

LAPPEENRANTA-LAHTI UNIVERSITY OF TECHNOLOGY LUT

LUT-School of Engineering Science

Master's degree Program in Chemical and Process Engineering

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PYROLYSIS OF HAZARDOUS PLASTIC WASTE

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ABSTRACT

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Pyrolysis of Hazardous Plastic Waste

Master's Thesis

2021

72 pages, 30 figures, 24 tables and 01 appendix

Examiner: Professor Tuomo Sainio
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Key words:

Pyrolysis, Halogenated plastic waste, WEEE, C&DW, Bubbling fluidized bed reactor.

In this study, the pyrolysis of expanded polystyrene, polypropylene/polyethylene, and high impact polystyrene plastic waste from WEEE (electronic & electrical equipment) and C&D (construction and demolition) are studied at various temperature (500-600 °C) using dolomite to determine the maximum liquid phase with minimum halogen content. The products are assessed by thermo gravimetric analysis, pyrolytic-gas chromatography mass spectrometry, X-Ray fluorescence analysis and gas chromatography flame ionization. Heating values are calculated by automated bomb calorimetry and differential scanning calorimetry. The outcome of the dehalogenation experiments exhibits lower halogenated contents with maximum liquid product at lower temperature and in the presence of dolomite additive.

ACKNOWLEDGEMENT

In the world of competition there is a race of actuality in which those are having will to come forward. Master thesis project is like a connection between theoretical and practical working. With this enthusiastic I joined this project. First, all the praises and gratitude to **Almighty ALLAH**, the omnipotent, the master of life and death, the ALL-Aware, who has knowledge of the most secret part of everything, the most merciful, who showered upon me blessings through thick and thin of my life and who blessed me courage, good health, company and support of good parents, teachers and friends to conceptualized, develop and complete my research, and bestowed me the opportunity and potential to make contribution to the existing ocean of knowledge.

Next to him are my parents, whom I am greatly obligated for me, brought up with love and inspiration to this stage. Without my parents I could not even think to reach that level of education, which I have today. I feel blessed and proud to have such parents. I am greatly thankful to my loving parents.

I am feeling oblige in taking the opportunity to sincerely thanks to my supervisors **Professor Tuomo Sainio** (LUT University) and **Muhammad Saad Qureshi** (Senior Scientist, VTT) for their continuous guidance, encouraging attitude, and motivation to complete this project timely. Their passion for imparting knowledge, unlimited patience and kindness has been a source of great motivation for me. Though I feel these lines are very small tribute indeed to all they have done for my academic as well as moral support.

I am greatly thankful to **Mr. Christian Lindfors** (Senior Scientist, VTT) for his corporation and support throughout my experimental work.

I am grateful to my prestigious and privileged **Mr. Alhalabi Tamer** (Research Scientist, VTT) for step-to-step guideline during whole experimental work.

I am overwhelmed to **Lab staff & attendant** of VTT lab. All of them open their doors every time, I need their guideline.

At last, I am appreciative to all my teachers and friends who have been always helping and encouraging me throughout the project. I have no valuable words to express my thanks, but my heart is still full of the favors received from every person.

Muhammad Hassam Khan

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List of Symbols & Abbreviations

ABS	Acrylonitrile butadiene styrene
ArX	Aromatic halide
Cd	Cadmium
CaBr ₂	Calcium bromide
CaCO ₃	Calcium carbonate
CaOHCl	Calcium hydroxide hypochlorite
CO	Carbon monoxide
C&DW	Construction and demolition waste
DBDPE	Decabromodiphenyl ethane
DSC	Differential scanning calorimetry
EEE	Electric and electronic equipment
EDX	Energy Dispersive X-ray spectroscopy
EU	Europe
FESEM	Field emission scanning electron microscopy
FCC	Fluid catalytic cracking
GC/MS	Gas chromatography/Mass spectrometry
GC/TOF-MS	Gas chromatography/time of flight-mass spectroscopy
GHG	Greenhouse gas
HCV	Higher calorific value
HHV	Higher heating value
HIPS	High impact polystyrene
HRGC	High resolution gas chromatography
HRMS	High resolution mass spectrometry
FeOOH	Iron (III) oxide-hydroxide
La ₂ O ₃	Lanthanum (III) chloride
LHV	Low heating value
LCV	Lower calorific value
MPa	Mega Pascal
NMR	Nuclear magnetic resonance spectroscopy
Pd	Palladium
PC	Poly carbonate
PBDD	Polybrominated dibenzo-p-dioxin
PBT	Polybutylene terephthalate
PCDF	Polychlorinated dibenzo furan
PCDD	Polychlorinated dibenzo-p-dioxin
PPE	Polyphenylene ether
PUR	Polyurethane
PVC	Polyvinyl chloride
PCBs	Printed circuit boards
Py-CG/MS	Pyrolysis gas chromatography mass spectrometry
PWS1	Plastic waste sample 1
PWS2	Plastic waste sample 2
PWS3	Plastic waste sample 3
NaBr	Sodium bromide

Na_2SiO_3

TG

TG-FTIR-MS

TX

Wi-Fi

WHO

XRD

Sodium silicate

Thermo-gravimetric

Thermo-gravimetric Fourier transform infrared
mass spectroscopy

Trace elemental instruments explorer

Wireless Fidelity

World health organization

X-Ray diffraction

1. INTRODUCTION

Plastics were first invented by Alexander Parkes in 1862. He introduced “Parkesine”, a first man-made plastic during an international London exhibition. Parkesine are commonly named as celluloid discovered during synthesis for substituent of shellac [1].

Plastics are also called as polymers because of their higher molecular weight formed by the repetition of simpler monomers. For example, the common and simplified expression of polypropylene (PP) is shown in Figure 1.

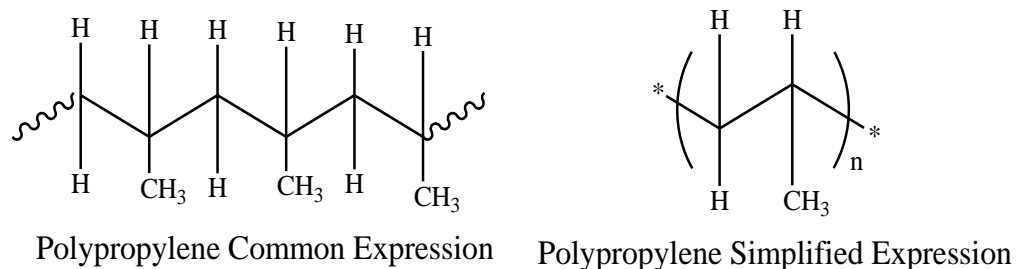


Figure 1: Chemical structure of polypropylene

The monomer for PP is in brackets where n subscript is used for number of repeating units for the polymer molecule.

SPI (Society of plastic industry) introduced identification code system for the division of plastic based on their chemical structure and specific properties. This code system was first introduced in 1988 to distinguish plastics for effective recovery. The code numbers are assigned specifically to the polymeric products possessing distinct properties [2]. Following are the seven groups of polymer groups based on their properties and applications [3].

