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Resource Recovery of Post-Consumer Plastic Waste Using Pyrolysis

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LIST OF SYMBOLS

H_c	Gross heat of combustion
T	Observed temperature rise
W	Energy equivalent of the calorimeter being used
e_1	Heat produced by burning the nitrogen portion of the air trapped in the bomb to form nitric acid
e_2	The heat produced by the formation of sulfuric acid from the reaction of sulfur dioxide, water and oxygen
e_3	Heat produced by the burning fuse
m	Mass of the sample

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ABSTRACT

The world today generates vast amount of post consumer plastic wastes, which causes many knotty issues and challenges on present plastic wastes management. Our fast exhausting hydrocarbon fossil fuels have increased the cost of plastic production. Recovering hydrocarbon resources from post consumer plastic wastes represents a more sustainable and holistic waste management alternative as compared to current incineration and landfilling for waste disposal. The aim of this study was to investigate the chemical compositions and energy content of the products yielded from the pyrolytic degradation of Polyethylene (PE), Polypropylene (PP), Polystyrene (PS) and the mixture of them in both clean and contaminated conditions. The results showed that degradation of the three plastic samples took place from 350°C to 550°C. Lower heating rate was observed to have better heat transfer achieving a narrower degradation window. PS degradation was observed to require lowest energy. Investigations on the product yields showed that solid residues generally reduced in yield with higher pyrolysis temperature, while liquid yield increased when pyrolysis temperature increases from 650°C to 950°C. In a single plastic pyrolysis, PE liquid yield consisted of saturated and unsaturated aliphatic compounds ranging from C₈ to C₂₃. PP liquid yield consisted of mainly n-methyl and cyclo-chain hydrocarbons and PS liquid yield made up of mainly styrene aromatics. The results from pyrolysis of plastic mixtures showed that plastic mixtures containing high PS content augmented the production of liquid yield while high PP content was observed to increase gas yield. Similar to single plastic material pyrolysis, PE favored formation of aliphatic hydrocarbons, while PP increased the n-methyl and cyclo-chain hydrocarbons and PS led to higher aromatic composition. These results demonstrated that the liquid and gases yield distributions had a certain degree of dependency on plastic waste mixture composition. From the studies on the influence of contamination on plastic wastes, the result showed that oil, salt and water present to mixed plastics had exhibited an inhibition impact on the range of

product yields while enhancing the yield of the aromatic component in mixed plastics. Pyrolytic oil was found to have an average content of 40MJ/kg demonstrating high calorific values of the pyrolysis liquid product. In conclusion, the product yields from the pyrolysis of single, mixed and contaminated plastics showed great potential for chemical and fuel recovery.

Chapter 1

Introduction

1.1 Background

Today, plastic packaging applications are so wide and versatile that their disposals not only constitute to a major fraction in the municipal solid waste (MSW) stream but their impacts on our environment are extremely wide and potent. However, current post-consumer plastic (PCP) recycled is considered low in comparison to other materials in the MSW. This unpopularity is due to many difficulties and limitations of the current mainstream mechanical recycling method that ultimately leads to poor economic return. Among the many difficulties faced in recycling PCP, the most costly and significant challenge lies in the area of separation and purification. Pyrolysis of PCP represents an attractive recycling alternative to produce valuable products of high consistency. This technique has potential of reducing operation cost by eliminating the separation and purification process of plastic recycling.

1.2 Objectives and scope of work

The main objective of this research study was to investigate the impact of food contaminated PCP through measuring the discrepancies in the pyrolysis products with clean plastic mixtures. The data generated will serve as a benchmark to justify the need for separation and purification process in the pyrolysis of PCP waste. The secondary objective of this research was to measure the calorific value of the pyrolysis product from mixed and food contaminated PCP. The data can be used as a preliminary justification for future fuel applications.

The scope of work covered in this research included:

- 1) The preparation stage which involve the design, construction and set up of the integrated pyrolysis system, the preliminary study on the properties of PE, PP and PS using several characterization tests, and the calibrations of the analytical equipment such as GC-MS and GC-FID

- 2) The thermogravimetric and pyrolysis yield study on the degradation behaviors of single plastic based on different pyrolysis temperature and heating rate.
- 3) The study on the product yield due to the co-pyrolysis of mixed PE, PP and PS.
- 4) The study on the product yield due to the co-pyrolysis of mixed plastics contaminated with synthetic food.

1.3 Thesis layout

Chapter 1 illustrates the overall background, intention and scope of work and layout out summary of this thesis.

Chapter 2 gives a brief history to the application of plastic, reviews on the magnitude of the PCP problems and highlights the issues and technologies challenges with current plastic recycling infrastructures.

Chapter 3 illustrates the preliminary work such as the sample plastic characterization and thermogravimetric studies carried out before the commencement of the actual pyrolysis experiments. The chapter also outlines the actual procedures of setting up and operating the integrated batch pyrolysis reactor. This chapter also explains the procedures of calibration of analytical equipment.

Chapter 4 reports and discusses on the chemical composition of the pyrolysis yield from the data derived from the various pyrolysis experimental work. This chapter also shares the calorific values of the different product from PCP pyrolysis. .

Chapter 5 draws a few conclusions based on the results obtained in Chapter 4. Some recommendations are suggested for future research endeavor.

Chapter 2

Literature Review

2.1 Introduction

Plastics with new improved performance characteristic are continually developed to meet different applications since its discovery by Alexander Parkes in 1862. Today's plastics packaging, played a key role in maintaining the cleanliness, freshness and portability of consumable products, has made PCP become one of the larger categories by volume in the MSW, particularly in highly industrialized countries [1].

The current disposal methods for plastic wastes by landfilling and incineration not only have great social and environmental impacts but they are also very expensive to build and maintain. Landfilling, which is considered as the worst option in the hierarchical approach to solid waste management [2], does not make use of the energy-rich disposed plastics as a raw resource and requires plentiful space. Moreover, the non-degradable nature of plastics inhibits the biological process within the landfill. Socially, the public "Not in my Backyard" movements, stricter regulations on groundwater contamination and directives to restrict landfilling applications has significantly reduced the number of active operating landfills especially in densely populated area [3, 4]. Alternatively, the disposal of plastics has been carried out by incinerations, which has many advantages. Firstly it reduces the volume and mass of the plastics to a fraction of its original size (more than 90%). Secondly, plastics are high in energy content, which allows greater offsets to the cost of operation by energy sales [5]. However, incineration of plastics without sorting results in the formation of dioxins [6]. Carcinogenic emission to air, toxic fly and bottom ash are also costly to remove and could cause social health repercussion if not dealt effectively.

Another option to plastic wastes disposal is recycling. In short term economic point of view, landfilling and incineration is more competitive than the recycling options. However, from a welfare economic view, it has less environmental impact and lower energy use, which in the long run generates greater benefits [7].

2.2 Recycling of post consumer plastics

Recycling in general is a process by which a product at the end of its service life is converted into another product. It usually encompasses separating, collecting, processing, marketing and ultimately using the material that could have been thrown away. Recycling of mixed plastics can result in a product to have inferior physical properties, thus an effective separation of mixed plastics from the MSW is always necessary. Despite the importance of public participation in the separation of PCPs in recycling scheme, there are many limitations on the extent of separation that was carried out [8]. Recycling schemes, such as kerbside collection, return of bottle bills, drop boxes and buy back centre, are usually targeted as the clean and easy way to separate PCP. Items, such as drinking bottles, detergent bottles, are usually recovered. However a large portion of the PCP consisting of disposable food packets, utensils and plastic bags are ignored or avoided by the recycling schemes. According to the Environmental Protection Agency (EPA), this PS, PP and LDPE portion represents 45% of the total plastics found in MSW [9]. These types of PCP collected are highly contaminated, assorted mixtures. These make their identifications, separation and purification very challenging [10]. For this reason, many pretreatment techniques prior to actual recycling have been developed to clean and sort out this mixture of PCP. The pre-treatment of plastic wastes usually includes volume reduction, separation/sorting, crashing, washing and drying. However, the enhancement of the separation process of PCP still remains the mainstream of the researches as it has the most significant impact. Most current strategies to separate plastics rely on gravity separation or hand-sorting. Manual separation is labor intensive and expensive while high quality automatic gravity segregation of plastics are almost exclusively limited to processes that separate polymers of different gravity [11]. A number of promising technologies for plastics sorting under investigations includes electrostatic techniques [12], air classifications, hydrocycloning [13], froth flotation [14], depolymerization, selective dissolution, sorting based on infrared analysis or laser scanning of polymer, and incorporation of chemical

markers into different polymer [15]. Another important pretreatment process is purification of the soiled PCP. This normally involves the use of chemical agents and large amount of water, which creates secondary effluents that require treatment before discharging [16]. The pretreatments prior to recycling not only increase the complexity of recycling operation but incur a direct bearing on the cost of PCP recycling. In some recycling plants, the costs of operation of this expensive pretreatment not only exceed the costs of earlier disposal methods, but also exceed the market value of competitive virgin raw materials [17]. As such, a recycling method that could eliminate or reduce the number of pretreatment process required would definitely make plastic recycling of PCP waste more economically viable and competitive.

2.3 Different types of recycling methods

Primary recycling is the most commonly used recycling method of post industrial plastic wastes. This method involves mainly mechanical means. In this recycling process, plastic wastes are melted and recycled into material that has equivalent characteristics of the original product. Only thermoplastic wastes can be directly reprocessed in this manner. Examples of such plastic material that can be re-utilized are edge trims, start-up and change-over scraps, finished products or parts fails to meet required standards, etc [18]. The recycled resins are usually resold to plastics manufacturers as a replacement of virgin material or added to virgin resin at various ratios. The main limitations that primary recycling have are the degradation of resin properties due to repeat processing and the possible contamination of the reprocessed plastics.

Secondary recycling or down-recycling is another mechanical recycling that reprocess scrap plastics through grinding, melting and reforming into plastic products with less demanding properties. Secondary recycling is usually applied to mixed or contaminated plastics that cannot be reprocessed through primary methods [19]. These plastics usually have properties inferior to those of the

original products. This reduction in quality can surface as a decrease in strength of the plastic due to polymer chain scissions during melting. A gray-green colored plastic is usually produced due to the mixing of different colored plastics, or contamination from dirt or chemicals that the plastic wastes feedstock once contained. One good example of secondary recycling plastics is plastic lumber. They are typically used for picnic tables, sign posts, and playground equipment [20].

Quaternary recycling or energy recycling, uses combustion to recover energy from used plastics products. Plastic wastes can be utilized for energy recovery in two distinct ways. Firstly, plastic wastes can be incinerated together with MSW with energy recovery or they can be separated from MSW, collected and processed for fuel preparation; plastics Derived Fuel (PDF). PDF originated from fossil fuels have very high calorific values and almost negligible moisture content. PDF in general has a larger pool of potential combustors than RDF (Refuse Derived Fuel) and MSW because there is no need for dedicated combustion plant. They are highly versatile and can be used for energy production by mono-combustion or by co-combustion or existing energy facilities [21]. All PDF performed technically well during combustion and their emissions were low [22]. Small particles size and stable feeding of PDF are important for effective combustion. PDF generally have heating values in the range of 7,000 to 1, 6000 Btu/lb [23]. Conventional Refuse Derived Fuel generally has a heating value of less than 6,500 Btu/lb [10]. Despite the high heating value of plastics, the prerequisites for the successful introduction of PDF still depend on several factors like the guaranteed quality, consistent long-term supply and public acceptance. The plastic wastes must be converted to a prepared form that makes it suitable for transportation and storage, and for feeding into the energy conversion plant [24]. Despite its versatility, in quaternary recycling, plastics are still destroyed; therefore potentially recoverable valuable materials are still considered lost. Table 2.1 summarizes the heating values of plastics compared with other fuel sources.

