (decomposition) and temperature ranges of the polymers.

Thermo gravimetric analysis (TGA)

Before filling the TGA sample pan, the samples were weighed on a Mettler Toredon weighing balance, and the weights were recorded. In the presence of liquid nitrogen, a Retsch shredder was utilized to shred plastic samples to 1.5 mm. To avoid contamination, the shredded samples were re-weighed and the weights recorded before being placed in a glove box. Using the pestle and mortar, a zeolite-type catalyst was crushed to 1.5mm and placed in a separate glovebox. The catalyst assisted in speeding up the reaction (Susastriawan & Sandria, 2020). To prevent oxidation of materials during analysis, the TGA furnace was purged for 5 minutes with nitrogen ($N_2 = 99.9999$ percent), which will displace air and oxygen in the furnace, providing pyrolysis-friendly conditions. Each plastic-type employed 25g of material put in a platinum pan, which

was combined with a catalyst at a 1:10 catalyst feed rate. The experiment was carried out in a nitrogen environment with a flow rate of 60 mL/min after purging, and the heating rate will be 10°C/min across the temperature range of 25-600°C. The heating rate, minimum and maximum temperatures employed in the pyrolysis analysis were determined by the TGA results.

Pyrolysis procedure

The pyrolysis tests for the various plastic types were carried out in a laboratory scale setup that included a stainless steel reactor with a fitted lid. A pressure gauge was placed to monitor the pressure of nitrogen flowing into and through the reactor.

The reactor was heated using a muffle furnace. The temperatures were chosen based on the TGA results. Nitrogen (99.9999 percent) was used to purge the reactor for 30 minutes to ensure an inert atmosphere (no air) before pre-weighed materials were mixed and added to the reactor at a catalyst feed ratio of 1:10. The reactor was built in the furnace, complete with a nitrogen inlet that will be continuously purged at 60mL/min and product outlet lines. Using the muffle furnace's programmable temperature controller, the reactor was slowly heated to the desired set point temperature.

Since N₂ was used to continuously purge the furnace, a hand-held thermometer was used to monitor the temperature in the furnace to ensure that the temperature indicated by the furnace is approximately the same inside the furnace. The sample was kept in the reactor at the set temperature until the reaction was finished. The condensable products were collected in collection bottles after cooling in another collection bottle filled with distilled water in an ice bath, and the gases produced were collected in a 0.5-liter gas Tedlar gas collection bag for analysis. The experiment was carried out in

two reactors, each containing 0.025kg of plastic sample, as shown in the diagram

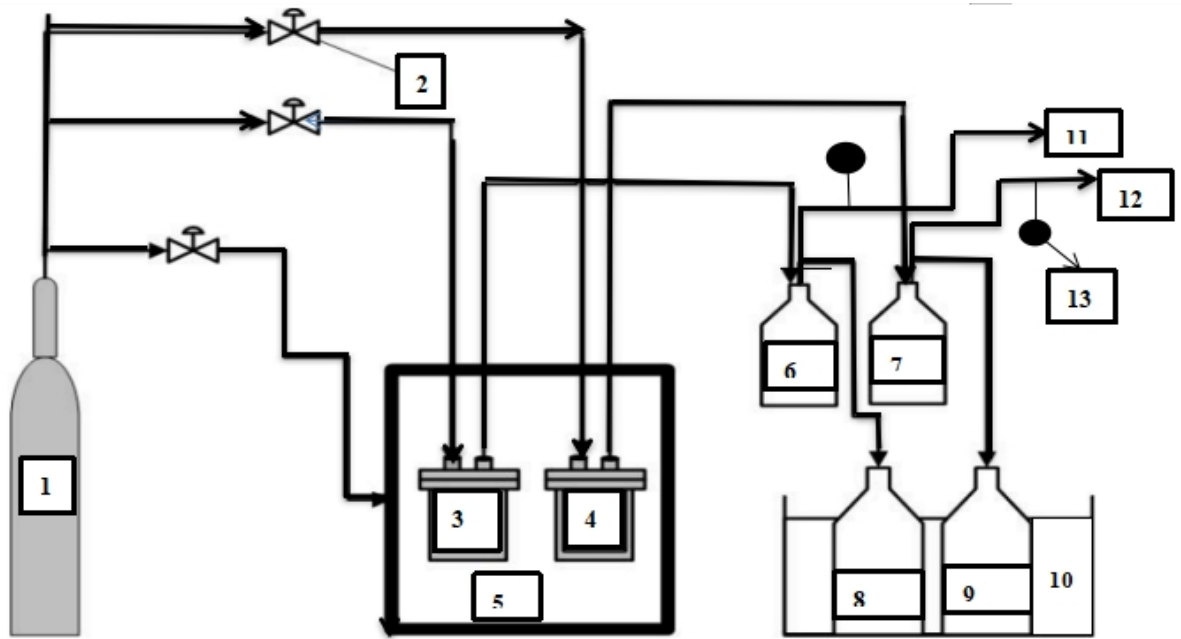


Figure 2: Pyrolysis equipment set-up

(1) Nitrogen cylinder, (2) Diaphragm valve, (3) 25g(A) plastic sample reactor, (4) 25g(B) plastic sample reactor, (5) Muffle furnace, (6) plastic sample A products collection, (7) Plastic sample B products collection container, (8) plastic sample A second product collection container, (9) plastic sample B second product collection tin, (10) Ice bath, (11) Tedlar gas collection bag A, (12) Tedlar gas collection bag B, (13) Tedlar gas collection bag