- Polyethylene Terephthalate (PETE)
- High Density Polyethylene (HDPE)
- Polyvinyl Chloride (PVC)
- Low Density Polyethylene (LDPE)
- Polypropylene (PP)
- Polystyrene (PS)
- Others



Figure 2: SPI codes for various plastic products [3]

Plastic consumption around the globe is growing rapidly because of its numerous applications in our daily lives. Many industries are utilizing plastics because of their material properties and flexibility to tune them. Plastics are usually reusable, low cost, easy to manufacture, thermally and electrically insulative, versatile, flexible, and resistant to corrosion, chemicals, and water [4]. The life cycle of plastic is important to understand because not all the plastic products are same. Some products are single use while some are long life and used in products like parts of electrical appliances and automobiles. Many plastics have a lifespan of less than one year whereas some of plastics remain useable for more than 50 years. Hence different plastic products are used in different applications within their individual value chains. Therefore, quantity of plastic waste collected does not co-relate with demand of plastic within same year.

Among all the plastic produced and consumed around the world polyolefins are the most used plastics while the plastic containing halogen atoms such as PVC, and flame retardants are quite common. Apart from the usage of halogenated plastics, the plastic discharge as municipal solid waste (MSW), automotive waste, household waste (HHW), waste electrical and electronic equipment (WEEE), and hospital waste (HW) contain huge number of hazardous compounds that are detrimental to environment if left untreated [5]. Hence treatment of plastic waste is a need of time. Instead of recycling plastic, mechanically, which is already facing challenges like cross contamination, degradation of polymer, presence of non-polymeric impurities and additives, much more reliable methods for the conversion of plastic waste into sustainable energy reserves could be taken into practice to fulfill future energy demand [6].

Plastic waste conversion to sustainable energy resources can be done by breaking down the plastics using:

- Pyrolysis
- Incineration
- Gasification
- Plasma process
- Hydrocracking

Among all these methods, pyrolysis is one of the significant methods because maximum waste is converted into energy, decomposition occurs at lower temperature, and it is inexpensive [7]. Pyrolysis is termed as thermal degradation of long polymeric chain into smaller and lower molecular weight compounds. This process occurs without oxygen under heat and results into formation of gas, oil, and char as major products. The working principle of pyrolysis includes feeding of feedstock into the reactor and heating it in the absence of oxygen. The feedstock may be an organic material like plastic, wood, rubber, or plant based. Thermal decomposition of feedstock turned into small molecules and condensed into liquid phase is termed as pyrolysis oil.

In this thesis, pyrolysis of three different feedstocks i.e expanded polystyrene, polypropylene/polyethylene, and high impact polystyrene was performed at different temperatures ranges from 500°C to 600°C with or without dolomite as an additive to get maximum liquid yield having minimum halogen content. Based on starting material, mode of operation, and other operational conditions, various product phases such as liquid, char, wax, pyrolysis oil and pyrolytic gas were produced. The feedstock and products were characterized by TGA, XRF, Py/GC-MS, GC-FID and other characterizing tools and it was determined that pyrolysis at lower temperature resulted in higher liquid phase with lower halogens in it.

Background of Plastics

Plastic materials are broadly used man made materials, among the world from water bottles to electronic devices. The first commercial production of plastics in 1950 was 1.5 million tons and it reached 260 million tons in 2007 however, exponential increase up to 335 million tons of plastic production and consumption was observed in 2016 followed by 359 million tons in 2018 with expectations of triple increase till 2050 [8]. The rate of plastic production all over the world rises from 1950 to 2018 with a steady increase from 2008. Meanwhile in Europe, plastic production falls from 64.4 million tons in 2017 to 61.8 million tons in 2018 [9]. According to PlasticEurope-2020, in 2019 China contributed 31% of world’s plastic production (368 million tons) whereas Asia reached highest level of 51% for production of plastic. In Europe, plastic demand in 2018-2019 was 50.7 million tons of which packaging, building and construction industries was 39.6% and 20.4% respectively likewise automotive industry, electronic industry, household appliances and agricultural industry demanded 9.6%, 6.2%, 4.1 and 3.4% respectively.

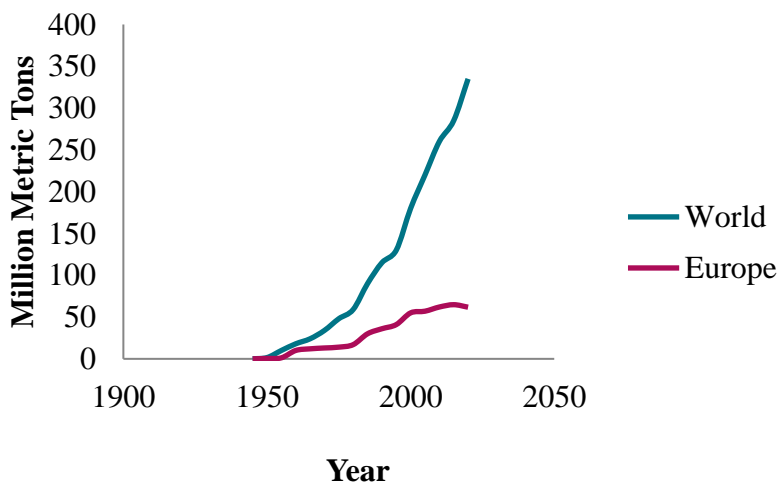


Figure 3: Global plastic production compared to Europe 1950-2018

Table 1: Plastic demand distribution based on resins.

Plastic	Demand %	Applications
PP	19.3	Packaging, hinged caps, automotive parts
LDPE	17.7	Reusable bags, trays, containers
HDPE	12.2	Toys, shampoo and milk bottles, housewares, pipes
PVC	10	Pipes, cables, profiles, wall and floor covering
PUR	7.9	Pillows, mattresses, insulating foams for fridges
PETE	7.7	Bottles for water, juices, soft drinks, cleaners
PS	6.4	Food packaging, building insulation, electronics, eyeglasses frames
Others	19	Optical fibers, hub caps, valves, seals, aerospace materials

Fossils and petrochemical feedstock are closely related with production of plastics [10]. The plastics industry is very much dependent on predetermined stocks of gas and oil, which makes up to 90% of its feedstock [11,12]. Hopewell et al [12] concluded that about 4% of global gas and oil generation is served as feedstock for plastic assembly whereas 3 to 4% fossil-fuel utilized as a source of energy for production of plastic. Geyer et al [8] reported that from global production of plastic, only 1% plastic is produced from bio-based and biodegradable sources per year.

1.1. Post-Consumer Treatment of Plastic Waste

The waste produced from plastic production reached 29.1 million tons around Europe in 2018 from which 42.6% of the waste was treated for energy recovery, 24.9% was treated inefficiently either open landfills, disposed in dumped or littered and remaining 32.5% recycled in useful products [PlasticEurope-2020]. If the same situation followed, it is predicted that 12 million tons plastic waste will end-up in nature or landfill till 2050 and 15% GHG emission from plastic waste [13, 14].