Table 2.1 Energy values of target plastic wastes compared with other fuel sources. [25]

Source	Energy value (KJ/Kg)
Municipal Waste	10,000
Wood	14,000
Newspaper	16,000
Rubber	22,000
Coal	27,000 – 30,000
Mixed Plastics	30,000 – 40,000
Polystyrene	37,000
Polypropylene	40,000
Polyethylene	41,000
Kerosene	42,600
Diesel Oil	44,400
Gasoline	46,000

Tertiary recycling is the breakdown of polymeric waste into reusable fractions for reincarnation as polymers, monomers, fuels, or chemicals [26]. This can be achieved chemically or thermally. Generally, polymeric materials in tertiary recycling are degraded into lower molecular weight compounds. In the chemical recycling or solvolysis, feed sample is dissolved and converted back to their monomers while in thermal recycling, heat energy is used to break the feed samples into smaller molecular weight components.

Chemical recycling or solvolysis is used to convert step-growth polymers, which are often made by reversible reactions to reusable chemical products. These step-growth polymers include polyester, polyamides, polyurethanes, and polyethers. The various solvolysis processes are summarized in Table 2.2;

Table 2.2 Various solvolysis processes in chemical recycling

Solvolysis Process	Applications	References
Glycolysis	PET, nylon	[27]
Hydolysis	Polyamides, polyesters, polycarbonates	[28]
Methanolysis	PET, nylon, polyurethanes	[29]
Aminolysis	PET	[30]
Alcoholysis	PET, nylon	[27]
Acidolysis	nylon	[31]

Although solvolysis is the predominant conversion route for step-growth plastics, there are still some limitations for this method of plastic recycling [21, 26, 32]:

- Requires the plastic to be relatively clean and cannot be used for mixed plastic streams
- Environmental concerns over the use of some solvents for depolymerization reactions
- Unsuitable for chain-growth polymers such as PE, PP, PS, PVC, etc.
- Step-growth polymers only contribute to 20% of all plastics sold in U.S.

Thermal recycling or thermolysis involves the use of high-temperature to cleave the bonds in the backbone of the polymer. This form of recycling essentially cleaves plastic wastes back into petrochemicals feedstock that can be used as raw materials in the production of new petrochemicals and plastics without any deterioration in their quality and without any restriction regarding their application [21]. The main forms of thermolysis polymer feedstock recycling are pyrolysis, hydrogenation and gasification. Pyrolysis is carried out in high temperature environment where there is an absence of air. There are four main advantages of this thermal recycling over incineration. Firstly, thermal recycling reduces the volume of product gases. This means a considerable reduction in capital expenditure in treating flue gas. Secondly, the pollutants become

concentrated in coke-like matrix solid residues which can be handled more easily. Thirdly, pyrolysis is conducted in a closed system, thus allowing no pollutants to escape. Lastly, instead of collecting ashes from incineration, the pyrolysis process recovers valuable hydrocarbon products, such as monomers, petrochemical feedstock and fuels from plastic wastes. When the process is carried out in an atmosphere of hydrogen gas, it is referred to as hydrogenation or hydocracking, and if it is carried out in the presence of a controlled amount of oxygen, it is known as gasification. The generic products of each process of thermolysis are listed in Table 2.3.

Table 2.3 Overview of the main forms of thermolysis processes in thermal recycling. [21]

Thermolysis	Products
Pyrolysis	Naphtha, high boiling oils, high value refinery product
Hydrogenation	Crude Oil, high value refinery product
Gasification	Syngas, Carbon Monoxide, Hydrogen

Plastic recycling lags behind the production of plastics despite mechanical and chemical recycling have matured over the years [33]. They are only economically viable up to 10 to 20% of the MSW plastics. Chemical recycling has limitations and deals only with step-growth polymers. These recycling methods require purification and separation pretreatments, which inflict high additional overheads. Moreover, their products are also low in market values. From past studies, tertiary recycling (pyrolysis) has demonstrated potential ability to produce high value products without the need of costly purification and separation from the highly contaminated heterogeneous PCP. The main purpose of this study is to verify this potential.

2.4 Polymers and monomers structures

Polyethylene, polypropylene and polystyrene investigated in this study are thermoplastics having a long chain structure with little branching produced from polymerization reactions. They are usually made by joining together into long chains a number of molecules which have the same kind of reactive points or grouping in their structure. These individual molecules are usually olefins or other compounds with double bonds, and are called monomers. The molecules of the polymer often contain hundreds of monomer units.

Monomer	Polymer
Ethylene = Ethene	Polyethylene
Propylene = Propene	Polypropylene
Styrene	Polystyrene

Figure 2.1 Polymer and monomer structure of target plastic wastes [34].

2.5 Pyrolysis mechanisms of plastics

Pyrolysis is a thermal decomposition occurring in the absence of oxygen [35]. Pyrolysis has been highly regarded as the potential tertiary recycling technology of interest in converting plastic wastes to useful hydrocarbon resources to counter increasing PCP volume in MSW [36, 37, 38]. Pyrolysis mechanism of plastics consists of at least three steps namely initiation, propagation and termination. In general, initiation creates radicals that start the chain reactions. Carbon to carbon in straight-chain hydrocarbons is generally weaker than the carbon to hydrogen bonds [39]. When a hydrocarbon molecule is subjected to a large energy source in the absence of oxygen, the weaker carbon to carbon bonds will break up, producing hydrocarbon radicals. Once generated from initiations reactions, the free radicals will transform through a series of propagation steps. These radicals have a reactive nature, which allows them to proceed through a large range of subsequent reactions. Most radicals will continue to thermally fragment through chain transfer or β -bond scission. In the chain transfer reactions, radical species attack the parent and produced hydrocarbon molecules promoting the release of more radicals. These radicals are stabilized by the β scission of the bond located at the β position as demonstrated in equation 2.1 [26].

The new radical can either transfer its single electron to a new hydrocarbon molecule to convert itself to paraffin, or undergo further β -bond scissions. Hence, the successive alkyl radical decomposition into olefin molecules until the remaining radical becomes either a hydrogen atom, or methyl or ethyl radical, which serves as an initiator, so that the cycle is repeated within the pyrolysis process of plastics. The mechanisms for pyrolysis process are summarized in equations 2.2 to 2.5, where M is the parent molecule, and R^* denotes the smallest

alkyl radicals. This general mechanism can be illustrated from the thermal degradation mechanism of polyethylene in Figure 2.2. [40].

Initiation:

Propagation:

Termination:

Termination

Figure 2.2 General mechanism of the thermal degradation of polyethylene [40].

Cullis and Hirschler proposed four decomposition mechanisms during pyrolysis of plastics [41].

- (a) End-chain scission or depolymerisation: The polymer is broken up from the end groups successively yielding the corresponding monomers. End-chain scissions are heterogeneous reactions, which promote the generation of volatile products in the gas-liquid interface as shown in Figure 2.3.
- (b) Random-chain scission: The polymer chain is broken up randomly into fragments of uneven length.
- (c) Chain-stripping: Elimination of reactive substitutes or side groups on the polymer chain, leading to the evolution of a cracking product on one hand, and a charring polymer chain on the other.
- (d) Cross-linking: Formation of a chain network, which often occurs for thermosetting polymers when heated.

These different mechanisms and product distributions are, to some extent, related to bond dissociation energies, the chain defects of the polymers, aromaticity degrees and the presence of halogen and other hetero-atoms in the polymer chains [38]. For the target PCP in this study, the decomposition mechanisms and associated monomer yield are listed in Table 2.4.

Figure 2.3 Proposed macroscopic mechanism of the end-chain scissions of polymers to produce products at gas-liquid interface [42].

Table 2.4 Decomposition mechanisms and monomeric yields of target polymers [41].

Polymers	Decomposition mechanisms	Monomeric yield, Wt %
Polystyrene	End-chain and random-chain scission	42-45
Polyethylene	Random-chain scission	0.03
Polypropylene	Random-chain scission	0-17

2.6 Review of different reactors for plastic wastes pyrolysis

The design and set-up of the pyrolysis process and reactors are flexible and a large variation of conditions can be achieved. Reactors to recycle plastics by pyrolysis include in vessels, autoclaves, rotary kilns and fluidized beds. Rotary kiln has been used widely in the incineration of solid wastes. With appropriate modifications, these furnaces can carry out the pyrolysis process to a satisfactory level on a large scale basis. Plastic wastes of various shape and size and heat values can be fed into the rotary kiln [43]. Rotary kiln processes are marked by relatively long residence time with large temperature gradient inside the rotary kiln. The pyrolysis products are usually very diverse [44].

Most studies on the pyrolysis of plastic wastes through fluidized bed are performed in the laboratory with a few at pilot scale. Fluidized bed has a number of special advantages for pyrolysis because it is characterized by an excellent heat and mass transfer as well as constant temperature throughout the reactor [44]. This provides a more uniform spectrum of products and allows shorter residence time at moderate temperatures. The absence of a moving part in the hot region reduces the maintenance time and cost [45]. However, it is known that stable, long-term operations of these fluidized reactors can be compromised by particle agglomeration phenomenon, which can generate worsening of fluidization and eventually lead to defluidization [46]. Table 2.5 highlights some of reactors that have been used in the investigation of different types of plastic pyrolysis. From Table 2.5, the reactors can actually be further categorized into two main groups based on residence time and temperature. The long residence time processes typically operate at a temperature range of 450-600°C and a residence time ranges from several tens of seconds to several minutes. The primary product is usually liquid fuel, and the conversion to base monomer is low. The product yield and composition is usually highly temperature dependent, while the effect of residence time is less significant [47]. The short residence time in plastic pyrolysis studies utilized the later generation pyrolysis reactor technology

including fast fluidized beds and other rapid fluid-particle contacting equipment. They typically operate at temperatures ranging from 750-1000°C and residence times ranging from a few hundred milliseconds to several seconds [47, 48]. The primary product usually has the potential of achieving high olefin yields, with adequate control of residence time [48].

Table 2.5 Pyrolysis reactors for plastic wastes

Reactor Type	Investigator	Plastics tested	Operation Parameters
Long Residence, low temperature			
Gray-King Static Bed Reactor	Kiran [49]	PS, PE	600°C at 5°C/min Hold time 15 minutes
Autoclave	Walendziewski [50]	PP, PS	370-450°C 90% gas yield Liquid fraction boiling point <360°C
Fluidized bed	Williams [51]	LDPE	500-700°C Gas yield increases with temperature Oil mainly aliphatic composition
Circulated-spheres reactor	Bockhorn [52]	PVC, PS, PE (1:1:1 by weight)	Stepwise pyrolysis 330°C dechlorination followed by 380°C and finally at 440°C
Short Residence, high temperature			
Internal circulating fluidized bed (ICFB)	Milne [47]	LDPE	780°C-860°C 400 – 600 milli seconds 90% Gas yield with 75%wt total olefins
Curie Point Pyrolysis Reactor	Sodero [48]	LDPE	800 -900°C 350-2500 milli seconds 75% weight light olefins
Free-fall reactor	Karaduman [53]	PS	700-875°C Liquid yield max at 750°C Styrene yield max at 850°C

2.7 Review of pyrolysis of mixed and contaminated plastic wastes

PCP found in MSW usually consists of more than one type of plastics. Most researches reported were based on the study of individual clean plastics. There is very little information available on the mixed plastics behavior on pyrolysis and their product yield for commingled plastics containing more than two polymers [54]. Pyrolysis studies carried out on contaminated plastics usually focused on the effects of polyvinyl chloride (PVC) on the product yield. This is because the formation of hydrogen chloride (HCl) not only causes deactivation of zeolite catalysts and corrosions of metal components of the pyrolysis reactor [21], but the chlorine content in the pyrolytic oil fraction makes the liquid product yield unsuitable for chemical feedstock [55]. The dehydrochlorination process of plastic mixture containing PVC can be achieved by catalytic steam reforming [56] or through an additional isothermal stepwise process at about 300-350°C [57]. The evolved HCl would then be removed by scrubbing using calcium oxide. In addition to PVC cross contamination, most PCPs collected from MSW stream are not only highly heterogeneous but also include contaminants such as food and dirt. This is the main barrier to the increase of the recycling rate of PCPs. As such, it would be highly desirable and relevant to understand interactions of different plastic mixtures [34, 58], and common post-consumer contaminations by food and dirt [59] on the stability of product yield as shown in Table 2.6.