The experiment was repeated using the same conditions, that is a temperature range of 450°C-900°C and a heating rate of 0.1-1°C/s

The percentage yield of the pyrolysis solid, liquid and gas collected at the end of the reaction were calculated by the Equations 1, 2 and 3 as shown below:

$$Y_{liquid} = \frac{M_2}{M_1} 100\% \quad (1)$$

$$Y_{residue} = \frac{M_3}{M_1} 100\% \quad (2)$$

$$Y_{gas} = 100\% - (Y_{liquid} + Y_{residue}) \quad (3)$$

Where:

M1: Mass of the sample,

M2: Mass of liquid product,

M3: Mass of residue.

Data showing the quantities of oil and char obtained after pyrolysis per 0.025kg of plastic type was measured and recorded (Appendix 2).

The average volume of pyrolytic oil acquired from pyrolysis of plastic type was determined by the formulae below and recorded (Appendix 2)

$$\text{Average volume of pyrolytic oil} = \frac{\sum \text{volume of pyrolytic oil}}{\text{number of samples}} \quad (4)$$

The average weight of char acquired pyrolysis of same plastic type was determined by formulae below and recorded as well (Appendix 2)

$$\text{Average weight of char} = \frac{\sum \text{weight of char}}{\text{number of samples}} \quad (5)$$

3.4.4.2 Determining toxic gas concentrations from pyrolysis process and from determining the energy value of fuels

In order to detect the type of the gas and its quantity, a thermo-gravimetric software printout was used to estimate the mass of each gases matter (Jesus et al., 2018).

After that the results were converted into mg/m³ in order to compare them with the EMA Act (SI 72 of 2009) standards using the formula;

$$P = (X * 1\,000\,000) / (1\,000) \quad (6)$$

Where, P=total mg/m³

X= gas amount in kg

1 000 000= mg

1000= m³

3.4.4.3 EMA Act (SI 72 of 2009) emission standards

EMA emissions standard SI 72 of 2009 prohibits the emission of $\text{SO}_2 > 50\text{mg/m}^3$, NO_x (NO_2) $> 150\text{mg/m}^3$ and $\text{CO} > 100\text{mg/m}^3$ into the atmosphere and it issues emission licences for those who produce within range as shown in table 3.

Licences on emission discharges issued by EMA are classified as shown on the table

Colour code	Narration
Blue	Environmentally safe
Green	Present low environmental hazard
Yellow	Presents a medium environmental hazard
Red	Present high environmental hazard

Table 3: Colour codes for licences on emission discharge issued by the EMA Agency

3.4.4.4 Data analysis

A statistical Package of social science (SPSS) version 20 was used for all statistical data analysis at $p > 0.05$. A One Way Analysis of Variance (ANOVA) was used to determine any significant difference on different plastic type quantities among three dumpsites. LSD Post-hoc was used to determine for any significance difference in the means of pyrolytic products quantity (char and oil) recovered from different plastic types, in mean concentrations of gases emitted during pyrolysis of the three different types of plastic and EMA emission standards and trace elements in the ash of pyrolytic char. Pearson correlation and regression analysis were performed to examine the relationship between the fuel quantity and different plastic-type. All statistical analysis were done at 95% confidence ($p > 0.05$).

CHAPTER 4: DATA PRESENTATION AND ANALYSIS

4.0 Introduction

This chapter is concerned with the presentation, discussion and analysis of research findings and it is in this chapter where disagreement and agreement with literature can be seen. Hence the following objectives will be presented, the three most abundant types of plastics within Chiwaridzo Phase 2 location waste streams, fuel quantities to be produced by each type through pyrolysis and air quality during pyrolysis as well as trace elements in pyrolysis char ash.