In Europe, 29.10 million tons of plastic waste was accumulated for treatment either by recycling, landfill or chemical treatment [Figure 4]. It is noticeable that export of plastic waste outside Europe fall by almost 39% from 2016 to 2018.

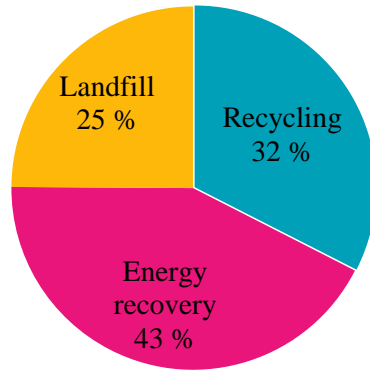


Figure 4: Treatment of plastic waste in Europe in 2018

2. LITERATURE SURVEY

2.1 Sources of Halogenated Plastic Waste

Waste electronic and electrical equipment, end-life-vehicle waste, and construction and demolition waste are source of numerous polymers and metals but also contain harmful elements. It comprises of 30% plastic most of which contains toxic additives, heavy metals (Pb, Hg, Cd etc), brominated flame retardant (BFR) like polybrominated diphenyl ether (PBDE), polybrominated biphenyls (PBB) and tetrabromobisphenyl A (TBBPA) that causes difficulty in recycling [15]. Actual composition of plastic in WEEE [Figure 5] revealed that larger portion of WEEE plastic constitutes of thermoplastic such as PP, PC, ABS and HIPS whereas remaining are present in lower proportion [16].

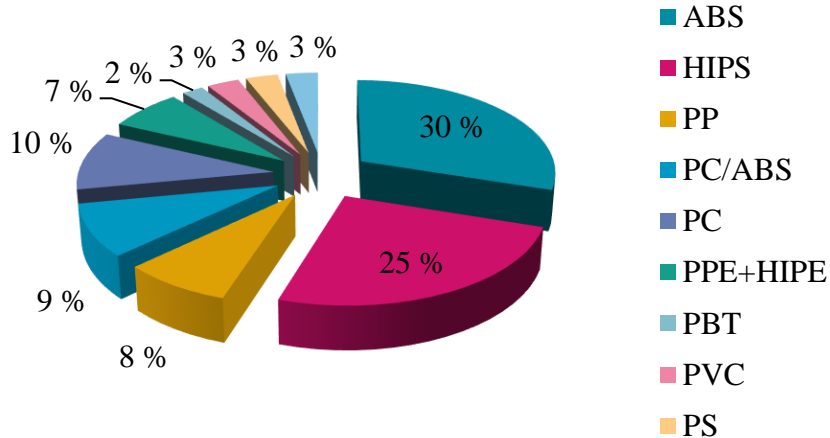


Figure 5: WEEE plastic composition [16]

Construction and demolition waste (C&DW) also contribute significantly toward formation of hazardous waste as it reaches up to 30 to 40% to the total solid waste due to large scale activities of construction and demolition as a results of city re-building and urbanization. The C&DW mostly comprised of timber, plastic, metal, brick, mortar, tiles, mineral aggregate, wood, bitumen, and block and showed adverse environmental effects due to dumping or landfilling. Recycled C&DW have applications in road pavement, subbase, and pipe bidding [103].

To reduce the flammability of plastic, fire or flame retardants are added. Flame retardants increase the resistance of plastic against ignition, lower spreading of flame and slower the process of combustion. WHO reported several deaths per year due to burning caused from EEE therefore flame retardants also lowers the death rate per annum [17]. Delva et al [17] reported main groups of flame-retardants as;

- *Halogenated flame retardants (HFR)*
- *Inorganic flame retardants*
- *Phosphorus containing flame retardants*
- *Nitrogen containing flame retardants*

As the main concern of this thesis is based on halogen containing plastics so only halogenated flame retardants will be discussed here. HFRs show potential fire resistance by capturing hydroxyl group from ignition medium and have widespread applications in our daily life. Incomplete combustion of these halogenated organic waste results in formation of PCDF, PBDD, and PCDD therefore complete burning and treatment of flame retardants are necessary.

Brominated flame retardants BFRs are among the most used HFR used in EEE, automotive industries, construction industries, furniture, and textile industries. There are 75 types of BFR in practice among them two (PBDE and PBB) are banned around world due to their toxic behavior on human being and environment [18]. Later, TBBPA was proposed as a substituent of PBDE and PBB which has not toxic effects on their further degradation [19].

PVC has been enormously used as a major constituent in rigid film sheets, building, construction, microelectronic appliance, domestic goods, fitting, pipe, health protection product, etc because of its high persistence and its ability for fire retardance as compared to another plastics. PVC waste has been treated by incineration and landfilling disposal methods; however, these techniques have met with commercial and environmental challenges due to more land utilization and other possible hazards [21]. PVC plastic waste can be treated and recycled by three variable processes from recent past years that includes mechanical, chemical, and energy recovery treatments. The featured advantage of chemical recycling is the value of products formed after PVC waste treatment. Moreover, energy recovery by incineration is important but give incomplete combustion of PVC waste into hydrogen chloride, acid gases and dioxins that are very toxic to both human being and environment, incineration also has low efficiency value [22, 23]

2.2 Current Recycling Techniques Applied for Plastic Waste

Plastics are usually non-biodegradable and have short lifespan which makes it essential to dispose it off properly. As a result, various techniques are in practice for recycling, recovery and recycle of plastic waste.

Current treatment techniques of plastic waste are divided into four major branches.

- *Landfilling*
- *Primary recycling*
- *Mechanical recycling*

- *Chemical recycling*
- *Energy recovery*

2.2.1 Land filling

Landfilling is a process applied for discarding of solid waste to landfills. It is an unattractive strategy for the managing of plastic waste because plastics have low biodegradability, higher volume to weight ratio, high cost and legislative pressure. However, this method of recycling is still in practice, but the trend has decreased. The amount of plastic landfilled has reduced by 44% since 2006, however 25% plastic waste was still sent to landfills in 2018. Landfilling pollutes the ground with leaching of contaminants which require several years to degrade naturally, until then it pollutes the environment [24]. Another crisis associated with land filling is emission of GHG and the disposal of useful material present in plastic waste. Due to all these adversities, current legislations restrict this method of disposal. EU commission has targeted to properly limit land filling by the year 2050 [25]

2.2.2 Primary recycling (re-extrusion)

Primary recycling is also known as re-extrusion; it is a technique in which plastic residue is mixed with fresh material to the extrusion process to manufacture the product having the same properties as the original products. Primary recycling is specified as a closed-loop recycling procedure that pertains to original waste either scrap or post-consumer [26]. For instance, if LDPE scrap does not lie on to given specification, it will be re-introduced to extrusion for further treatment.