Table 2.6 Studies on pyrolysis of commingled plastic wastes

Investigator	Plastics mixtures	Interaction effects
Pinto [34]	68%PE,16%PP,16%PS	<ul style="list-style-type: none">• PE increase alkane content
- Autoclave	16%PE,68%PP,16%PS	<ul style="list-style-type: none">• PS led to higher aromatic content
- Pyrolysis at 430°C	16%PE,16%PP,68%PS	<ul style="list-style-type: none">• PP favored alkene formation
	33%PE,33%PP,33%PS	<ul style="list-style-type: none">• PS and PP increase octane number in end product• Yield high dependency on plastic waste blending
Predel [58]	60% PE, 40% PP	<ul style="list-style-type: none">• Products are mostly aliphatic waxes
- Hamburg fluidized bed	40%PE,60%PP	<ul style="list-style-type: none">• Addition of PS to PP favored formation of more unsaturated waxes
	90%PE,10%PS	
	90%PP,10%PS	<ul style="list-style-type: none">• PS to Polyolefines lead to more products with shorter chain lengths
- Pyrolysis at 510°C	54%PE,%36%P, 10%PP	
Kiran [59]	PE:PP	<ul style="list-style-type: none">• Increasing PP suppress liquid yield in co-pyrolysis of PE:PP and PS:PP mixtures
- Gray King Assay pyrolysis reactor	PS:PP	<ul style="list-style-type: none">• Polyaromatic formation of PE:PP mixture is suppressed at a 1:1 mixing ration• C₃ – C₄ formation increase in PE:PP mixture with increase of PP content• Additional PP to waste mixtures increase alkene/alkane ration for C₂ and C₃
- 700 °C		<ul style="list-style-type: none">• Decrease in onset, half-life and end temperature for PP degradation• Cracking of gaseous molecules is favored as there is higher amount of gas yields
	On Effects of Dirt and Food Contaminations	Formation of higher C numbers hydrocarbon compounds

Chapter 3

Materials & Methodology

3.1 Introduction

The sample polymers of interest in this study were PE, PP, and PS. Today, these plastics represent a huge portion of plastic wastes in Singapore's MSW. These polymers are light, cheap, flexible, and have very short useful lifespan. These favorable characteristics allow them to be used commonly in the domestic markets serving multipurpose especially in the food and beverages sectors. However these useful properties also become the main culprits to cause white pollution, disposal and conservation issues. In this chapter, characterization of the target plastic samples, set-up of the batch run pyrolysis reactor and the analytical methods to determine the composition of the product yields are discussed.

3.2 Materials Characterization

PE samples were acquired in the form of common plastic bags (LDPE) from a major shopping center. PS and PP samples were obtained from Canteen A of the university, in various forms of disposable food packaging, cups and utensils. Photographs of the polymers in their original form are shown in Figures 3.1 to Figure 3.3. The samples were cut into approximate size of 2-5 mm² manually to facilitate the proceedings of the different experiment analysis. Particle density, ash content and ultimate analysis were carried out as part of the preliminary study on the composition of the polymer samples. This step would provide valuable information for the analysis and evaluation of the physical and chemical transformation from the original polymer samples with the final pyrolysis products.

Figure 3.1 Photographs of LDPE in original form and after pretreatment

Figure 3.2 Photographs of PS in original forms and after pretreatment

Figure 3.3 Photographs of PP in original forms and after pretreatment

3.2.1 Particle density

Quantachrome Corporation’s Ultrapycnometer was used to determine the particle density of the waste plastic samples. The Ultrapycnometer employs Archimedes’ principle of fluid displacement and Boyle’s law to determine the volume of the sample. Gas is used as the displaced fluid as it can penetrate the finest pores maximizing accuracy. Helium gas was used for the determination of the particle density for the waste plastic samples. Helium is an ideal inert gas and its small atomic dimensions assure penetration into crevices and pores approaching one Angstrom (10^{-10} m in dimension). Determinations of particle densities were conducted 5 times for each sample at a temperature of 26.6°C and pressure at 17psi. Table 3.1 presents the recorded results.

Table 3.1 Average particle density of the polymer samples

Sample Type	Average Density (kg/m ³)
Polyethylene	924
Expanded Polystyrene	182
Polypropylene	921

3.2.2 Ash content

PS and PP basically constituted into volatile and ash portion. The volatile portion is composed of the combustible organic material while the ash part is composed of inert inorganic such as additives of plastics polymer and possibly contaminants. The ash contents of the samples were determined. Approximately 200mg of the shredded samples were ignited in a muffle furnace at 550°C for 20 minutes. After cooling, the residue was taken as the non-combustible ash, and calculated as a percentage of the oven dried weight of samples. Each sample was tested for 5 times. The results are summarized in Table 3.2, while diagrams of the ash contents after combustion are shown in Figure 3.4.

Table 3.2 Ash content and volatile material from the plastic waste samples

Sample	Ash content, dry weight (%)	Volatile Material, dry weight (%)
PE	± 1.95	98.05
PS	± 0.24	99.76
PP	Negligible	100.00

Figure 3.4 Photographs of waste plastic ash content

3.2.3 Ultimate analysis

The chemical compositions of the sample polymers were determined by a Perkin-Elmer Series II CHNS/O elemental analyzer 2400. The elemental analyzer is a self-contained, microprocessor-controlled and capable of simultaneous determination of carbon, hydrogen, sulphur and oxygen. The process of sample analysis consists of a series of automated steps: combustion and reduction, homogenization of product gases, separation and detection. The average results from the elemental analyzers and the C/H ratios by weight and moles are presented in Table 3.3. Trace amounts of sulphur and nitrogen elements were detected. This could probably be due to the contamination by organic compounds (food substances) attached to the surface of the polymer samples during their useful life.

Table 3.3 CHNS compositions of sample polymers presented in % dry weight

Element (weight %)	PE	PS	PP
C	82.5	91.2	84.8
H	17.6	9.3	18.1
N	1.6	1.5	1.9
S	1.8	0.9	1.8
C/H Ratio by weight	4.7	9.8	4.7
C/H Ratio by moles	0.40	0.82	0.40

The preliminary study of the target plastic samples of PE, PS and PP gives basic information on the plastic material particle density, volatile material content and their basic chemical composition. The basic information is served as a platform when evaluating the results of the pyrolysis product yield.

3.3 Thermogravimetric Study

Thermogravimetric study was carried out to understand the degradation kinetics during pyrolysis of the sample polymers. Isothermal and dynamic degradations of polymers were conducted in this study. The advantage of dynamic measurement is that all parameters can be obtained from one experiment. However, the strong correlation between temperature and degree of conversion requires a careful analysis of the sample temperature. This requires a lot of additional information concerning the heat transfer. Therefore, validation of dynamic measurements with isothermal measurement is necessary [60]. With that knowledge, isothermal measurements can be performed within the determined temperature ranges and kinetic parameters can be determined. These kinetics parameters can directly be used to describe isothermal decomposition processes and to design isothermal reactors [52].

The Thermogravimetric analysis was conducted using a TGA/FTIR system consisting of a Perkin-Elmer Thermogravimetric Analyzer (TG Analyzer, model TGA7) coupled to a Perkin-Elmer FTIR Spectrometer (Fourier transform infrared, model: Spectrum GX FTIR). When thermogravimetric analysis is coupled with gas-analysis instrument, the application can provide information on the type and quantity of gases evolved during polymer degradation [61, 62]. This equipment was used in the analysis of the thermal degradation and evolved gases products from the sample polymers. The coupled TGA/FTIR equipment used a specially designed accessory which was made up by a heated stainless steel gas cell. The evolved gases were led into the accessory through an inert heated transfer line. The temperature of both the cell and the transfer line was maintained at 155°C during the experiments in order to eliminate condensation.

Weighed waste plastic samples were placed in a small platinum dish. The sample weight varied from 4mg to 25mg. Different volume weight ratios of the sample polymer used to load into the TG's platinum pan disc resulted in these weight variations. As the weights of the sample were very small and relatively light, heat and mass transfer effects can be reasonably ignored [63]. After the plastic samples had been loaded into the platinum disc and hoisted to the target position a small furnace was then raised to the platinum disc position and brought to a predetermined temperature by application of an electric current. The waste plastics would rapidly be heated up to the required temperature. The dynamic thermal degradation of the plastics starts at 30°C and end at a temperature of 900°C. Higher end temperature was used to ensure full degradation of the sample polymer. The heating rates for all dynamic experiments of the 3 type of waste plastic samples were shown in Table 3.4 and Table 3.5 list the general heating programs for isothermal analysis.

Table 3.4 Heating rates for dynamic thermal decomposition

Sample Types	Heating Rates					
Plastic samples	1°C/min	5°C/min	10°C/min	20°C/min	30°C/min	50°C/min

Table 3.5 Heating programs for isothermal decomposition

Initial temperature starts at	Heating rate to 300°C	Heating rate after 300°C to target temperature	Hold time after reaching target temperature
25°C	10°C/min	5°C/min	1 hour
Temperature Range			
300°C 350°C	400°C 450°C	500°C 600°C	700°C 900°C

The sample weight was recorded against time and temperature at 2 seconds intervals to produce the thermogram (TG). Pyris proprietary software was used to calculate the rate of weight loss against time and temperature, the derivative thermogram (DTG).The temperatures at the start, maximum and end of peaks in the DTG were then found using the Pyris software, together with the percentage mass loss during each peak. During the heating of the waste plastic samples, the atmosphere around the furnace was fluxed by nitrogen at a flow rate of 20.0ml/min. Nitrogen act as the carrier gas sweeping the pyrolysis gaseous products to the Infrared (IR) Spectrometer for analysis. Gram Schmidt profile, Specific gas profile and absorbance spectrum averaged over specified time duration can be obtained using the software available in the IR spectrometer.

3.4 Experimental set-up

A batch run Integrated Horizontal Batch Pyrolysis Reactor (IHBP) reactor was set up to carry out the pyrolysis of the targeted plastics waste samples. A schematic representation of the apparatus used is shown in Figure 3.5. It comprises of the furnace reactor system, condensing system, the sample collection units and the piping, valves and fitting system.

The furnace reactor system comprises of a Lenton tube furnace, LTF 12/50/300 and a pyrolysis chamber. The single zone wire-wounded heating element can achieved up to a maximum temperature of 1600°C. The specifications of the Lenton tube furnace is given in Appendix B. The pyrolysis chamber consist of 595 mm length 48 mm external diameter and 42 mm internal diameter Schunk , Alusik-90 2A high temperature open ceramic tube with both ends secured air tight with stainless screw capping and high temperature rubber O-rings. Plastic samples are feed into a narrow cylindrical stainless steel container within the ceramic tube as illustrated in Figure 3.6 which also shows the effective heating zone. Figure 3.7 exemplify the delay between the program temperature and the actual temperature experienced by the plastic samples.

A BÜCHI Recirculating Chiller B740 and a BÜCHI Glass Condenser unit are used for condensing and collection of the pyrolysis oil product. Water at 5°C is used as the coolant. Water is pumped from the chiller to the bottom of the condenser unit and received back from the top of the condenser to preserve effective and efficient heat exchange. As the hot mixtures of gaseous hydrocarbons flow along the circulating glass wall, thermal energy is lost causing condensation of these gaseous hydrocarbons along the inner surface of the circulating transportation tube. These condensed liquid hydrocarbons then flow slowly down via the slopping glass tube to the bottom of the condenser unit for collection.

Swagelock Grade 316 Stainless Steel tubings with outer diameter of quarter inch and nominal wall thickness of 1mm were used for interconnecting the IHBP reactor. Platon gas flow meter with a flow range of 0.2 to 2 mL/min was set to 0.2 mL/min to regulate the flow rate of the nitrogen carrier gas from NOX Pte Ltd (Singapore). IBEDA flashback arrestor, model GG EN730-1 was also installed as a safety measure against the possibility of pressure built up in pyrolysis chamber. Nuts and ferrule sets connecting the system were from Hy-Lok while the open/close valves were from BOLA-TEK, WOG1000 CFM with NPT threading.