4.1 The three most abundant types of plastics within Chiwaridzo Phase 2 location waste streams.

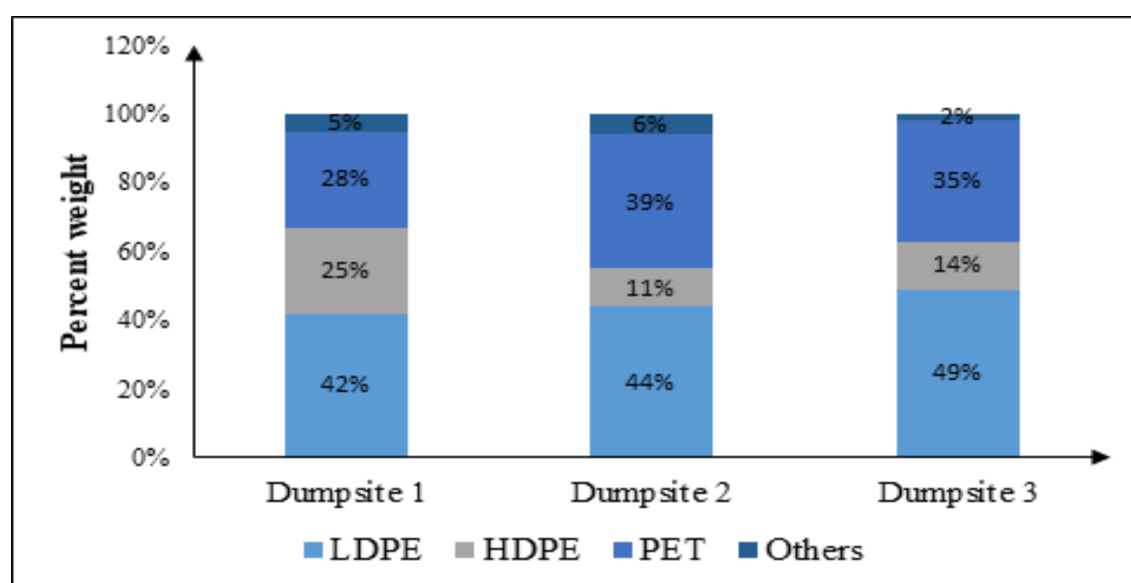


Figure 3: Plastic quantities across dumpsites

Results show that LDPE was significantly higher (45%) than all plastic types followed by PET (34%), HDPE (16.7%) and other plastic types (4.3%) respectively.

4.3 Fuel quantities to be produced by each type through pyrolysis

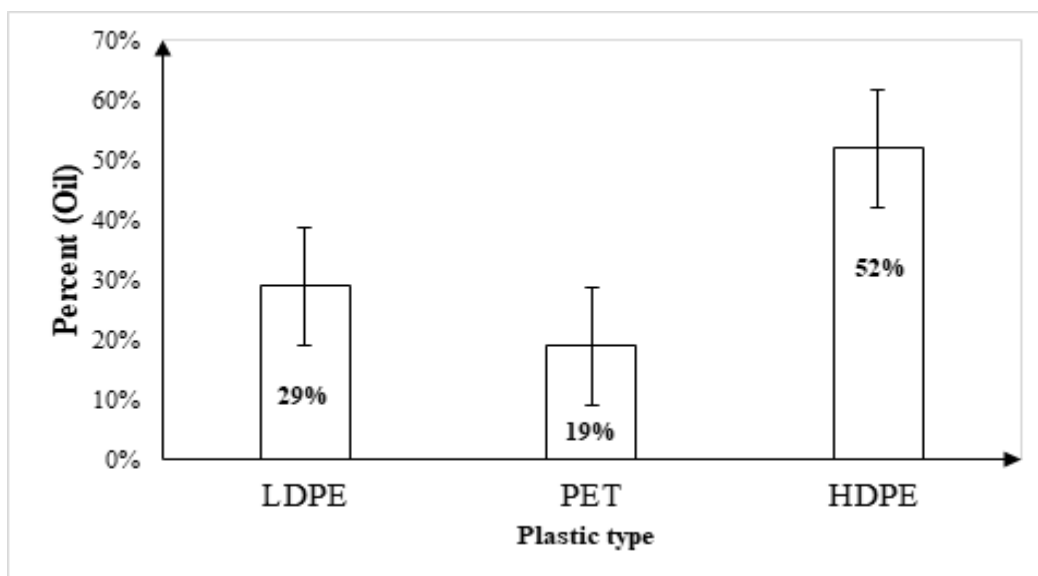


Figure 4: % oil yield per plastic type

Fig 4 above shows that HDPE has the highest concentration of oil (52%) followed by LDPE (29%) and PET recorded the least with 19%. Results show that there was a significant difference in the concentration of oil in all types of plastic ($p < 0.05$).