2.2.3 Mechanical recycling

Mechanical recycling is known as secondary recycling; involves mechanical treatment of plastic waste to recycle plastic into similar, or new plastic products with almost the same or to some extent lower quantity [27]. The mechanical recycling of WEEE can be done firstly by shredding electronic scrap followed by sorting via various ways (either manual or by eddy-current separator) and then lastly the melting of plastic via extrusion into small pellets [25]. Polymer separation, de-contamination, size reduction, and extrusion are some mechanical ways to treating plastics. Higher energy consumption and strict quality parameters are the key challenges of mechanical recycling along with sorting of waste capability. However, many waste sorting techniques are in practice such as infrared spectroscopy, X-rays' fluorescence, flotation process and electrostatic techniques.

Product degradation during whole recycling process and the selectivity of polymers are two other problems linked with this method of recycling hence it is also termed as down-cycling or downgrading recycling method [28].

2.2.4 Chemical recycling (feedstock recycling)

Chemical recycling is classified as tertiary recycling; involves the decomposition of plastic waste into valuable hydrocarbons via chemical reactions such as gasification, pyrolysis, etc. Energy recovery into vulnerable products like fuel, diesel, or chemicals can be processed by these methods [25]. This process is mainly proceeding at pilot plants due to large energy consumption [28]. In comparison to others, this method does not require strict pretreatment or sorting of waste and products are mostly in the form of char, wax, gas, or liquids [29].

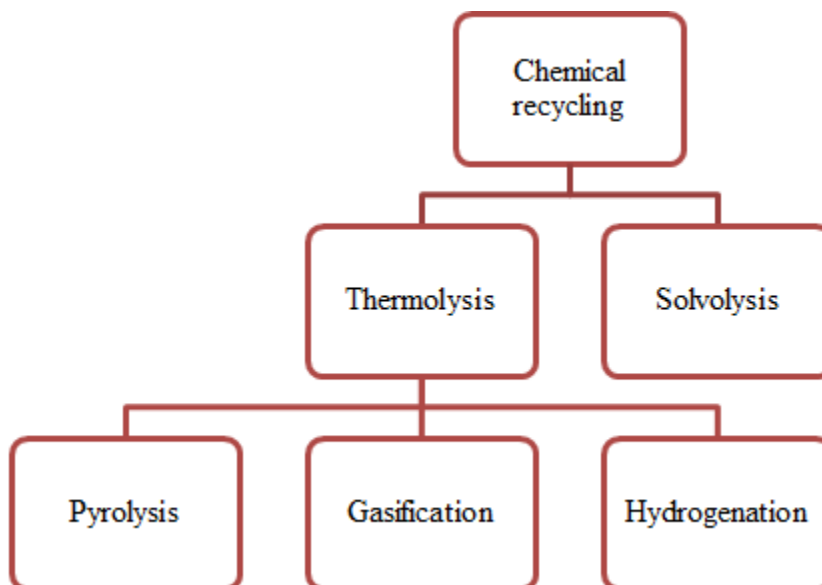


Figure 6: Schematic presentation of chemical recycling [30]

Chemical recycling is broadly classified into two processes i-e solvolysis and thermolysis [Figure 6]. During solvolysis, plastic waste dissolves into a solvent with or without the presence of initiators or catalysts. Solvolysis can also be applied as a pre-treatment step done before thermolysis [30]. Thermolysis (pyrolysis) also lies in this category of chemical recycling can be done by heating feedstock without oxygen in an inert atmosphere. Various parameters like temperature, catalyst, rate of reaction, type of reactors, etc effects thermolysis and its applications [31]. Gasification is referred to as partial oxidation or indirect combustion of organic compounds in presence of oxygen/air at higher temperatures (e.g., Up to 1600 °C). Gasification's main products include CO and H₂ synthesis gas (syngas) [32].

Hydrogenation/hydrocracking is a process in which heating takes place in the presence of hydrogen at higher pressure (approx. 100atm) and low temperature (150 to 400°C). Hydrogenation allows larger amount of feedstock to process as compared to catalytic cracking. It reduces the higher molecular weight compounds into lower ones and also decreases the boiling point of heavy oils from feedstock to produce saturated hydrocarbons [33]

Pyrolysis is one of the suitable methods for the recovery of material energy from the residual plastic waste. Pyrolysis consumes only 10 percent of the energy of the polymer waste in conversion to useful hydrocarbons.[34].

2.2.5 Energy recovery

During energy recovery, plastic waste gets incinerated and produces energy in the term of heat, electricity, or steam. One of the most common advantage associated with this process is that it decreases the space required for landfilling and the higher calorific values of feedstock. Incineration is suitable option for energy recovery due to financial recovery of waste as a fuel [25].

However, one major impediment linked with energy recovery is that incomplete incineration results into formation toxic products such as PCBP, PCBF or dioxins that could be released to atmosphere if not treated. [12].

2.3 Effect of reactor type during pyrolysis

Heating of plastic waste at high temperature (400° C to 600° C) in an inert atmosphere either with (catalytic pyrolysis) or without (thermal pyrolysis) catalyst is termed as pyrolysis. Pyrolysis products include char, oil, and gases characterized by techniques like GC/MS and/or NMR (either 1D or 2D) [32]. Pyrolysis can be classified as slow or fast depend upon heating rate.

- *Slow pyrolysis (300-600°C)*
- *Fast pyrolysis (400-600°C)*

Many researchers have done research on pyrolysis of plastic waste for their conversion in valuable products and studies of parameters affecting them [Table 02]. Slow pyrolysis is the oldest technique applied for thermal treatment of carbonaceous material with charcoal and char as main products. During this process, organic substance is heated in dearth of oxygen at relatively lower temperature (from 300 to 600 °C) and with slow heating rate (5-80°C/minute) which optimizes the char yield [35]. Fast pyrolysis yields different

amounts of liquid and gases depending upon temperature and residence time of vapors in reactor. Lower temperature and longer vapor residence time result into formation of secondary products such as charcoal. Recently liquid production through fast pyrolysis is in practice due to convenient liquid storage, transportation and energy or chemical production. Reactors are the heart of pyrolysis although it only costs 10 to 15% to total capital cost of the whole process [36]. Choice for reactor depends upon following criteria [37].

- Targeted product (char, liquid, gas)
- Operation mode (batch or continuous)
- Source of heat (electric or gas heater)
- Mechanism of heating (direct, indirect or microwave)

Mostly used reactors for fast pyrolysis are fixed bed bubbling fluidized reactors, circulating-bed reactors, rotating cone, ablative plus conical spouted bed to yield optimum pyrolysis oil.