Figure 3.5 Schematic diagram of the integrated horizontal batch pyrolysis (IHBP) reactor

Figure 3.6 Furnace temperature program during operation of IBHP reactor

Figure 3.7 Pyrolysis chamber containing plastic waste samples and temperature gradient along pyrolysis chamber

3.5 Operating procedures of the IHBP reactor

The experimental studies carried out using the IHBP reactor followed a set of standard operating procedures. The operating procedures were followed strictly to ensure repeatability and reliability of the pyrolysis results to minimize discrepancies. An operation checklist was used to ensure procedures were strictly adhered to. The operating procedures were grouped into four phrases as illustrated in Figure 3.7

Figure 3.8 Work flow diagrams of standard operating procedures of the IHBP reactor

Phase 1: Setting up of the IHBP reactor

Prepared plastic samples were fed into the steel container which in turn were inserted into the ceramic tube such that the plastic samples were positioned in the effective heating zone. Both ends of the ceramic tube were then sealed by tightening the screwed stainless steel caps, forming the pyrolysis chamber. The inlet of the pyrolysis chamber was the attached and secured with the fittings from the incoming carrier gas piping while the outlet of the pyrolysis chamber was coupled with the inlet of the BÜCHI gas condenser unit. Gas sampling bag was finally attached to the end to the IHBP reactor for sampling. The next step was to check for leakage and blockages in the IHBP reactor to ensure zero oxygen environment and smooth transportation of gaseous pyrolysis products to its correct destination. Once all these have been done, the IHBP reactor set up has

been considered completed. A pyrolysis experimental record sheet is shown in Appendix A to facilitate the reactor set up.

Phase2: Running operation of IHBP reactor

Once the reactor set-up had been completed, the temperature program was keyed into the temperature controller. The furnace was to increase its temperature from the current temperature to 350°C at a heating rate of 10°C/min. When the temperature reached 350°C, the gas sampling bag is attached to the sampling point for collection of the uncondensed pyrolysis flue gas. The collection of the gas sampling window lasted from 350°C to the target temperature. After which the excess gas from the pyrolysis chamber would be vented off. It would then increase at 5°C/min to its target temperature. The system was held at the final temperature for an hour to counter for any delay effects, Figure 3.8 After which the system is left to cool down for 24 hours.

Phase3: Collection of the pyrolysis product for analysis

After the experiment had been completed, the gas sampling bag was retrieved and was left at room temperature for at least 24 hours for the gas mixture within the sampling bag to mix thoroughly. Liquid hydrocarbon that was condensed and collected from the condenser units was poured into a small glass container and weighed. Heavier liquid hydrocarbons of darker color that were found inside in inner surface of the pyrolysis chamber were also carefully extracted with pipette. The liquid hydrocarbons were then diluted with methylene chloride and stored at 5°C before analysis. Solid residues were scraped from the stainless steel container.

Phase 4: Cleaning of the IHBP reactor and preparation for new set up

After the collection of the pyrolysis products, components and parts of the IHBP reactor were cleaned to ensure there is no bring-over contamination to the subsequent runs. Stainless steel container and the ceramic tube were placed in the tube furnace and heated up to 900°C for 20 minutes to burn off contaminants attached to their surfaces. Left over carbon was scaped off during washing. Methylene chloride was used to dissolve and clean the hydrocarbon products that were attached onto the inner surfaces of the condenser glass walls after collection. The condenser unit was then placed in an oven at 110°C for 30 minutes to ensure the condenser was free from organic solvents. Methylene chloride was also used to clear blockages found in the pipers and fittings of the IHBP reactor. Once all components have been cleaned, they were ready for the next run of the pyrolysis experiments. Generally, the standard operating procedures are adhered strictly to preserve repeatability and reliability of the experimental results.

3.6 Pyrolysis Study

The experimental studies on pyrolysis can be grouped into 3 different parts. The first part was the pyrolysis carried out on the clean plastic samples at different temperatures. This experiment was carried out to provide a reference platform for comparison between single clean plastic pyrolysis, mixed plastic pyrolysis and contaminated mixed plastic pyrolysis studies. The second part of pyrolysis runs focused on the effects of mixed plastics pyrolysis. The aim was to find out if there was any optimum interaction in the product yield during pyrolysis. This would provide valuable information on the necessity for sorting of PCP later in large scale applications. The final pyrolysis runs aimed to investigate the impact of food contaminations on the mixed plastics. The plastics mixture was mixed with synthesized food waste consisting of salt, oil and water. This approach simulated the actual contamination frequently found in PCP. The information served to provide relevant data to seek the need of preliminary washing prior to pyrolysis

in industrial scale operations. Table 3.6 summarizes the operating temperatures and the plastic mix ratios for the pyrolysis studies carried out in the different group studies.

Table 3.6: Feedstock compositions for pyrolysis studies

Feedstock	Temperature (°C)	PE	PP	PS
PE450	450	100	-	-
PE650	650	100	-	-
PE950	950	100	-	-
PP450	450	-	100	-
PP650	650	-	100	-
PP950	950	-	100	-
PS450	450	-	-	100
PS650	650	-	-	100
PS950	950	-	-	100
Mix 1:1:1 (mix)	950	33	33	33
3PE:1:1 (3PE)	950	60	20	20
3PP:1:1 (3PP)	950	20	60	20
3PS:1:1 (3PS)	950	20	20	60
Contaminated mix	950	33	33 (5g)	33 (5g)
1:1:1 with 16% food		(5g)	Salt	Water
contamination		Oil	(1g)	(1g)
		(1g)		

3.7 Analytical methodologies

In each experiment, gas, oil and solid residue were obtained as pyrolytic products. The gas and oil products were analyzed by Gas Chromatography coupled with Flame Ionized Detector (GC-FID) and Gas Chromatography Mass Spectrometry (GC-MS) respectively. Analytical methods and procedures were developed for evaluating the liquid and gaseous products using Gas Chromatography. The

decisions for selection of the appropriate apparatus and components are summarized in Table 3.7

Table 3.7 Method development for gas chromatography

Procedures	Gaseous Products	Oil Products
Step 1:	Gaseous Compositions	Oil Compositions
Determine Goal of Analysis		
Step 2: Component Selections		
Detector	Flame Ionized Detector	Mass Spectrometry
Column	Agilent J&W GS-Alumina	Agilent J&W DB-1
Injection Method	Manual Injection	Automatic Liquid Sampler
Step 3: Calibrations	National Oxygen Pte Ltd. Standard Gas	Manual preparation
Step 4: Temperature Program	Figure 3.9	Figure 3.10
Step 5: Sample Preparation	Direct from Tedlar Bag through gas syringe	Dilution with Methylene Chloride
Step 6: Analysis of Sample

Figure 3.9 Temperature program for gas analysis using GC-FID

Figure 3.10 Temperature program for oil analysis using GC-MS

3.8 GC-FID calibration

It was found that peak areas based on FID were roughly proportional to the weight of the unoxidized carbon in the component detected [64]. Standard of known concentrations would generate signals which were interpreted as the measured area counts. Generally, higher concentration compounds would correspond to larger area counts.

Calibration curves are plotted with area count against its concentration in parts per million (ppm). It was observed that for all gases, the behavior trend of the calibration points at lower concentration was different from that of the higher concentrations. As such the calibration of each standard gas was divided into 2 parts namely the lower and upper calibration curve. Figure 3.11 and Figure 3.12 show the methane calibration curves. For each concentration there were at least 5 points and the standard errors were shown. Using the equation of the trendline for the calibration curves concentration-area conversions are generated and used to calculate the actual concentration of the gaseous products from the pyrolysis experiment. The calibration curves of other selected gases can be found in Appendix D.

In this study, standard gas mixtures were used to generate the calibration curves. The standard gas mixtures were obtained from National Oxygen Pte Ltd in pressurized cylinders (2000 Psi/7.6m³) with blending tolerance of $\pm 5\%$. Compositions of the standard gas mixture can be found in Table 3.7 For the gas calibrations, the standard gas mixtures were filled into a 3 liter *SKC series 232* Gas Sample bag at atmospheric pressure. Using a *SGE Australia* 100 μ L gas tight syringe, sample gas is withdrawn and injected manually into GC-FID. Volumes of 10 μ L to 500 μ L were injected and areas were obtained. Hewlett Packard 5890 series II plus Gas Chromatograph coupled with FID is utilized for both calibrations and analysis of the pyrolysis product. Constant switching in columns resulted in column cutting

and different positioning of the column due to new installation. These resulted in shifting of retention time of the target compounds. As such calibration checks were always performed prior to analyzing the pyrolysis products to counter any possible discrepancies. Hewlett Packard Chemstation software then directly interprets and calculates the mass of the sample injected using the calibrated data as reference.

Table 3.8 Standard gas mixture composition for calibration gas

Component	Gas Concentration (ppm/ mole percent)
Methane	20,000 / 2
Carbon Monoxide	20,000/ 2
Ethylene	15,000/ 1.5
Ethane	5,000/ 0.5
Propane	5,000/ 0.5
Propylene	5,000/ 0.5
1- Butene	5,000/ 0.5
1,3 Butadiene	5,000/ 0.5
Nitrogen	Balance/ 92%

Figure 3.11 Methane calibration curve for lower concentration using GC-FID

Figure 3.12 Methane calibration curve for higher concentration using GC-FID

3.9 GC-MS calibration

Calibration of the Mass Spectrometer (MS) is required to perform quantitative analysis on the pyrolysis oil products. Calibration standards of known concentration and the area under their corresponding peaks in the Total Ion Chromatogram (TIC), a mass/area conversion factor are determined. TIC is a plot of sum of the abundances of all mass peaks at each time or scan number as a function of time. Similar to gas calibration curve of GC-FID, the GC-MS curves plot abundance against mass of component. Large numbers of hydrocarbon compounds are speculated to be detected and identified by GC-MS. However it would not be efficient and feasible to quantify all identified products. Furthermore some of the compounds might not have any economical value for recovery. Therefore only certain hydrocarbon compounds of interest were quantified.

The hydrocarbons compounds selected for quantification were generally divided into two main classes namely the aliphatic and aromatic groups as listed in Table 3.9. There were at least 5 calibration points for each mass and the calibration curves were produced to cover the range of expected product mass results for all the pyrolysis experiment. Standards of the target compounds were produced at different concentrations.

The calibration standards were prepared by using methyl chloride (Dichloromethane) as the solvent. They were prepared by adding known quantity of the calibration material of high purity to methyl chloride. A 10 μ L auto-sampler liquid syringe was used to inject 1 μ L of solution into GC-MS for analysis. Similar to GC-FID, Hewlett Packard Chemstation software for GC-MS was used to interpret and calculate the mass of the sample injected using the calibrated data as reference. Figure 3.13 shows standard benzene calibration curves, and it was observed that all liquid calibration curves exhibited a linear trend. Liquid calibration standards were produced to determine the quantity of possible

products in the pyrolysis oil. The parameter settings of the Mass Detector can be referred in Appendix C.