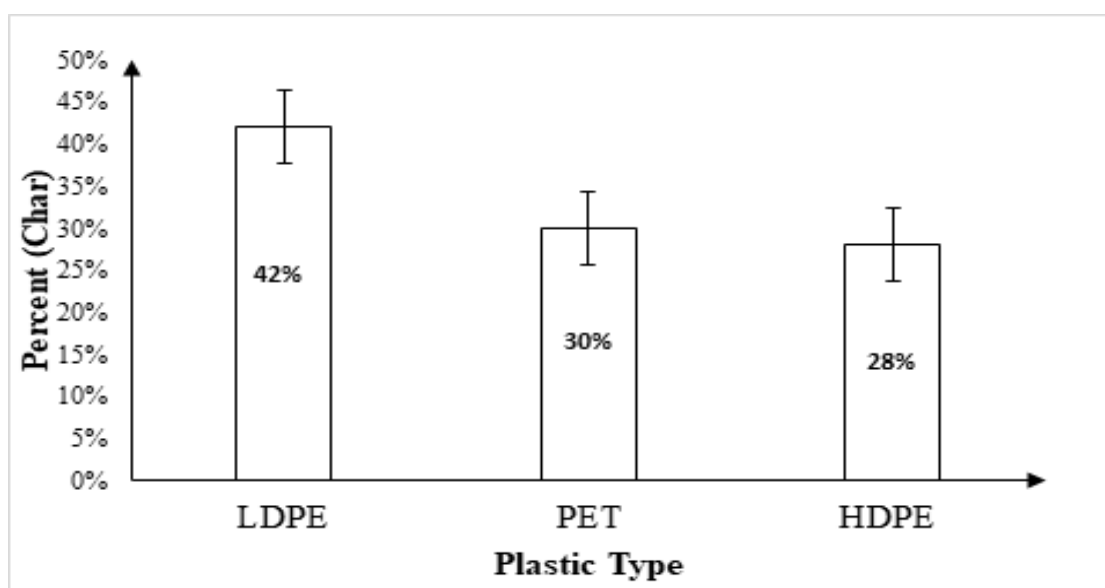


Figure 5: % char yield across plastic types

The results indicate that LDPE has the highest weight in terms of char with an average of 42%. PET (30%) was significantly different from HDPE (28%) and LDPE (42%) in relation to the weight of char ($p < 0.05$). The results also show that the weight of char between LDPE and HDPE was not statistically significant ($p > 0.05$).

4.4 Determination of air quality during pyrolysis

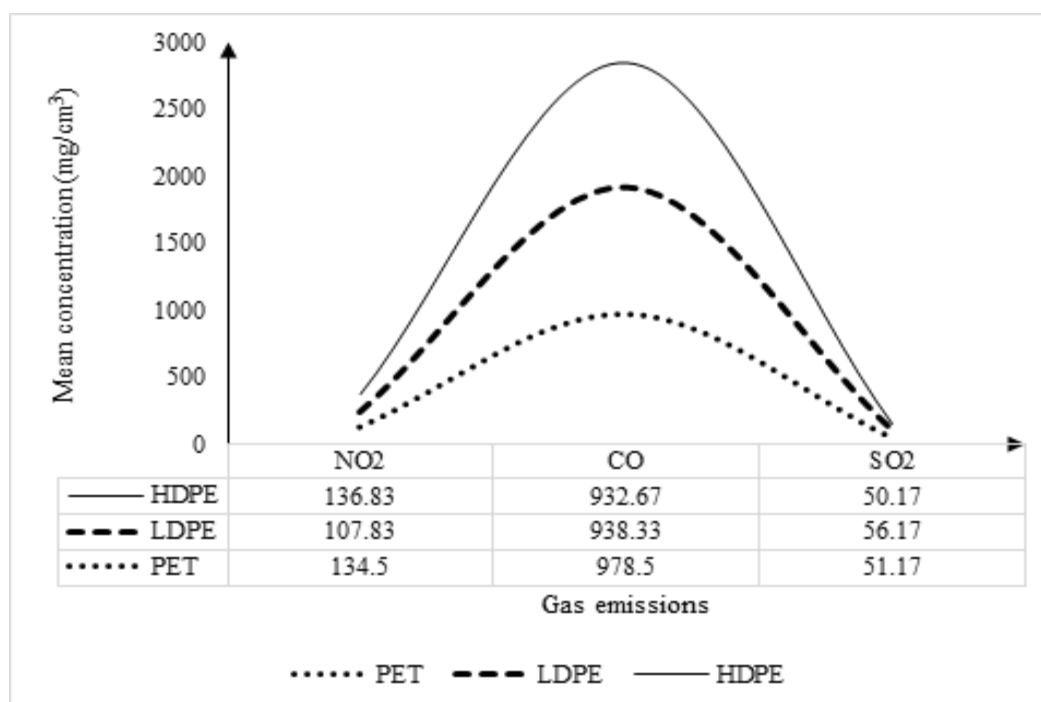


Figure 6: Gas emissions across plastic types

Results show that the concentration of NO₂ was high on HDPE with an average of 136.83mg/cm³. The least concentration of NO₂ was recorded on LDPE (107.83mg/cm³). It is evident that HDPE produce more NO₂ as compared to other plastic types. Results show that PET recorded the highest concentration of CO (978.50mg/cm³) followed by LDPE (938.33mg/cm³) and the least was recorded on HDPE (932.67mg/cm³). The results imply that all types of plastics constitute high levels of CO. Results indicate that LDPE recorded the highest concentration of SO₂ (56.17mg/cm³) followed by PET (51.17 mg/cm³) and HDPE has the least concentration with an average of 50.17 mg/cm³. This serves to confirm that, LDPE contains more SO₂ than other plastic types. Results also show that LDPE has the highest concentration on SO₂ (56.167mg/cm³) followed by PET (51.167mg/cm³) and HDPE has the least with 50.167mg/cm³. The concentration of CO is significantly high on PET (978.500mg/cm³)

Figure 5 also shows that; HDPE has the highest level of NO₂ (136.833mg/cm³), followed by PET with an average of 134.500mg/cm³ and LDPE has the least concentration of NO₂. The concentration of CO is significantly high in HDPE than any other gas (932.667mg/cm³).