Table 2: Studies on pyrolysis of halogenated plastic

Plastic	Reactor	Process Parameters				Yield wt%			Products	Ref*
		T, °C	P, MPa	ΔT, °C/min	t, min	Oil	Gas	Solid		
PVC	Fixed Bed	500	-	10	-	12.3	87.7	0	-	[75]
PVC	Vacuum batch	520	0.0022	10	-	12.8	0.34	28.13	HCl=58.2 wt%	[95]
PS	Pressurized batch	425	1.6	10	60	97	2.5	0.5	-	[96]
PS	Batch	500	-	-	150	96.7	3.27	0	-	[97]
PS	Batch	581	-	-	-	89.5	10	0.9	Liq styrene=65 wt%	[98]
PS	Semi-batch	400	0.101	7	-	90	6	4	-	[99]
CO ₂ and Fe ₂ O ₃ coupled PVC		900	-	10	-	-	-	-	H ₂ and syngas	[21]
WPCBs (BFR)	Fixed bed	500	1.5bar	50	60	60 to 79%	21 to 40%	-	NaBr, KBr	[100]

						char	volatile matter	
ABS (BFR)	Bench-scaled FBR	430 to 510	13.3K Pa	-	-	45 to 64		Dehalogenated oil [101]

*Nitrogen fluidizing medium in very experiment

2.3.1 Bubbling Fluidized Bed Reactors

Bubbling fluid bed (BFB) technology has simpler construction, easy to operate, efficient heat transfer to feedstock and temperature controller [36]. Martinez et al [38] worked on designing of first pilot scale bubbling fluidized bed reactor for plastic waste [Figure 7]. They worked on thermal processing of plastic waste by considering sand as a bed material or mixture of sand and catalysts like dolomite as a bed. For the regular temperature and pre-heating of reactor, electric heaters were located near the bed zone and free-board zone. It was observed after the analysis of plastic fuels that in the free-board, larger number of chemical reactions was take place. This factor implies on the correct dimension of reactor as well as the velocity of gas in the free-board to gets the longer residence of gas inside it. There is also the higher production of tar by this pilot scale BFB reactor. However, the feeding input of plastic waste requires special attention, a continuous feeding of fuel from storage tank to the bottom of reactor by rotary or screw feeders is essential because hot gas coming from inside of the reactor gets in contact with the feed as a result the fuel gets warms and un-desired side reaction will start occurring. In order to avoid these side reactions, water coolers are inserted with screw feeders but still it causes problem for plastic waste feed [39-40].

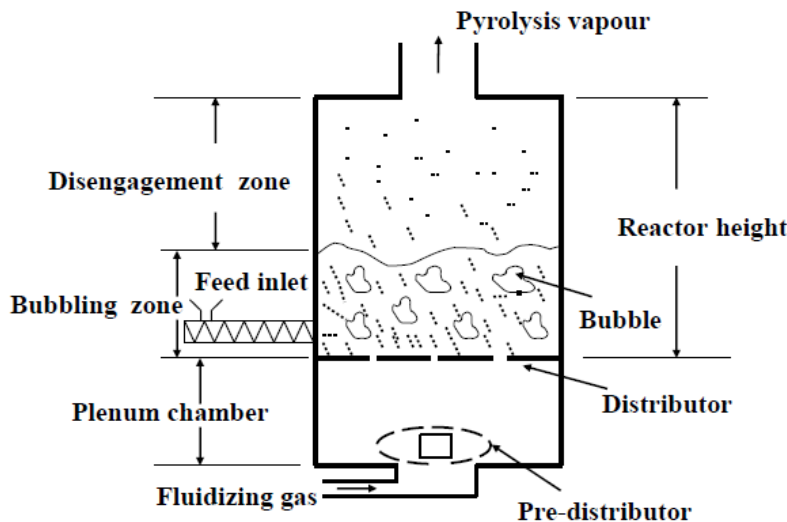


Figure 7: Typical Schematic diagram of BFB [38]

Some advantages and dis-advantages of BFB technology are stated in Table 3.

Table 3: Benefits and drawbacks of BFB [36]

Benefits of Bubbling fluidized bed reactor	Drawbacks of Bubbling fluidized bed reactor
Temperature control is stable.	Higher probability of coalescence phenomena
Works at various pressures	Higher particle entrainment in reactor
Variable particle sizes can be accommodated.	-
High ash content can be tolerated.	-

2.3.2 Fixed Bed Reactors

In a fixed bed reactor, bed material is stationary. Fixed bed reactors are commonly used but in the case of plastic feedstock, their usage becomes complicated and challenging. Plastics have high viscosity and poor thermal conductivity in a molten state; both characteristic properties of plastic feedstock make it difficult to feed it into a fixed bed reactor. Usually, plastic in the molten state is fed into the reactor with the help of a capillary tube from a pressurized tank. However, the feedstock in a liquid or gaseous state can be fed comparatively more easily [37]. Temperature gradients and channeling are most common problems associated with fixed bed reactor systems. Small scale units are easy to set up and operate for initial screening of operational conditions.

2.3.3 Rotating Cone Reactor

Rotating cone reactors has been invented by University of Twente, Netherland in early 1990's [36]. Recently, system scaling up to 200 kg/hr is in practice. Rotating cone technology works on the same principle as of transported bed. In rotating cone, hot sand is mixed with the feedstock affecting the thermal properties of pyrolysis reaction. This transporting of feed and hot sand is supported by the centrifugal force exerted by the rotating cones instead of carrier gas used in CFB technology. The sand and feed are introduced from the bottom of reactor where force (centrifugal) allowed solid particles to get separated and move upward to the lip of the cone as a result vapors are conducted toward condenser. Subsequently, char and the sand directed toward combustor where re-introduction of feed take place along with re-heating of sand at the bottom of cone reactor [Figure 8] [41].

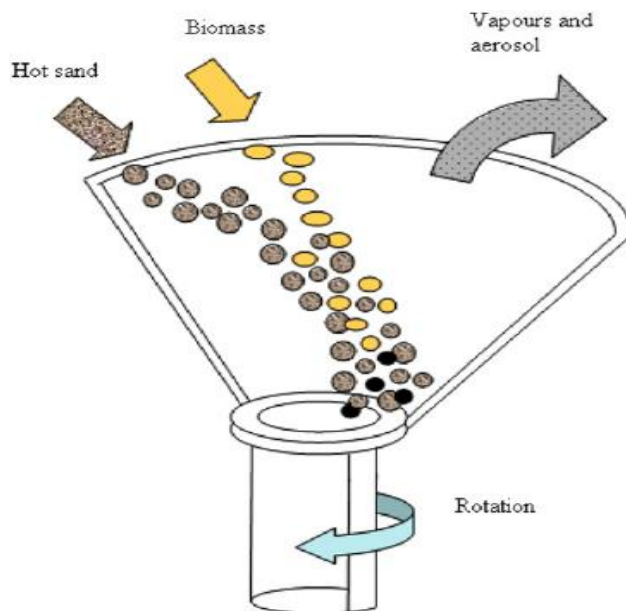


Figure 8: Schematic diagram of rotating cone [41]

Some benefits and drawbacks of rotating cone remain concise in Table 4.