Figure 3.13 Standard calibration curves for GC-MS aromatics

Table 3.9 Compound of interest in the analysis of pyrolysis liquid

Chemical	Formula	Specific Density	Boiling point (°C)
Benzene	C_6H_6	0.8787	80.1
Toluene (Methylbenzene)	C_7H_8	0.866	110.6
m- Xylene (Dimethylbenzene)	C_8H_{10}	0.8684	139.3
O- Xylene	C_8H_{10}	0.8801	144.0
p- Xylene	C_8H_{10}	0.86104	137.5
Ethylbenzene	C_8H_{10}	0.866	136.25
	$C_6H_5C_2H_5$		
Styrene (Ethenylbenzene)	C_8H_8	0.9059	145.5
(vinylbenzene)	$C_6H_5CH=CH_2$		
Indan (2,3-Dihydro-1H-idene)	C_9H_{10}	0.9639	177
Indene (Indonaphthene)	C_9H_8	0.9968	182
Naphthalene (Naphthalin)	$C_{10}H_8$	0.9628	218
(naphthene)			

3.10 Sample preparation

No contaminants or dirty particles were observed visually from the condensed pyrolysis oil and it was important since samples must be clean to achieve good chromatography results [65]. The condensed pyrolysis oil was relatively clean as the contaminants were left as residues in the ceramic tube and were too heavy to be carried away by the carrier nitrogen gas. 200 μ L of the condensed oil samples were dissolved in 25 mL of methylene chloride. Methylene chloride was chosen as the solvent because it has high vapor pressure and do not react with the solute. The liquid mixture was first agitated for 24 hours to ensure uniform dissolution of the oil sample in the solvent (Methylene Chloride). The samples were then transferred into a 5mL fiber glass valves and keep at 5°C in a large refrigerator. Before analysis, the prepared sample would then be placed on a shaker again for an hour. This was to ensure that the sample liquid reached room temperature and achieved uniform distribution. After which the samples were put in order and

injected to GC-MS by Agilent 7683 Series Automatic Liquid Sampler. For each experiment run of the pyrolysis reactor, the pyrolysis gases after passing through the condenser and silica gel were collected using a 100 liter Gas Sample bag. No sample preparations were required. Gas tight syringe was used to retrieve 100 μL of the collected gas and the sample gases were injected directly into the GC-FID for quantitative analysis.

3.11 Bomb Calorimeter set-up

A Bomb Calorimeter was used to evaluate the heating values of the pyrolysis oil product. Generally, this device burns a fuel sample and transfers the heat generated into a known mass of water. From the measured weight of the fuel and temperature rise of water, the heating value can be determined using the first law of thermodynamics for control mass. Figure 3.14 shows the schematic diagram of the bomb calorimeter system used and Figure 3.15 illustrates the details of the bomb vessel within the system of the bomb calorimeter. The apparatus consisted of a precision mass balance for weighing fuse and fuel samples, an oxygen bomb, and the bomb calorimeter. Firstly, the pyrolysis oil sample in the cup and the fuse were weighed on the precision mass balance. After weighing, the cup was placed in a wire cradle which hanged from the top of the bomb vessel. The fuse wire was then attached between the two arms of this cradle and dipped into the fuel without touching the sides of the fuel cup. This assembly was placed inside the oxygen bomb, which consist of a rigid, constant volume, steel vessel. Following these, oxygen was injected into the oxygen bomb. The prepared bomb was placed in a stainless steel bucket with two liters of pure, deionized water and ignition leads are attached to the bomb. Care was taken that the bucket sat firmly on the grooves at the bottom of the bucket. Next, the calorimeter cover was closed and the combustion program was initiated. This cover has a hole that allows a precision thermometer and thermocouple to be lowered down into the water to measure the temperature changes. In addition, a small electrically driven paddle

wheel was engaged by a drive belt to stir the water and homogenize its temperature.

Figure 3.14 Schematic diagram of the complete bomb calorimeter

Figure 3.15 Schematic of the bomb vessel details

The sensible way to evaluate a fuel's heating value (HV) would be in terms of the energy it would produce per unit mass of fuel. Ideally, in a calorimeter, a carefully weighed liquid or solid fuel sample would be completely burned. All of the heat released would be conducted into a known mass of water. From the resulting rise in water temperature, the amount of energy released, the heating values can be determined using the following equations.

$$HV = \frac{\Delta J_{\text{water}}}{m_{\text{fuel}}} = \frac{(mC_v \Delta T)_{\text{water}}}{m_{\text{fuel}}} \quad (3.1)$$

However, in practice, there are complications which should be taken into consideration for calculation. The complications are accounted as follows;

$$HV = \frac{(mC_v \Delta T_{\text{corrected}})_{\text{water}} - \Delta m_{\text{wire}} HV_{\text{wire}}}{m_{\text{fuel}}} \quad (3.2)$$

Chapter 4

Results & Discussions

4.1 Introduction

Three plastic pyrolysis studies were conducted utilizing PE, PS and PP, in the food service industry for packaging. The primary focus of the first study was to understand the degradation behaviors of single plastic based on the pyrolysis temperature and heating rate. These data served as a reference to determine optimum temperature and heating rate for the IHBP reactor and for comparison with the results of the following two studies.

The second study on mixed plastic pyrolysis aimed to find the impact of mixed plastic interactions on the products yielded. It would provide important information for deciding the need of sorting, or extent of sorting plastic wastes prior to pyrolysis for large scale applications.

The third study focused on the impacts of common food (synthetic) contaminants on plastic pyrolysis. This study would provide as understanding on the pyrolysis products when food packaging plastics were pyrolyzed together with food left leftovers. This study would provide information on the necessary needs of pre-washing, or extent of pre-washing required prior to the pyrolysis of plastic wastes mixtures.

In each study, thermogravimetric analyses were carried. Overall yields of liquid and residue fractions were determined by the weight difference of the pyrolysis chamber and condenser unit. The yield of gas fraction was determined by mass balance. Gaseous composition and chemical composition of product were carried out by GC-FID and GC-MS, respectively. Calorific values of solid and oil product were carried out on bomb-calorific meter. All the results are discussed in this chapter.

4.2.1 Impact of temperature and heating rate on single plastics pyrolysis

Figures 4.1, 4.2 and 4.3 illustrate the thermogravimetric studies of degradation behavior under isothermal conditions for PE, PP and PS, respectively. It should be noted that only PP and PS achieved full degradation while PE only achieved 92% of degradation. This is probably due to the inorganic content such as additives and coloring admixtures, found in PE plastics polymers. The straight line in the weight lost (Y-axis) over a period of time (X-axis) shows minimal drop in mass. This clearly indicates that the applied temperature at 300 °C does not have sufficient energy to break up the carbon to carbon (C-C) bonds in the plastics polymers. As the pyrolysis temperature is increased to 350°C, weight loss is not significant in PE which is less than 5%, PP which accounted for 5% after 80 minutes, and PS which has a 15% loss in weight. The degradation behavior of PS compared to the other 2 polymers can be more clearly differentiated as the heating temperature is furthered increased to 400°C. PE achieves only 5% weight loss, PP achieves 12% weight loss and PS achieves almost 90% weight loss in 80minutes. The differences in weight loss behavior for PS with PE and PS may be explained by the decomposition mechanisms proposed by Cullis [41]. His study suggested that decomposition of PE and PP undergo only random-chain scission process. However, PS decomposition involved an additional end-chain scission which greatly enhanced the degradation process with lesser application of heat.

The experimental results in this study showed that all polymers tested underwent full degradations as the pyrolysis temperature increased to 450°C and 500°C with the fastest full degradation occurring in PS followed by PP and finally by PE. This probably showed that the bonding strength in PE polymers could be higher than the other polymers tested. The time difference

for full degradation at 500°C and 450°C was observed to be around 20 minutes while it was observed to be around 15 minutes for PP. There is no time difference for PS. The results suggested that it would not be operationally productive and economical to carry out pyrolysis of these polymers mixture under 500°C as it probably would requires more energy as a result of extended time required.

Figure 4.1 Isothermal degradations of PE at different temperature

Figure4.2 Isothermal degradations of PP at different temperature

Figure 4.3 Isothermal degradations of PS at different temperature

Figure 4.4 Yield distribution of single plastics at different pyrolysis temperatures

Figure 4.4 shows the variations of solid, liquid and gas distributions of the pyrolyzed polymer products at 450°C, 650°C and 950°C. The distributions were worked out from the weights of pyrolyzed solid and liquid products. The weight of the gas fractions were determined by mass balance.

From the mass distributions of PE at different pyrolysis temperatures, it was observed that the solid products decreased with increasing temperature. There was no liquid formed at 450°C. Liquid content of PE was observed to increase from 26% at 650°C to 36% mass at 950°C. Gaseous evolution of PE is found highest at 650°C with 63% mass.

For the mass distributions of PP, the solid residues mass reduced from 78% to 2% when the pyrolysis temperature increased from 450°C to 650°C. Beyond 650°C, there was no decrease in solid residues mass. Liquid mass increased slightly from 6.3% to 8.25% as the temperature increased from 450°C to 650°C. PP liquid mass distribution was observed to be highest at 950°C with 57.3%. Gaseous mass distribution was highest at 650°C achieving approximately 90%. Gaseous output was considered low at 450°C with 16% mass and achieves 40% mass at 950°C.

For the PS mass distributions, the solid residue content was the lowest among the three constituents. No solid residue was found at 950°C. Despite increasing mass content of liquid with increasing pyrolysis temperature, its composition is considered rather low. This phenomenon is probably contributed by the high gaseous output of PS.

From observations, it is interesting to note that the mass distribution of gas does not always increase with increasing temperature. Instead, the mass distribution of gas is highest from 450°C to 650°C. The mass distribution of gaseous output would then decrease again as temperature increased from 650°C to 950°C. This phenomenon was probably due to the secondary reactions within the reactor that caused the light carbon compounds that was initially broken up at a lower temperature to recombine again in the reactor to

become heavier carbon compound, explaining the drop in gaseous output at higher temperatures. This recombination of light carbon compounds was probably due to the design of the experimental pyrolysis reactor (IHBP reactor) where it did not readily allowed gaseous products to move out of the pyrolysis chamber. Generally, the overall behavior observed from PE, PP and PS was that pyrolysis would reduce the solid residue mass distributions and increase the liquid product distributions as the pyrolysis temperature increased.

Figures 4.5, 4.6 and 4.7 show the results of the derivative thermogravimetric studies. This study helps to evaluate and understand the impacts of heating rates and degradation behaviors on the selected polymers. Plastics polymers namely PE, PP and PS were pyrolyzed at 1°C/min, 5°C/min, 10°C/min, 20°C/min, 30°C/min, and 50°C/min. Figures 4.5, 4.6 and 4.7 are plots of weight loss and derivative weight loss against temperature.

Figure 4.5 Degradation behaviors of different heating rates of PE

Figure 4.6 Derivative weight loss (DTG) dynamic degradation of PE at different heating rate

Figure 4.7 Comparison between DTG of different plastics at 5°C/min

Figure 4.5 shows the degradation behaviors for the different heating rates on PE. The left inner most curves represents 1°C/min and the right outermost curve represents 50°C/min. It is clearly shown that the degradation of PE commences at a lower temperature of about 200°C for a 1°C/min heating, achieves 50% weight loss at approximately 440°C and reach full degradation at about 460 °C. However for heating rate at 50°C/min, initial degradation was very minimal from 200 °C to 400°C and it achieves 50% weight loss at about

515°C and finally reach full degradation with very little increase in temperature at about 525 °C . The observation showed that the temperature window for degradation reduces with decreasing heating rate especially before 50% weight loss is achieved. This phenomenon was also observed in the pyrolysis of PP & PS.

From further investigation, it is observed in Figure 4.5 that it requires only additional 10°C increase in pyrolysis temperature to reach 100% degradation at 450°C for 1°C/min heating rate when compared to an additional of 33°C at 548°C for 50°C/min heating rate. This observation showed that lower heating rates generate steeper degradation curves. This phenomenon is clearly observed in Figure 4.6 which plots the derivative weight loss of PE at different heating rates. The lower heating rate curves clearly reinforced that they require a shorter pyrolysis temperature window to reach full degradation when compared to those of faster heating rates.

Typically, all derivatives weight loss curves in Figure 4.6 show that the degradation rates are gentler at the initial stage and then slowly become steeper until the rate of weight lost reaches the peak degradation rate. The more gentle curves at the initial stage are probably due to the polymer molecules gaining the necessary kinetic energy where the breakdown of the molecules from the polymers is gradual. However, as the molecules gain more kinetic energy , they become more readily to be broken off from the polymer chain. This phenomenon is illustrated by a change from gentle slopes to steeper curves as the heating rates increase. Upon reaching the peak, the degradation rate abruptly reduced to zero as full degradation is reached very quickly at higher heating rates.