CHAPTER 5: DISCUSSION

5.0 Introduction

This chapter is concerned with the discussion of research findings with the existing frame of literature on objectives of this study. It is in this chapter where disagreement and agreement with literature can be seen.

5.1 The three most abundant types of plastics within Chiwaridzo Phase 2 location waste streams.

Results show that LDPE was significantly higher (45%) than all plastic types followed by PET (34%), HDPE (16.7%) and other plastic types (4.3%) respectively. Because of its water resistance, LDPE plastic has a wide range of applications in the home. This is in agreement with Mejia et al. 2019, who observed LDPE's high content in household waste streams as a result of its use in plastic bags, rubbish bags, and wrapping foils for packaging. Gwada et al. (2019) investigated the plastic waste discarded by households in Kenya's Watamu ward, finding that LDPE was discarded at a significantly higher rate than other types of plastic waste, accounting for 55 percent of all plastic waste discarded, with PET combined LDPE accounting for 40.7 percent.

PET was second common plastic within Chiwaridzo Phase 2 residential waste stream because it is commonly used for light and easy beverage packaging owing to its low cost, sustainability, and reusability in comparison to other plastic kinds. This is in line with the American Chemistry Council's 2018 findings that PET is the most widely used packaging material today, with 62 percent of PET bottles produced annually. However, these findings were in contrast to those of Bodzay and Bánhegyi (2016), who found that LDPE (23 percent), HDPE (19 percent), and PET (11 percent) were all present after conducting a waste sort. The difference was due to the fact that the waste sort for their study was done at a municipal dumpsite where both residential and industrial waste is collected. The difference is also attributed to PET plastic waste being

commonly recycled by small scale informal recyclers so it is less common because it is taken by scavengers (Feresu, 2014)

PET was significantly higher than HDPE and other plastic types which include PP, PVC, and PS, whereas, HDPE was slightly above other plastic types. HDPE is fewer among plastics discarded from households due to its high strength to density ratio which supports reusing. This was supported by Merkl (2016) who reported HDPE from a residential waste sort to be 2.9% with the most abundant being LDPE (55%). Due to its large molecular mass, HDPE is less concentrated than the concentration of LDPE in the household waste stream. HDPE is collected for recycling by scavengers for informal recycling because it is easy to achieve goal weights and provides high-quality oil when recycled (Feresu, 2014). As a result, there was a major disparity between HDPE and other plastic kinds.

Other plastics, such as PVC, PS, and PP, had significantly lower concentrations than the rest of the plastics because they are used extensively in industries and medical fields, as supported by Janajreh et al. (2015) and Jonbi et al. (2019), and their presence in residential waste streams is due to worn out electrical appliances and health inhibitors.

5.2 Fuel quantities produced by each plastic type through pyrolysis

5.2.1 Pyrolytic oil quantities

HDPE has the highest concentration of oil (52%) followed by LDPE (29%) and PET recorded the least with 19%. Results show that there was a significant difference in the concentration of oil in all types of plastic ($p < 0.05$). The differences in pyrolysis oils were attributable mostly to the various melting points and thermal degradation rates of different plastic kinds. According to Jaboska et al. (2019), the melting point of PET is 260°C, the melting point of HDPE is 130.8°C (Constantinescu et al., 2019), and the melting point of LDPE is 110°C (Fotopoulou and Karapanagioti, 2017). Sogancioglu et al. (2017) discovered that degradation temperatures and differences in particle size of plastic type impact pyrolysis oil yields among plastic kinds in an experiment. This was in agreement with a study conducted by Straka et al. (2022), who discovered that during pyrolysis of HDPE and LDPE under the same conditions produced oil yields of 54% and 23% respectively indicating a statistical difference in the yields. However, this contradicts with a study conducted by Singh et al. (2019) in which oil yields from

pyrolysis of HDPE plastic to be 57%. The variations were attributed to rise in pyrolysis temperature in his experiment which facilitated the production of liquid oil.