Table 4: Benefits and drawbacks of rotating cone reactor [41]

Benefits of rotating cone reactor	Drawbacks of rotating cone reactor
60 to 70% liquid yield	Complex integrated process
Ease in recovery of product	Difficult to scale up.
Reduced wearing problems.	-
No carrier gas required.	-

2.3.4 Ablative Pyrolysis

It is comparably different from other technologies of fast pyrolysis. It works on the principle of melting butter in frying pan, by spreading butter over more surface area and by pressing it frequently causing fast melting. In the same way, organic feedstock is melted by the heat transferred to it from the walls of reactor consequently; molten layer of feedstock vaporizes into product. As compared to other technologies, ablative pyrolysis operates with higher particle size of feedstock, more quantity of feed, without need of carrier gas and re-circulation [42]. The key feature of ablative pyrolysis is when feedstock encounters hot walls of reactor; ablation take place. The molten layer is vaporized into product when the feed moves away. However, scaling of ablative

pyrolysis is not much effective due to controlled surface area and it is a complex process because mechanical force is required to drive reactor [36].

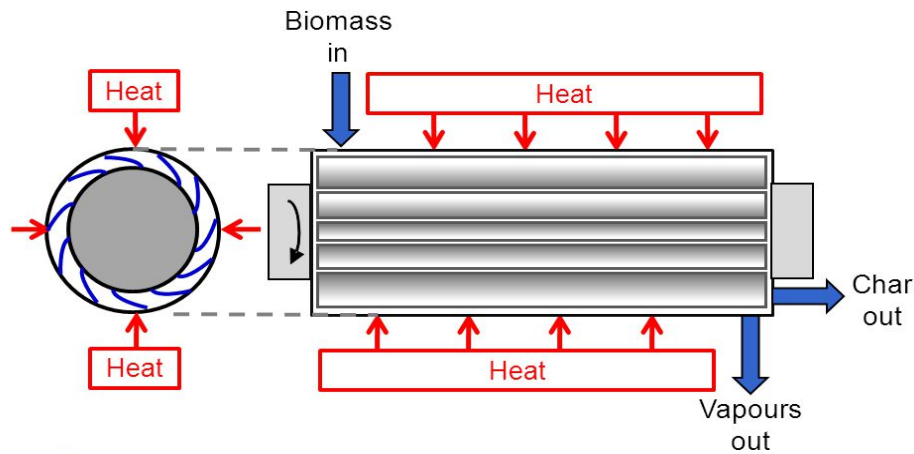


Figure 9: Schematic diagram of ablative pyrolysis reactor

2.3.5 Conical Spouted Bed Reactor

The conical spouted bed reactors (CSBR) are potentially used for particles that require vigorous mixing. Particle size may vary from smaller to larger with variable texture. CSBR technology involves conical shape reactors; feed is introduced at the base of cone reactor and directed toward gush and drift onto fountain where it moves toward the back into annulus [Figure 10]. This featured movement of feedstock in the CSBR technology makes it different from others and allowed desired reaction to occur. CSBR has been successfully used by many industries for fast and flash pyrolysis of biomass due to silent features like for designing of spouted bed, distributed plates are not required which makes it easy to design [43, 44].

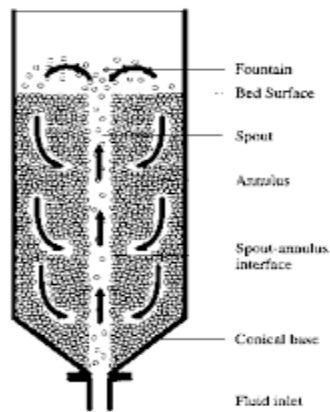


Figure 10: Schematic diagram of CSBR [45]

2.3.6 Fluidized Bed Reactor

Fluidized bed reactors (FBR) are typically operated in fast or flash pyrolysis. FBR technology has characteristic high rate of heating with fine mixing to feedstock. FBR operates on principle of reactor filling with bed of solid raw-material particles along with steady flow of fluidizing gas which fluidizes the particles. Pyrolysis reaction occurs right after the induction of feedstock into a reactor and the residence time can be regulated with the flow of fluidizing gas into the reactor [46].

Some benefits and limits of FBR are listed in Table 5.

Table 5: Advantages and limitations of FBR technology [46]

Advantages of fluidized bed reactor	Limitations of fluidized bed reactor
Enhanced mixing	Complicated separation between bed material and coke
High heat transfer rate between gas and particles	Choice of fluidizing gas
It requires low maintenance time.	External heating and recirculation cause complication
FBR are easy to operate.	-
	-

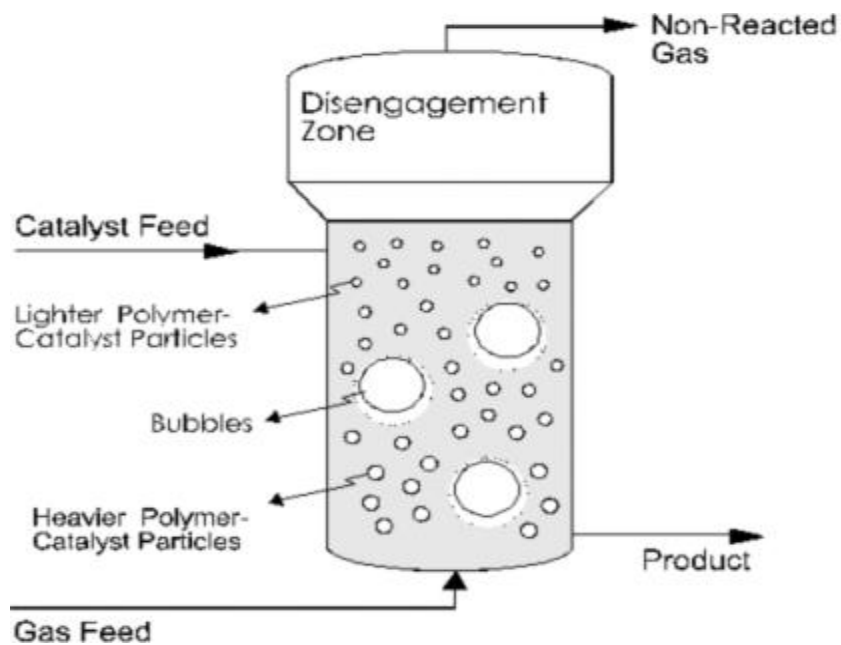


Figure 11: Schematic diagram of FBR [47]

2.4 Significance of Types of Reactors for Plastic Pyrolysis

The choice of reactor for specific pyrolytic reaction at specific conditions is very important due to high thermal conductivity and viscosity of plastic which result in heat-mass transfer constraints. This factor highly influences the distribution of products formed. Ishihara et al [48] for the first time described feeding of plastic waste in FBR, plastic waste sample were first melted at about 230°C and then introduced into the top of reactor. N₂ gas was introduced as a carrier gas and silica-alumina as a catalyst. 31% to 74% parallel augmentation of hydrocarbons (gaseous state) was observed due to steady raise in temperature from 340°C to 475°C also decline in space/residence time causes reduce gas yield.