Figure 4.7 illustrates the derivative weight loss curves for PE, PS and PP at heating rate of 5°C/min. It is clearly shown that PS requires the smallest pyrolysis temperature window from 350°C to 450°C for full degradation to occur. This reveal that PS requires lowest heat energy application to achieve full degradation. PE and PP shared similar but larger pyrolysis temperature window from 350°C to about 500°C. This means that PE and PP needs higher amount of heat energy for full degradation. Similar pyrolysis temperature windows of PE and PP recommend the suitability and economics of pyrolyzing then together rather than with PS.

The rate of degradation is fastest in PS reaching the peak of 18% weight loss/min followed by PP at 16% weight loss/min and PE at 12.5% weight loss/min. Higher degradation rate is probably due to the double scission actions. More gradual slope in PP at the initial degradation process also exhibited the greater amount of energy requirement to trigger the degradation process in comparison with PE. However, the curves show that beyond this stage, the rate of degradation of PP would become higher. This slow down in PE degradations could be due to the presents of coloring agent or other chemical additives found in the PE samples..

4.2.2 Composition analysis of pyrolytic liquid for single plastic at different temperatures

The influence of temperature on the pyrolysis liquid yield distribution of single plastic waste was investigated in this study. Plastic wastes were pyrolyzed at 450 °C, 650 °C and 950 °C. The compositions were compared. Differences in the compound type and amount in the liquid yields were identified. Figure 4.8 illustrates a typical total ion chromatographs (TIC) of the pyrolytic liquid composition when a sample plastic was pyrolyzed. Each peak

in the TIC corresponds to a certain compound detected by the mass spectrometer when these compounds elute from the column at different retention time. These peaks are labeled in number and their corresponding chemical structure name, formula and molecular weight and the quality of match with the mass detector database is shown in Appendix E. The heights of peak in the TIC are measured by the abundance number representing the strength of signal identified by the mass detector. The greater the abundance number represents the higher is the concentration at the particular compound in the pyrolytic liquid sample. The quantity of the compound in the pyrolytic liquid is directly proportional to the area counts under the peak, producing a mass/area relationship with an appropriate conversion factor. Thus by integrating all the peak areas in the TICs by using the HP Chemstation software, individual compound concentration can be expressed as percentage of the total pyrolytic liquid composition by weight. These percentages are presented in the form of a bar chart to allow clear and reliable comparison of the product distributions and indication of statistical errors when evaluating the pyrolytic liquids.

Figure 4.8 Typical total ion chromatograph of PE's pyrolysis liquid yield

Figure 4.9 Liquid composition and constituent distributions of PE at 950°C

Figure 4.10 Liquid composition and constituent distributions of PE at different pyrolysis temperatures

Figure 4.8 shows a typical TIC for a PE pyrolytic liquid. The undulating peaks resemble an erlang bell curve distribution, with abundance number declining towards the end of the analytical window. Figure 4.8 shows that PE pyrolytic liquid produces a large number of saturated and unsaturated aliphatic hydrocarbons with 50 compounds (peaks) detected. This is probably because PE aliphatic molecular structure allows production of more intermediates during pyrolysis. Figure 4.9, shows the composition of the compounds, expressed as a percentage of the original weight of pyrolytic liquid analyzed. It should be noted that the number of compounds represented in the bar chart are less than the actual number of peaks shown in the TIC. This is observed in all the TIC and corresponding bar chart. This is because peaks with abundance number less than 5000 are regard as noise disturbance and therefore filtered away during calculations. Only peaks with abundance number more than 5000 are presented in the bar charts.

In general, PE pyrolytic liquid consists of hydrocarbon ranging from C_8 to C_{23} , showing a good mix of alkanes and alkenes. This highlights the potential of using PE pyrolytic liquid fraction as fuel which kerosene consists of hydrocarbons ranging from C_9 to C_{16} , and diesel fuel hydrocarbons range from C_{15} to C_{25} . Generally speaking, the compounds mass distribution is relatively uniform ranging from 6% to 10%. The small error bars highlighted the stability and consistency of the product compositions. This demonstrates that pyrolysis of PE is able to produce products of relatively high consistency, making it a potentially scaleable and economical process.

In the pyrolysis of PE at 450°C , no liquid was produced. Instead, white colored solids were found attached to the side of the pyrolysis chamber. The shredded PE waste melted and hardened during the pyrolysis process as the

energy supplied at 450°C was not sufficient to crack the plastic polymer into liquid form.

Figure 4.10 illustrates the chemical compositions of PE pyrolyzed at 650°C and 950°C. It was observed that PE produced a larger range of heavy hydrocarbons (C_{12} - C_{28}) products when pyrolyzed at high temperature as compared to the medium temperature. Each of these heavier hydrocarbons yield was less than 10% of the total composition in weight with small statistical errors. This demonstrates the high repeatability and consistency of product yields when PE is pyrolyzed at a high temperature of 950°C. PE pyrolyzed at 650°C produced lighter hydrocarbons ranging from C_6 to C_{12} . The major liquid product was cyclohexane. Fewer compounds were compiled for this medium temperature. It was observed that these hydrocarbon products contained high statistical errors indicating that the resulting products were neither consistent nor stable at 650°C. At higher pyrolysis temperature, Figure 4.10 showed that there are more heavy products formed when pyrolyzed at 950°C. This suggests that the light intermediates formed at 650°C most probably have recombined to form more stable and heavier compounds as the pyrolysis temperature increases. This shows that it is favorable for PE pyrolysis to be carried out at higher temperature to achieve more reliable resulting products.

In comparison with TIC for PE, Figure 4.11 shows that PP has fewer peaks, i.e., 21 aliphatic hydrocarbon compounds detected. This could probably be due to the propylene molecular structure that discourages the formation of more intermediate radicals. In association with the fewer peaks in the TIC for PP, the abundance numbers of the PP peaks are concentrated at peaks 3 and 6 as shown in Figure 4.11. Figure 4.12 shows that 2,4-Dimethyl-1-heptane is the

main products from the pyrolysis of PP. The bar chart clearly shows an uneven distribution with most compounds having less than 5% in weight. On the whole, propylene monomer contain methyl group which most likely influences the formation of methyl hydrocarbon products during pyrolysis. This is clearly shown in Figure 4.12 where most of the pyrolytic compounds contain n-methyl group. The bar chart also reports large amount of cycloalkanes identified in PP's pyrolytic liquid composition. Liquid compositions and constituent distributions of PP when pyrolyzed at 450°C, 650°C and 950°C are illustrated in Figure 4.13. 2, 4 Dimethyl-1-heptene is observed to be the dominant constituent standing 43% to 51% of the total liquid yield composition. Cyclohexane yields were found to be high at 450°C (22%) and at 650°C (28%) for pyrolysis of PP. However, almost negligible was detected in the yield of PP at 950°C. The low yield of cyclohexane is replaced by a larger range of hydrocarbon products that are not detected in the lower pyrolysis temperature. It should be noted that these special yields were mostly less than 5% in mass distributions.

Figure 4.11 Typical total ion chromatograph of PP's pyrolysis liquid yield

Figure 4.12 Liquid composition and constituent distributions of PP at 950°C

Figure 4.13 Liquid composition and constituent distributions of PP at different pyrolysis temperatures

The TIC from the pyrolysis of PS is illustrated in Figure 4.14 while Figure 4.15 shows the PS's pyrolytic composition make-up at 950°C. Both diagrams clearly show that the dominant product from the pyrolysis of PS is styrene monomer. This is probably because PS pyrolysis is controlled by intra-molecular transfer and PS itself has an aromatic structure that has a high bond energy making it very stable and very difficult to breakdown into other smaller compounds.

The bar chart in Figure 4.16 shows PS composition and constituent distributions when pyrolyzed at different temperatures. In general, besides cyclohexane, all the products are aromatic hydrocarbons. Unlike the large variations in the product distributions of PE and PP, the product distributions of PS pyrolyzed at the three different temperatures are very similar and consistent. Styrene is the dominant product from the pyrolysis of polystyrene comprising of 75 % at 650°C to up to 85% at 950°C. The results also showed that the largest styrene yield occurred at a temperature of 450°C. Benzene, (3-nitroropropyl) made up the second largest product for all PS pyrolysis temperature. It represents around 5 to 20% of the total liquid composition. The presence of nitrogen compound is probably due to the use of nitrogen as a carrier gas in the pyrolysis process.

Figure 4.14 Total ion chromatograph of PS's pyrolysis liquid yield

Figure 4.15 Liquid composition and constituent distributions of PS at 950°C

Figure 4.16 Liquid composition and constituent distributions of PS at different temperatures

4.3 Analysis of the liquid composition for mixed plastic pyrolysis

Plastic wastes collected in Singapore are usually are not sorted or cleaned. It greatly discourage the efforts of plastic recycling based on current technologies. It is currently a difficult task in recycling municipal post-consumer plastic wastes. These plastic wastes consist of several commodity polymers with various degrees of contaminations and damages [66] making their identification, separation and purification very challenging [10]. It is often necessary to separate mixtures of plastic wastes into respective categories in order to recovery useable plastics products, since certain plastics are not usable after re-processing [67]. This often requires additional investments on the separation technologies. Washing of municipal post-consumer plastics also produces secondary by-products such as wastewater. Thus efforts for separation and cleaning of these municipal

post-consumer plastics simply incur additional operation costs, making it economically unattractive. Day [68] commented that pyrolysis is a recycling technology particularly applicable to mixed and contaminated plastic wastes. It can convert these polymeric plastic wastes back to petrochemical feedstock, along with some carbonaceous char. Through pyrolysis, no sorting and washing of the collected post-consumer plastic wastes are required. Thus, thermal cracking (pyrolysis) of polymer wastes back to useful hydrocarbons is perceived as being an environmentally desirable and promising option for plastic recycling [69, 70]. In this chapter, the effects of mixed plastic compositions and contamination of plastics samples with synthetic food leftover consisting of oil, salt and water on the liquid composition of the pyrolyzed plastics are discussed. The liquid compositions would provide valuable fundamental information in verifying the feasibility of using pyrolysis technologies on unsorted and unwashed post-consumer plastic wastes. To study the effects of plastic wastes composition on the product yield, the three main plastics PE, PP and PS present in the MSW were selected. The plastics samples were shredded to a particle size of 3mm and the thermal decomposition was carried out in presence of nitrogen at a flow rate of 20ml/min. The pyrolysis temperature was set at 950°C to achieve full degradation of plastic feed. The plastics were mixed in different proportions as shown in Table 4.1.

Table 4.1 Plastic waste compositions tested in pyrolysis studies

Test Run	PE (% weight)	PP (% weight)	PS (% weight)
Mix 1:1:1 (mix)	33	33	33
3PE:1:1 (3PE)	60	20	20
3PP:1:1 (3PP)	20	60	20
3PS:1:1 (3PS)	20	20	60

The reference plastic mix had an equal distribution of PE, PP and PS. This mixture composition served as a control reference to distinguish possible yield differences from co-pyrolysis of other plastics mix. Figure 4.17 shows the solid, liquid and gas mass balance of the pyrolysis yield. 3PE:1PP:1PS yield was reported to show high solid residues which was probably contributed by higher chemical additives in the plastic sample. It was observed in 1PE:1PP:3PS mix that higher PS content promotes higher liquid yield. 1PE:3PP:1PS shows that the high content of PP probably inhibited the formation of liquid yield while it increased the yield of the gases output. Generally, very little difference was observed from the bar charts of solid, liquid and gas mass balance. Solid residues basically contributed to approximately 3-5% mass, liquid yields contributed to approximately 35 – 40% mass and gas contributed around 50-60% mass.