5.2.2 Pyrolysis char quantities

The results also indicated that LDPE has the highest weight in terms of char with an average of 42%, with PET (30%) significantly different from HDPE (28%) and LDPE (42%) in relation to the weight of char ($p < 0.05$). This is in agreement with a study conducted by Sogancioglu et al. (2017). This study's findings corroborate the fact that LDPE plastic waste produces a larger percentage of gas and char products than HDPE waste. In another experiment, Istoto and Saptadi (2019) found that the quantities of char produced by pyrolysis of HDPE and LDPE were 18.06g and 19g, respectively. Because the two plastics are made of the same monomers, there are no statistical variations in the char formed by them. However, LDPE has greater monomer branching than HDPE, which explains larger char amounts in LDPE (Salih et al., 2013).

PET differed considerably from HDPE and LDPE in terms of char weight ($p > 0.05$). The discrepancy was ascribed to the polymers' differing reaction processes, Dastanian and FakhrHoseini (2013). PET plastic has a lower carbon fix than HDPE and LDPE because it is created from different monomers. Ügdüler et al. (2020) ascribed this to an increase in the usage of various detergents and disinfectants as a result of the covid-19 epidemic. These are generally packed in HDPE and PET bottles, which are then re-used as storage containers. Disinfections are often composed of iodine and chlorine components, which may infiltrate into the structure of the plastic and influence its qualities. This influences the pyrolysis products of various polymers, resulting in variances.

5.3 Determination of air quality during pyrolysis.

5.3.1 Concentration of NO₂ across pyrolysis of all plastic types

The results revealed that HDPE plastic produced the most NO₂ with an average concentration of 136.83mg/cm³. According to Alsaleh et al. (2014), the components of gases produced during HDPE plastic pyrolysis were methane (CH₄), hydrogen (H₂),

carbon monoxide (CO), sulphur oxides (SO_x), and nitrogen oxides (NO_x including NO₂), with NO₂ being the volatile gas with the highest concentration, followed by SO₂. This high NO₂ content was related to the usage of HDPE plastic prior to pyrolysis. Because of its great strength, HDPE may have been used to store ammonia, resulting in the integration of the nitrogen element into its structure, which is released when the plastic is pyrolyzed. The employment of nitrogen gas as a reducing agent in a steel reactor resulted in a high NO₂ concentration. This contradicts the findings of Laskar and Kumar (2019), who measured CO and SO₂ concentrations only solely due to the use of carbon as a reducing agent in the reactor. .

The lowest NO₂ concentration was measured on LDPE (107.83mg/cm³), this agrees with Sharuddin et al. (2016), in which the largest concentrations of gases generated during LDPE pyrolysis were CO, CO₂, and SO₂, as well as hydrocarbons in the C₁-C₅ range.

5.3.2 Concentration of SO₂ across all plastic types

The results showed that LDPE had the greatest SO₂ content (56.17 mg/cm³), followed by PET (51.17 mg/cm³), and HDPE had the lowest concentration with an average of 50.17 mg/cm³. This is consistent with a study done by Santaweek and Janyalertadun (2018), in which LDPE had the greatest amounts of SO₂, CO, and NO₂ in the order of dominance, with the inks and dye discovered on waste LDPE trademarks and labels. Ink and dyes are believed to be manufactured from coal and petroleum, both of which include considerable amounts of sulphur; this serves to prove that LDPE pyrolysis has more SO₂ than other plastic types

5.3.3 Concentration of CO across all plastic types

The results revealed that PET had the highest CO content (978.50mg/cm³), followed by LDPE (938.33mg/cm³), and HDPE had the lowest (932.67mg/cm³). This is consistent with the findings of Straka et al. (2022), who discovered large amounts of CO during PET pyrolysis, followed by NO₂ and a variety of hydrocarbon gases (C₁-C₅). The large carbon monoxide emissions are related to the plastic's vast range of

carbon and oxygen atoms, as shown by its monomer $(C_{10}H_8O_4)_n$ (Jaboska et al., 2021). Because of the presence of carbon and oxygen atoms obtained from crude oil and natural gas, which are used to manufacture synthetic plastics, all forms of plastics include significant quantities of CO when used for pyrolysis (Hacker et al., 2019).

The concentration of CO in HDPE was substantially higher than in any other gas (932.667mg/cm³), this contrasts the findings of Anene et al. (2018), who found that the experiment produced more NO₂ gas than any other volatile gas, followed by CH₄ and C₂H₄. This is because nitrogen gas, which was purged during TGA analysis and the pyrolysis process, was absorbed by HDPE samples prior to pyrolysis as a result of variations in process parameters (pressure, temperature, and heating rate) and nitrogen element as incorporated into its structure from the storage of nitrogen-containing chemicals/disinfectants prior to pyrolysis.

CHAPTER 6: CONCLUSION AND RECOMMENDATIONS

6.0 Conclusion

The main aim of the study was to examine the potential use of pyrolysis as an environmentally friendly method of reducing plastic waste in Chiwaridzo Phase 2 waste stream. Considering the results of comparison between the pyrolysis gas and the EMA Act (SI 72 of 2009) emission standards, the study concluded that plastic waste pyrolysis is an environmental friendly option for plastic waste management since the obtained results were within the blue band of the standard limits.