Kaminsky et al [49] worked on fluidized bed (Hamburg Process) by using spent FCC catalyst with PE and PS at temperature 370 to 515°C with feeding capacity 1kg/hr. Author concluded that presence of catalyst changes the distribution of product in comparison to thermal decomposition. Hence various parameters like presence of catalyst, residence time of vapors, temperature, type of reactor, and rate of heating affect the quality and distribution of products obtained by pyrolysis. From all these parameters, temperature and residence times plays a crucial role in a way that temperature above 500°C produces gases and char products whereas temperature between 300°C to 500°C favors liquid products [50].

2.5 Techniques to treat hazardous plastic

Pyrolysis of plastic waste containing brominated flame retardants, produces organobromine compounds in the oil which makes it unusable for downstream application unless treated otherwise. To overcome this problem, halogens must be removed either before or during the pyrolysis to get product with minimum halogen content. Several researchers have discussed different methods of recycling hazardous plastic waste. Some of them are discussed below.

2.5.1 Solvent extraction

Extraction of brominated flame retardants from plastics can be done using solvent extraction. Vilaplana et al [51] experimented the identification and removal of BFR more specifically decabromodiphenyl ether (deca-BDE) and TBBPA from HIPS sample by the application of MAE (Microwave-assisted extraction). Authors performed comparative experiment on BFR incorporated HIPS in presence of tetrahydro furane (THF) and raw HIPS directly from WEEE waste. They concluded that deca-BDE gave lower yield for extraction because of its non-polar nature and higher molecular weight whereas in presence of polar and non-polar mixture of solvent (iso-propanol and n-hexane), maximum extraction was observed at 130°C.

Extensively deployed brominated flame retardant is TBBPA and its removal from WEEE was studied by Evangelopoulos et al [52]. They adopted solvent extraction pretreatment before pyrolysis by soxhlet extraction instrument. The solvents they used were isopropanol due to its high polarity relative to others and low toxicity along with non-polar toluene. This study was performed on three different WEEE fractions (PCB, modem Wi-Fi router plastic and brominated plastic) collected from recycling plants. It was concluded that brominated plastics were efficiently removed by isopropanol solvent from solid fraction and TBBPA removed from liquid fraction by toluene.

Extraction of BFR from WEEE plastic by solvent treatment is mostly preferable because it is non-destructive technique with easy recovery and recycling of plastic. Choice of solvent critically affects the productivity of method. Other studies performed by Zhong and Huang [53] for removal of BFR mainly TBBPA from plastic WEEE based on solvent extraction method by using methanol, acetone, and toluene. They also conducted a comparative study on BFR containing plastics having high solubility and low boiling point with BFR plastic having lowest reactivity for given solvents. Their result revealed that methanol and toluene did not affect the decomposition of TBBPA whereas 20% TBBPA converted into high molar weight components with acetone as a solvent.

2.5.2 Mechanochemical treatment (MCT) (co-pyrolysis)

In this process, plastic waste is mechanically treated using additives in a ball mill. The impact of balls on the plastic particles in the presence of the additives release the halogens from the polymer matrix. MCT co-pyrolysis have several advantages for example, it is simple process, ecologically safe, and stable product is obtained. It is promising technique for destruction of halogenated polymers especially PVC, and retardants PCDD/F, PBT. A significant attribute of MCT is that it detoxifies polymers without complete destruction of whole molecule [54-56].

Saeki et al and Inoue et al [57-58] studied MCT for poly vinyl chloride by using alkali additives (like NaOH, KOH and CaO). During co-grinding, dehydrochlorination of PVC occurred by CaO additive. As a result, HCl react with CaO to form CaOHCl. Additionally, HCl was produced during crushing of PVC and SiO (additive) mixture. The experimental result of Saeki et al summarized that artificially synthesized slag was most effective additive as compared to others with CaCO₃ as least effective. Molar ratio of PVC directly affects the rate of de-chlorination [Figure 12] as maximum de-chlorination was observed after 4 hrs of MCT at 2 molar ratios.

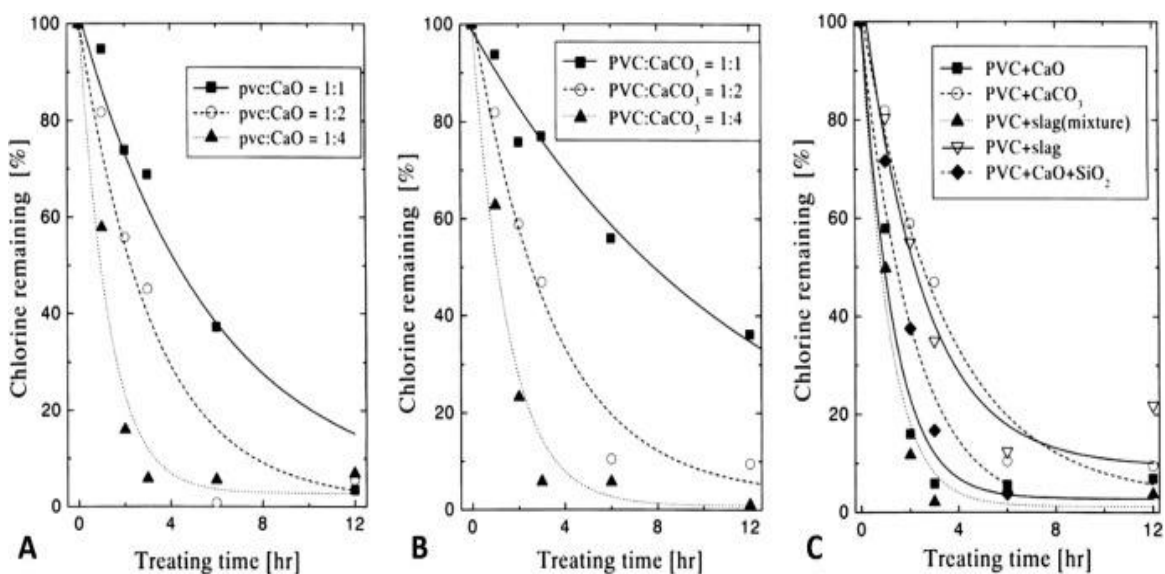


Figure 12: A: percentage of remaining chlorine in PVC and CaO mixture, B: percentage of remaining chlorine in PVC and CaCO₃ mixture, C: percentage of remaining chlorine in mixture of PVC with various catalyst/additives as a function of treatment time [57]

MCT has capability for removal of TBBPA from plastic waste. Study performed by Zhang et al in 2012 [59] for co-pyrolysis of TBBPA by co-grinding with CaO or mixture of sand quartz (Fe + SiO) with powdered iron as an additive at room temperature in ball mill. Experimental studies revealed 98% removal of bromine initially after 3 hrs while 95% after 5 hrs from TBBPA and showed better results as compared to specifically CaO additive. Promising results were due to fine particles activation of sand quartz and iron powder after MCT. These fine particles have high energy and reactivity and act as electron donor species. This electron transfer mechanism promotes bond cleavage of C

and Br and formed bromine radical which become so reactive to start propagation until it gets terminated.