Figure 4.17 Yield distributions of mixed plastics

Figure 4.18 Liquid composition and constituent distributions of evenly mixed plastics

Figure 4.19 Liquid composition and constituent distributions of different mixed plastics

Figure 4.20 Weight percentages of selected chemicals from mixed plastics

Figure 4.18 shows the pyrolysis constituent distribution of 1PE:1PP:1PS plastic mix. Certain compounds were similar to those of single plastic pyrolysis. However the quantities yielded were different. New compounds were detected. This meant that co-pyrolysis of plastic mixture probably induced interactions with the free-radicals, influencing the formation of the yield composition. Figure 4.19 further point out the high dependency of plastic mixture composition on the co-pyrolysis distribution. The presence of high PE content favored the formation for alkanes and alkenes ranging from C_8 to C_{13} . Almost negligible content of the aliphatic was detected from the yield product of other plastic waste composition low in PE. The results agreed with Pinto [34] & William [71]. Their co-pyrolysis studies of plastic mixture were similar to the 3PE:1PP:1PS mix, producing liquid yields of a mixture mainly of aliphatic compounds.

In our study, the dominant liquid yield for 3PE:1PP:1PS was styrene monomer consisting of almost 50% mass. A difference of the yield products with Pinto [34] was probably due to the use of different the reactor design. The autoclave reactor utilized by Pinto probably encouraged the cracking of the alkane group from polystyrene's benzene ring. The IHBP reactor used in these studies only accumulated sufficient energy to break the polymeric bonds that bind the styrene monomers together. After which, the gaseous styrene monomers in the IHBP pyrolysis chamber were carried to the condenser unit for collection via nitrogen carrier gas. The data in Figures 4.12 and 4.19 highlighted that the presence of PE is likely to be responsible for the formation of chloroform in the co-pyrolysis of plastic mixture. However, further investigations would be required to verify this observation.

The presence of the methyl group on the PP polymeric structure probably contributed to the formation of large number of n-methyl hydrocarbons compounds. Several cycloalkanes and alkylcycloalkanes compounds were detected in the liquid yield of plastic mixture high in PP content. However, these compounds only present a small fraction of the total liquid yielded. Detection of these cyclo-hydrocarbons suggested that there were activities on the rearrangement of the intermediates after the initial break down of the PP structure. The dominant liquid constituent in 1PE:3PP:1PS was styrene monomer comprising of 42% mass. It was observed that 1PE:3PP:1PS had the lowest yield of styrene monomers suggesting possible inhibition on styrene by the increment of the PP ratio.

Higher PS content in the plastic mix resulted in a rise in the aromatic content in the liquid yield. This is illustrated by the high styrene monomers (67%), alpha-methylstyrene (4.5%), benzene, 1, 1' (1, 3-Propanediyl) (3%) and

benzene 3-nitropropyl (14%) as shown in Figure 4.20. The figure also highlights that the increase in PP and PE content probably inhibited the aromatic hydrocarbon yield. In general, the presence of PE favored formation of aliphatic hydrocarbons (alkanes & alkanes), while PP increased the n-methyl group and cyclo-hydrocarbon content and PS led to higher aromatic compositions.

4.4 Analysis of the liquid composition yields on mixed plastics pyrolysis with salt, oil and water as synthesized food contaminants.

Many research studies done on the pyrolysis of plastic wastes were based on clean virgin plastics. However very little research data are available on the pyrolysis of contaminated plastics. This study explored the yield products of plastic wastes contaminated by oil, salt and water. These mixtures were used to simulate the actual food contaminations adhered onto disposed plastics utensils in the food service industries. A yield distribution of the synthesized contaminated plastics was compared against the yield distributions of clean plastic mix. The contaminated plastics samples were prepared by mixing 1g of salt, 1g of oil, 1g of water and mixed thoroughly with 5g of PE, 5g of PP and 5g of PS. Figure 4.21 shows the solid, liquid and gaseous product yield distributions of a clean evenly mixed plastic sample and the contaminated mixed plastic sample. Result show that the gaseous yields remained almost similar. Higher solid residue accompanied by lower liquid yield in the contaminated mix yields was probably contributed by the inorganic content in the contaminants.

Figure 4.21 Yield distributions for clean and contaminated mixed plastics

Figure 4.22 Liquid composition and constituent distributions of clean and contaminated mixed plastics

It was observed that the synthesized food contaminants did not favor the yield of liquid and gas. Instead higher content of solid residues was formed within

the pyrolysis chamber. Unlike the solid residues of clean mixed plastics which were black and powdery, the solid residues of the contamination mixed plastics were black crystallized lumps with glossy and shiny surfaces. The crystallized solid residues are likely to be a mixture of melted salt and black carbon. Figure 4.22 illustrates that the mixture of oil, salt and water contaminants enhanced the yield of aromatic products. Increase in styrene composition from 56% to 63%, toluene from 3.5% to 7.5%, alpha.-Methylstyrene from 3.3% to 3.6% and the detection of naphthalene were observed. It implies that the contaminations probably have a catalytic effect on the aromatic yield. In general, the total compounds detected in contaminated plastics were lower. The results demonstrated that the catalytic effect of synthesized food contaminants on aromatic yield possibly inhibited the yield of other alkane and alkene compounds.

4.5 Gas product analysis

Table 4.2 showed that fluidized-bed reactor produced greater amount of gases at a lower pyrolysis temperature than the batch reactor used in this study. It might be because the fluidized media are able to provide more uniform and effective heat transfer to the plastic samples. It could mean more savings in operational and energy costs. The result showed that the pyrolysis of PP generated greater gas yield for both reactors than that of PE. This is contributed by the larger quantity of methane, ethane and propylene formed.

Figures 4.23 and 4.24 give a good visual description on the non-condensable gas yield. The bar charts show that methane, ethane, ethylene and propylene contribute to the main composition of the gas yield. PE gas yield shows higher

content in ethylene, propane, 1-Butene and 1,3 Butadiene yield while PP gas yield show higher content in methane and propylene yield.

Table 4.2 Comparison of target gas yields from IHBP and fluidized-bed reactor

Temperature	IHBP reactor		Fluidized- bed reactor [58]	
	900°C		510°C	
Sample	PE	PP	PE	PP
Methane	0.12	0.81	0.19	0.42
Ethane	0.13	0.39	0.34	0.9
Ethylene	0.34	0.61	0.46	0.37
Propane	0.08	0.05	0.44	0.45
Propylene	0.29	1.98	0.53	3.5
1-Butene	0.09	0.01	0.032	1.0
1,3 Butadiene	0.03	0.06	0.035	0.0081

(Yields are expressed as weight % of feed)

Figure 4.23 Gas composition and constituent distributions of single and mixed plastics

Figure 4.24 Relative distributions of target gas yield

It is observed that although propane, 1-Butene and 1,3 Butadiene were detected, they presented a small component of the gas products in all plastics mixtures. The cracking of plastic waste polymeric structure at high temperature probably favors the formation of the lighter gaseous hydrocarbons and discourages possible secondary reactions from taking place. This prevents formation of heavier compounds. Generally, propane, 1-Butene and 1, 3 Butadiene generated were observed to be less than 5% mass each. Figure 4.23 showed that the increase in PE and PS content in the evenly mixed plastics did not inflict much change in the gas yield compositions.

Figure 4.24 shows that propylene productions is the highest followed by ethylene and methane. The generation of propylene is particularly high in 3PP:1PP:1PS plastic mix. This suggests that the co-pyrolysis of PP with PE and PS not only have catalytic effect on the quantity of propylene produced

but PP also suppressed the formation of other gases, especially to methane, ethane and ethylene. However further verification on this phenomenon is required. It is observed that the oil, salt and water contaminants displayed inhibition effects on propylene formation but encouraged the formation of methane.

The pyrolysis gas yield in Figure 4.23 agrees with Walendziewski experimental results [50]. Walendziewski reported that 70-80% of the pyrolysis gases from mixed plastics generated were from C_1 to C_3 hydrocarbons. Liquid and gas pyrolysis products showed high dependency on plastic mixture composition.

4.6 Evaluation of energy content of plastic samples using bomb calorific meter

Table 4.3 shows the energy content of the different pyrolysis products obtained under varying plastic mix and temperature combinations. The calorific values of most condensed liquids from the pyrolysis process are above 40MJ/kg. It was observed that the energy values were comparable to that of the original plastic samples before pyrolysis. These products have high content of hydrocarbons, which represent greater flexibility and convenience in applications and further processing for higher quality fuel. It was observed that the values of the energy content of PP450, PP650 and PP950 were close. It was observed that low temperature pyrolysis of PE, PP and PS produced solid fuel with very high calorific values.

Higher pyrolysis temperature produced more liquid products. The liquid products generated from pyrolysis at 650°C and 950°C contain high energy values, while the solid residues were found to have very low energy content. However, when the plastic samples were pyrolyzed at lower 450°C, most of

the products were in the form of solid residues which retained most of the calorific energy. Liquid products from co-pyrolysis of mixed plastics of varying ratios gave high calorific values averaging above 40MJ/kg. There are insufficient solid residues in the pyrolysis chamber to evaluate their solid residues energy content.

Pyrolysis liquid yielded from the contaminated samples gave a high energy content of approximately 44MJ/kg. It confirms that mild food contamination adhered onto the plastics surfaces do not affect the calorific energy content of the product yielded. The results suggested that the plastics waste collected from MSW does not require additional cleaning and washing pretreatments, which would be laborious, costly and time-consuming when energy recovery is the primary concern. In conclusion, pyrolysis can be considered as an attractive technology for energy recovery.

Table 4.3 Calorific values of samples measured by bomb calorimeter

Sample type	Gross heat energy (MJ/kg)
Raw plastics feedstock	
PE	45.945
PP	47.286
PS	48.811
Condensed pyrolysis liquid yield	
PE450	-
PE650	46.462
PE950	46.648
PP450	46.935
PP650	46.245
PP950	47.511
PS450	42.617
PS650	42.187
PS950	42.392
1PE:1PP:1PS	44.10
3PE:1PP:1PS	45.295
1PE:3PP:1PS	43.866

1PE:1PP:3PS	46.933
Contaminated 1PE:1PP:1PS	44.064
Solid residues	
PE450	42.749
PE650	16.768
PE950	2.853
PP450	46.513
PP650	-
PP950	-
PS350	41.687
PS450	41.784
PS650	-
PS950	-
Contaminated 1PE:1PP:1PS	7.38

Chapter 5

Conclusions & Recommendations

5.1 Conclusion

Three studies of plastic pyrolysis were conducted in this research work. The conclusions of each study are stated in point form in the following paragraphs.

The first study examined the impact of temperature, heating rate on the plastic degradations. Product yields from the pyrolysis products of three single plastics, namely, PE, PP and PS were evaluated. The conclusions are:

- In the thermogravimetric studies, it was observed that all degradations carried out at lower heating rate achieved lower initiation and completion temperature during thermal decomposition when the IHBP reactor was used.
- PS required less activation energy for thermal degradation, while PE and PP required about the same heat energy to initiate decomposition.
- At higher pyrolysis temperature, PP and PS generated more liquid yields while PE generated more gas yield.
- PE's pyrolytic liquid consisted of a good mix of alkanes and alkenes ranging from C₈ to C₂₃.
- PP's pyrolytic liquid yield consisted mainly of two chemicals namely 2,4-Dimethyl-1-heptane ranging from 42 to 50% in weight, and cyclohexane ranging from 22 to 28% in weight.
- Pyrolytic liquid from PS comprised mainly of only styrene monomer ranging from 75 to 90%.
- Trace amount of inorganic additives and coloring, approximately 5% in weight, were left behind from the degradation of PE.
- Solid residues reduced with increasing pyrolysis temperature.
- On the whole, the pyrolysis liquid yields of individual plastics showed low statistical error range demonstrating high repeatability and consistency.

The second study investigated the effects of co-pyrolysis of PE, PP and PP mixtures at different ratios on the liquid yield's chemical composition. The aim was to determine if there was a need to the sorting of contaminants if pyrolysis were to be used to recover resources from municipal plastic wastes. The conclusions are:

- The presence of higher PE portion favored the formation of aliphatic hydrocarbons.
- Higher PP ratio inhibited the formation of styrene.
- Higher PS ratio led to higher aromatic and liquid yields.
- Liquid and gaseous yield distribution demonstrated certain dependency on plastic wastes composition.
- Higher PP portion increased the n-methyl and cyclo-hydrocarbon content and the overall gaseous yield.