The study concluded that there was a significance difference ($p < 0.05$) in the quantity of pyrolysis oil recovered from different plastics types with HDPE having the highest concentration of oil (52%) followed by LDPE (29%) and PET (19%) respectively. A significance difference was also concluded between char quantities produced from different plastic types with LDPE plastic having the highest weight (42%) followed by PET (30%) and HDPE (28%) respectively. ANOVA LSD post-hoc showed that there is a strong relationship between the pyrolysis oil, pyrolysis char and plastic type.

In addition, trace elements were found to be present in char obtained from different plastic wastes. Study results showed that Zn across plastic types was statistically significant ($p = 0.002$) with no significant difference on the level of lead (Pb) ($p = 0.084$) and in terms of Cr concentration there was a statistical significant ($p = 0.008$). The elemental concentration of trace elements were obtained in small quantity which also aid the environmentally friendly use of char for production of energy.

6.1 Recommendations

- Further treatment of pyrolysis oil and char before use for the removal of trace elements which may harm environment.
- Use of specialized landfills for the disposal of ash from pyrolysis char.
- As the process temperature is the primary variable that can affect the quality and quantity of pyrolysis products, the process should be performed under

isothermal conditions by keeping the process temperature within the range of 450°C–900°C.

- To ensure that no hazardous emissions make their way back into the environment, control of CO, SO₂, and NO₂ emissions using extraction fans in the operation areas into bag houses, electrostatic precipitators, and installed scrubbers is required.
- Plastic waste should be thoroughly washed prior to pyrolysis to reduce the concentrations of trace elements in pyrolysis products which may be acquired from dumpsites
- Virgin and post-consumer plastics on the process and the distribution of the products should be explored as the number of times plastic waste was recycled also affects products.

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APPENDICES

APPENDIX 1: WASTE SORT PLAN

BINDURA UNIVERSITY OF SCIENCE EDUCATION

FACULTY OF ENVIRONMENTAL SCIENCES

WASTE SORTING PLAN



A WASTE SORT TO DETERMINE THE MOST ABUNDANT PLASTIC WASTE IN URBAN AREAS: A CASE STUDY OF CHIWARIDZO PHASE TWO

Please note that the information found upon completion of this waste sort will be used for academic purposes and can also be used by Chiwaridzo Phase Two authorities in making decisions that concern plastic waste management.

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BRIEF DETAILS ON THE WASTE SORT

Date of waste sort	/22
Place of sort	ONSITE (CHIWARIDZO PHASE TWO DUMPSITE)
Duration of waste sort	