The third study investigated the difference in the pyrolyzed liquid yield distributions of contaminated mixed plastics with those of clean plastic mixtures. The mixed plastics are contaminated with synthesized food wastes, which are made from a blend of oil, water and salt. The aim was to understand the impact of common food contaminants on the composition of the pyrolysis liquid yields. The conclusions are:

- Synthesized food contaminants resulted in higher solid residue formed
- Synthesized food contaminants exhibited inhibition on the range of yielded products
- Synthesized food contaminants were found to increase the yield of aromatic compound

Other general observations made in the three studies include;

- Methane, ethane, ethylene and propylene were the major gaseous compounds detected.
- Cracking of plastic wastes at high temperature favored the formation of lighter hydrocarbon gas.
- Average calorific value of the pyrolytic oils measured by the bomb calorific meter was about 40MJ/kg.
- High calorific oils were produced at low temperature.
- No sorting and cleaning of municipal plastic wastes are required if primary objective is energy recovery.

5.2 Recommendations

Future works on the development of pyrolysis technologies to recover useful resources from the municipal plastic wastes are;

- Poor thermal conductivity and high energy requirement for PCP cracking made pyrolysis to be highly energy intensive and expensive. Some studies indicated that catalysts can lower pyrolysis temperature and improve product yields significantly. It is proposed to carry out investigations using a mixture of different catalysts, with diverse characteristics, at different stages of PCP cracking to enhance the overall pyrolysis product yield.
- Investigation on co-pyrolysis of municipal plastic wastes with more variety and greater blends of plastic mixtures. Research carried out in this study was practically done on only three plastic polymers namely PE, PP and PS, which are the major plastic wastes disposed today. However, the plastics found in the municipal waste stream are much more diverse with a

large variety of plastic wastes. The proposed study is a natural step to provide vital information on the possible products generated from the co-pyrolysis of a more diversified feedstock.

- PVC plastics are commonly present in the MSW stream. Chlorine present would contaminate the pyrolysis products eliminating or reducing the product for potential usage. It is proposed to conduct investigation on the integration of appropriate chlorine removal to the current pyrolysis system.

Chapter 6

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6.1 References

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Appendices

APPENDIX A: Pyrolysis Experiment Record Sheet

Experiment Record Sheet

Type of Sample Feed: _____
Data Code: _____

Date: _____

1. Assembling Reactor (Before Heating)

(a) Weight of Working Tube (WT) + 4 sample divider (4SD) = _____ g

(b) Weight of WT + 4SD + Total Sample = _____ g

Weight of actual sample Feed = _____ g

aluminium foil must not be included in weighing.

2. During Pyrolysis Operation

Checklist

- (a) Check for consistent flow rate of carrier gas _____
- (b) Check for leakage using soap bubble _____
- (c) Check for carrier gas bubble output at end of pipe _____
- (d) Switch on Condenser Unit _____
- (e) Program (idle mode) and run temperature Program (Run mode) _____
- (f) *Gas bag installation after temperature hit 350°C @ _____ min _____
- (g) * Gas bag Detachment @ _____ min _____ hours _____

Time start reactor: _____ Time install gas bag: _____ Time Detach gas bag: _____

3. After Pyrolysis Operation
feed _____

Type of sample

(c) Weight of WT + 4SD + Total Sample = _____ g **Code name:**

(d) Weight of front residue oil = _____ g

(e) Weight of back residue oil = _____ g

(f) Weight of condensed pyrolytic oil = _____ g

(g) Weight of recovered ash = _____ g

Weight % of Pyrolytic Product:

Total Liquid _____ %
Gas _____ %

Total Solid _____ %

Total

4. Post Test Analysis:

Checklist

a. GC-MS

1. Density of sample

2. Sample preparation: dilution with methylene Chloride 50uL/500uL/1mL

3. Analysis with GC-MS

b. GC-FID

1. Sample collection left 24 hours for well mixing

2. Analysis with GC-FID

c. Bomb Calorific meter

1. Liquid Sample

2. Solid/ Wax Residue

d. CHNS Analyzer

1. Liquid Sample

2. Solid/ Wax Residue

e. TG-FTIR with similar condition

f. ICP (oil/ash)

f. SEM (morphology study)

g. BET (Ash)

h. Particle sizing (Ash)

APPENDIX B: Specification of Lenton tube furnace, model LTF 12/50/300

Lenton Furnace Model : LTF 12/50/300		
Temperature Controller – Main Zone		808P
Temperature Controller – End Zone		-
Over Temperature Controller		-
Electrical Supply	Supply	1PH/1N
	Voltage	240 V
	Frequency	50-60Hz
	Maximum Power Rating	1800 Watts
	Power Setting (Factor Sets)	100%
Normal Weight		15Kg
Wiring Diagram		WD-2092

APPENDIX C: Parameter settings of Agilent 5973 Network Mass Detector

<u>Parameter Settings of Agilent 5973 Network Mass</u>						
<u>Detector</u>						
Solvent Delay : 4.8 EM Volts: Rel 1388						
min						
Acquisition Mode:						
Scan						
Start	Low mass	High mass	Scan Threshold	Sampling Rate	Scan/ Sec	
time				(2^N)		
4.8 min	50	550	150	2	2.94	
<u>MS Temp</u>						
<u>Total Ion Scale</u>						
MS Window 1 : 2 000 000						
MS Window 2 : 100 000						

APPENDIX D: GC-FID Standard Gas Calibrations

Figure D1: Ethane calibration curve for lower concentration using GC-FID

Figure D2: Ethane calibration curve for upper concentration using GC-FID

Figure D3: Ethylene calibration curve for lower concentration using GC-FID

Figure D4: Ethylene calibration curve for upper concentration using GC-FID

Figure D5: Propane calibration curve for lower concentration using GC-FID

Figure D6: Propane calibration curve for upper concentration using GC-FID

Figure D7: Propylene calibration curve for lower concentration using GC-FID

Figure D8: Propylene calibration curve for upper concentration using GC-FID

Figure D9: 1-Butene calibration curve for lower concentration using GC-FID

Figure D10: 1-Butene calibration curve for upper concentration using GC-FID

Figure D11: 1, 3 Butadiene calibration curve for lower concentration using GC-FID

Figure D12: 1, 3 Butadiene calibration curve for upper concentration using GC-FID

APPENNDIX E: Chemical composition of PE, PP and PS pyrolytic fractions**Chemical composition of PE pyrolytic liquid organic fraction**

Peak No.	GC-MS Tentative Chemical Structure	Formula	Molecular Weight	Match Quality
1	3-Buten-1-ol, 2-methyl-	C5H10O	86.07	12
2	Cyclohexane, methyl-	C7H14	98.11	43
3	Cyclohexene, 4-methyl-	C7H12	96.09	52
4	Toluene	C7H8	92.06	72
5	Cyclohexene, 4-methyl-	C6H10	82.08	93
6	1-Heptene	C7H14	98.11	90
7	Heptane	C7H16	100.13	22
8	1-Octene	C8H16	112.13	97
9	Octane	C8H18	114.14	72
10	1,3,5-Cycloheptatriene	C7H8	92.06	7
11	Cyclohexene, 3-methyl-	C7H12	96.09	78
12	1-Octene	C8H16	112.13	90
13	Cyclopentane, 1,2,3-trimethyl-	C8H16	112.13	38
14	1,8-Nonadiene	C9H16	124.13	64
15	1-Nonene	C9H18	126.14	97
16	Nonane	C9H20	128.16	91
17	1-Nonene	C9H18	126.14	95
18	Nonane	C9H20	128.16	90
19	1,12-Tridecadiene	C13H24	180.19	78
20	1-Decene	C10H20	140.16	96
21	1-Decene	C10H20	140.16	93
22	Octane, 2-methyl-	C9H20	128.16	40
23	Bicyclo [4.1.0] heptane	C7H12	96.09	52
24	1-Undecene	C11H22	154.17	96
25	Cyclopropane, 1-heptyl-2-methy-	C11H22	154.17	94
26	Undecane	C11H24	156.19	91
27	Ether, hexyl pentyl	C11H24O	172.18	50
28	Bicyclo [4.1.0] heptane	C7H12	96.09	52
29	1-Dodecene	C12H24	168.19	96
30	2-Dodecene	C12H24	168.19	96
31	Dodecane	C12H26	170.20	91
32	Dodecane	C12H26	170.20	91
33	Cyclohexane, methylene-	C7H12	96.09	49
34	6-tridecene	C13H26	182.20	95
35	Tridecane	C13H28	184.22	94
36	Pentane, 3-methylene-	C6H12	84.09	9
37	Cyclohexane, methylene-	C7H12	96.09	49
38	2-Tetradecene	C14H28	196.22	98
39	Tetradecane	C14H30	198.24	97
40	E-9-Tetradecenyl acetate	C16H30O2	254.22	78
41	1-Hexadecene	C16H32	224.25	91

42	Pentadecane	C15H32	212.25	97
43	9-Eicosene	C20H40	280.31	91
44	Hexadecane	C16H34	226.27	95
45	1-Heptadecene	C17H34	238.27	94
46	10-Methylnonadecane	C20H42	282.33	86
47	1-Octadecene	C18H36	252.28	81
48	10-Methylnonadecane	C20H42	282.33	64
49	1-Nonadecene	C19H38	266.30	60
50	Eicosane, 9-octyl-	C28H58	394.45	50

Chemical composition of PP pyrolytic liquid organic fraction

Peak No.	GC-MS Tentative Chemical Structure	Molecular Formula	Molecular Weight	Match Quality
1	1-Pentane, 2-methyl-	C6H12	84.09	90
2	2,4-Dimethyl 1,4-pentadiene	C7H12	96.09	78
3	Cyclohexene	C6H10	82.08	93
4	Heptane, 4-methyl-	C8H18	114.14	87
5	Cyclohexane, 1,3,5-trimethyl-	C9H18	126.14	91
6	1,3-Cyclopentanedione, 2,2-dimethyl-	C7H10O2	126.07	50
7	Cyclohexane, 1,3,5-trimethyl-	C9H18	126.14	94
8	Cyclopentane, 1,2,3,4,5-pentamethyl-	C10H20	140.16	23
9	Heptane, 3,3,5-trimethyl-	C10H22	142.17	59
10	2-Undecene, 4-methyl-	C12H24	168.19	46
11	1R, 2c, 3t, 4t-Tetramethyl-cyclohexane	C10H20	140.16	64
12	(2,4,6-Trimethylcyclohexyl) methanol	C10H20O	156.15	56
13	Cyclooctane, butyl-	C12H24	168.19	35
14	Cyclohexane, 1,1-dimethyl-2-propyl-	C11H22	154.17	46
15	3-Ethyl-6-heptafluorobutyryloxyoctane	C14H21F7O2	354.14	47
16	Phosphonic acid, dioctadecyl ester	C36H75O3P	586.54	37
17	2-Decanol	C10H22O	158.17	50
18	Cyclohexane, 1,2,4-trimethyl-	C9H18	126.14	38
19	Triallylsilane	C9H16Si	152.10	38
20	2-Tetradecanol	C14H30O	214.23	53
21	Cyclohexane, 1-ethyl-2-propyl	C11H22	154.17	38
22	1,1'-Bicyclohexyl, 2-propyl-,cis-	C15H28	208.22	46

Chemical composition of PS pyrolytic liquid organic fraction

Peak No.	GC-MS Tentative Chemical Structure	Molecular Formula	Molecular Weight	Match Quality
1	Cyclobutane, ethenyl-	C6H10	82.08	93
2	Toluene	C7H8	92.06	91
3	Styrene	C8H8	104.06	95
4	.alpha.-methylstyrene	C9H10	118.08	94
5	Benzene, 1,1'-(1,3-propanediyl)bis-	C15H16	196.13	91
6	Benzene, (3-nitropropyl)-	C9H22NO2	165.08	25
7	Benzonitrile, m-phenethyl-	C15H13N	207.1	38