A	Main activity of a waste sort: Hand-sorting selected waste sample at Chiwaridzo Phase 2 dumpsite Waste sort objectives:
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	-Collecting baseline data regarding the amount and type plastic waste within Chiwaridzo phase 2. -Come up with three most abundant types of plastic within the location for recycling through pyrolysis																			
B	SORT SYSTEM Location of sort Country: ZIMBABWE Province: MASHONALAND CENTRAL Town: BINDURA Location: CHIWARIDZO PHASE 2 Sort team Number of participants: 4 <table><tr><td>Participant</td><td>Responsibility</td></tr><tr><td>A</td><td>Supervising team</td></tr><tr><td>B</td><td>Sorting PETE and PE and weighing the waste streams</td></tr><tr><td>C</td><td>Sorting HDPE and LDPE and weighing the waste streams</td></tr><tr><td>D</td><td>Sorting PVC, other plastic waste and weighing</td></tr></table>						Participant	Responsibility	A	Supervising team	B	Sorting PETE and PE and weighing the waste streams	C	Sorting HDPE and LDPE and weighing the waste streams	D	Sorting PVC, other plastic waste and weighing				
Participant	Responsibility																			
A	Supervising team																			
B	Sorting PETE and PE and weighing the waste streams																			
C	Sorting HDPE and LDPE and weighing the waste streams																			
D	Sorting PVC, other plastic waste and weighing																			
C	SAMPLING PROTOCOL Waste Segregation according to: Plastic type Expected waste heaps: <table><tr><td>HDPE</td><td>LDPE</td><td>PETE</td><td>PE</td><td>PVC</td><td>Other</td></tr></table> Sampling method for selection of dumpsite Available dumpsites: 3 Sample selection method: Purposive Sampling method for sorting pile. Method: Strata sampling Number of strata: 4 Strata sample weight: 15kg Overall sorting sample weight :60						HDPE	LDPE	PETE	PE	PVC	Other								
HDPE	LDPE	PETE	PE	PVC	Other															
D	CONDUCTING THE WASTE SORT A short briefing on the project objectives, equipment to be used and safety measures during the process will be proffered to participants. Any questions raised will be answered before commencing with sorting. Equipment to be used <table><tr><th>Equipment</th><th>Use</th></tr><tr><td>Labeled gallon sized bags</td><td>Collection bag for each category of sorted plastic</td></tr><tr><td>Sorting table</td><td>For sorting, promote ergonomics</td></tr><tr><td>Litter grabbers</td><td>Reaching waste underneath</td></tr><tr><td>Pens and paper</td><td>Recording weights</td></tr><tr><td>Hand sanitizer</td><td>Cleaning up after sorting</td></tr><tr><td>Scale</td><td>Weighing or sorted plastic</td></tr></table> Safety procedures during the sort 1. No eating, smoking, or drinking during sorting activities. Food and liquids should be away from the sorting area. If the event lasts over a meal period, hands and faces should be washed before eating or drinking. 2. The following safety equipment will be onsite and utilized by sorting participants: first Aid Kit , nit-rile gloves – two pair for each participant, eye protection, work suits and safety shoes/gumboots(participants can bring their own) Sorting will be conducted from top to bottom to avoid being cut by sharp objects which may be found in the waste stream						Equipment	Use	Labeled gallon sized bags	Collection bag for each category of sorted plastic	Sorting table	For sorting, promote ergonomics	Litter grabbers	Reaching waste underneath	Pens and paper	Recording weights	Hand sanitizer	Cleaning up after sorting	Scale	Weighing or sorted plastic
Equipment	Use																			
Labeled gallon sized bags	Collection bag for each category of sorted plastic																			
Sorting table	For sorting, promote ergonomics																			
Litter grabbers	Reaching waste underneath																			
Pens and paper	Recording weights																			
Hand sanitizer	Cleaning up after sorting																			
Scale	Weighing or sorted plastic																			
E	MEASURING SAMPLES After sorting, weights of sorted material will be recorded on the columns below provided on every copy of this plan given to every participant, followed by cleaning up of working area and thanking participants for their participation. Participant will sign up upon completion of responsibilities. <table><tr><td>Plastic waste type</td><td>A</td><td>B</td><td>C</td><td>D</td><td>E</td><td>F</td></tr><tr><td>Weight(kg)</td><td></td><td></td><td></td><td></td><td></td><td></td></tr></table>						Plastic waste type	A	B	C	D	E	F	Weight(kg)						
Plastic waste type	A	B	C	D	E	F														
Weight(kg)																				
F	DATA ANALYSIS The data shall be analyzed to obtain a snapshot of plastic waste produced. Percentage weight of each waste stream shall be calculated. The data obtained from calculations of percentage weight can be incorporated into a pie chart thus giving a clear image of the three most abundant types of plastic which can be used for pyrolysis to attain project objectives																			

G	USING THE DATA When the three most abundant plastic types are obtained, the researcher will take a sample of 5kg of each type for experimental pyrolysis analysis
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APPENDIX 2: RESULTS FROM RAW DATA

Data showing the quantity of oil and char obtained after tyre pyrolysis.

Sample	Sample weight (g)	Volume of pyrolytic oil (ml)	Weight of Char(g)
PET1	25	5.1	3.1
2	25	4.3	2.8
3	25	5.1	2.4
4	25	4.3	2.2
5	25	5.3	2.3
6	25	4.4	2.7
LDPE7	25	8.2	3.2
8	25	7.3	4.3
9	25	6.9	3.7
10	25	5.9	2.8
11	25	6.8	3.5
12	25	7.5	4.1
HDPE13	25	14.1	1.8
14	25	13.2	1.9
15	25	9.4	2.3
16	25	13.5	2.5
17	25	11.3	2.9
18	25	15.1	3.1

Volume of pyrolytic oil and weight of char

Sample number	Plastic type	Average volume of pyrolytic oil (ml)	Average weight of char(g)
1-6	PET	4.75	23.58
7-12	LDPE	7.10	3.60
13-18	HDPE	12.77	2.42

Volatile gases released during plastic pyrolysis and char trace elements

plastic	NO2(mg/cm3)	CO(mg/cm3)	SO2(mg/cm3)	Cr(mg/cm3)	Pb(mg/cm3)	Zn(mg/cm3)
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PET	159	967	48	0.061	0.062	0.052
1	160	978	51	0.045	0.01	0.016
1	171	976	53	0.133	0.047	0.039
1	108	998	50	0.182	0.014	0.019
1	107	988	52	0.091	0.01	0.022
1	102	964	53	0.143	0.019	0.042
LDPE2	110	955	55	0.181	0.003	0.006
2	104	978	56	0.224	0.003	0.009
2	106	943	55	0.185	0.003	0.005
2	112	932	55	0.624	0.045	0.016
2	111	911	58	0.627	0.046	0.0139
2	104	911	58	0.486	0.048	0.009
HDPE3	99	911	45	0.291	0.281	0.14
3	103	911	49	0.251	0.231	0.1
3	111	941	48	0.161	0.14	0.089
3	155	943	48	0.213	0.01	0.588
3	188	945	59	0.2	0.013	0.621
3	165	945	52	0.23	0.009	0.573