2.5.3 *Solvothermal/ hydrothermal treatment (STT/HTT)*

A thermochemical process for the conversion of polymeric organic samples into high carbon content products; is termed hydrothermal carbonization (HTC). The mechanism of HTC involves heating of submerged biomass in water at temperature 180°C to 260°C under high pressure of 2 to 6 MPa which is generally not controllable but varies with degree of saturation for water vapor pressure analogous to temperature of reaction. Currently researchers are looking forward to producing solid hydro-char product to make it significant for industrial applications and environment friendly [63, 64]. As organic feedstock already submerged in water hence the content of moisture into feedstock does not affect the process of HTC. This unique feature reduces the cost and energy input of treatment as compared to others by eliminating pre-drying of wet feedstock and resulted mainly in three products: solid (hydro-char), liquid (biooil + water) and minor amount of gases (CO₂) depending upon reaction conditions [65]. The capability of STT for pyrolysis of WEEE containing BFR was studied by Zhang and Zhang [66]. They demonstrated about the mechanism for debromination and the factors affecting the efficiency of STT. They also concluded that solvents like methyl, ethyl and iso-propyl alcohol have no main difference in efficiency of BFR removal with different bromine losses. Recycling of common plastics with maintained structure after STT was main outcome of the authors [66].

2.5.4 *Supercritical fluid technology*

Fluids beyond critical state temperature and pressure are termed as supercritical fluids. Physical properties of these fluids like their diffusion coefficient, viscosity, solvation capacity, density and others show sensitivity toward variable temperature and pressure conditions. This unique behavior of supercritical fluid technology along with eco-friendly characteristic makes it interesting for BFR removal from WEEE [68]. Water as supercritical fluid showed potential to degradation of bromine in BFR to give bromine-free oil, organic solvents like methanol, methanol and acetone also act as supercritical fluid for treatment of WEEE. Zhang and Wang [69] examined degradation of waste computer housing plastic containing BFR, by applying several supercritical fluid environments. Their results revealed the effectiveness of supercritical technology for debromination as well as decomposition of brominated plastic followed by reprocessing of bromine-free oil. They also found that water showed maximum efficiency for debromination as compared to methanol, isopropanol and acetone.

2.6 Effect of Additives

Several researchers have investigated the effect of additives during the pyrolysis of WEEE since several years. The presence of additive improves the quality of pyrolysis product by reducing halogen contents. Calcium based additives commonly used because of its efficiency for binding of halogen acids formed during pyrolysis process. Bhaskar et al [105] used novel calcium-based sorbents in 2002 for the process of dehalogenation of mixed halogenated plastics (PP/PE/PS/PVC) during pyrolysis. Halogen free liquid was obtained which could be used as a fuel or feed for refinery. The experiments were carried out in bench scale pyrolysis unit at 430°C in presence of calcium-based sorbent like calcium carbonate carbon composite (Ca-C) sorbent. They concluded that the degradation products (Liquid, gas), average carbon number, residue, liquid product density obtained without calcium-based sorbent was 71 wt% liquid products with 0.82 gcm⁻³ density and 13.7 carbon number whereas the same products in the presence of 2 g and 4 g Ca-C was 62 wt% and 66 wt% respectively however, the liquid products density was not affected by the presence of Ca-C [105]. Jung et al [101] performed thermal degradation of ABS containing flame retardants by utilizing fluidized fixed bed reactor (FBR) at temperature range of 430°C to 510°C to get oil yield with reduced halogen content. They also studied the effect of calcium-based additives like calcium hydroxide, calcium carbonate and oyster shells. They carried out the experiments in both absence and presence of additives pyrolysis. They concluded that reduction of bromine and chlorine in oil yield by 0.05 wt% and 0.04 wt% respectively. The authors summarized that from all of three additives used, calcium hydroxide proved to be best one for the removal of halogen as the content of antimony in oil yield was 0.001 ppm in presence of calcium hydroxide. Moreover, a significant route for recycling of oyster shell was also studied by them [101].

Hlaing and co-workers [106] demonstrated the effect of scallop shell, calcium and sodium hydroxide during pyrolysis of computer casing plastics for the reduction of bromine content in oil yield. The reactions were performed in glass reactor at 450°C both in presence and absence of additives. They concluded that in NaOH presence for pyrolysis of Br-ABS, minimum bromine content in oil yield was obtained [106]. Cho et al [107] mentioned in their study about the consequence of various additives while pyrolysis of mixed plastic (PP, PE, PS, PVC and other small polymers) for the recovery of Benzene, Toluene, and Xylene (BTX). The experiment was carried out in fluidized bed reactor at 660°C to 780°C temperature with or without additives i-e calcium oxide, calcium hydroxide, rice straw and squeezed oyster shells. The formation of HCl during pyrolysis of PVC strongly affects the process as well as the yield products, the applications of pyrolysis oil in petrochemical industry reduce significantly due to it. For the absorption of HCl, calcium-based additives were added to the feed and reduction in chlorine content up to 50 ppm was observed by additives.

2.7 Influencing operational parameters on pyrolysis

Chemical processes are strongly dependent on process parameters. In pyrolysis, process parameters direct the formation of final output like oil, gases, and char. These operational parameters are pressure, temperature, residence time, catalyst, fluidizing gas type and their rate of flow. The required products can be produced by varying the parameters. Further explanation of the influence of operating parameters is mentioned in the following texts.

2.7.1 *Temperature, pressure and space/residence time*

Temperature in pyrolysis process controls cracking reaction [74]. Overall decomposition of polymeric waste depends upon temperature applied during pyrolysis. Cracking of plastic involves the breakage of carbon chain. The effect on plastic degradation with respect to change in temperature can be analyzed by thermo-gravimetric analyzer which gives information on the degradation profile of material i.e loss of mass w.r.t temperature. TGA measures the change in mass of substance with respect to time and temperature. As a general rule of thumb, higher temperatures $>500^{\circ}\text{C}$ leads to excessive formation of gases. Liquid share is reduced consequently. The effect of temperature is directly related to the residence time of decomposition. Short residence times in the case of fluidized bed pyrolysis with high temperatures leads to excess gas formation whereas high temperatures with very low residence times (minutes) leads to secondary and more stable products such as aromatics in liquids and char.

Most of the researcher conducted their experimental work at atmospheric pressure so pressure effects are not reported well in literature and there is a need to fully understand the effect of these parameters in pyrolysis findings. Murata et al. [77] examined the pressure effect in between of 0.1 to 0.8 MPa on thermal pyrolysis of HDPE in a continuous stirred-tank reactor. They noticed by the rise in pressure, the gas formation increased at 410°C . It was concluded in the results that pressure has greater impact at reduced temperatures. They also suggested that degree of product unsaturation decreases by increasing the pressure and more residence time of vapors at lower temperature. This means that rate of C-C bond breakage in polymer is directly linked with pressure applied. Lopes et al [78] done the continuous pyrolysis of waste from tires in atmospheric and vacuum (25 to 50 KPa) in CSBR pilot plant by using temperature range from 425 to 500°C . As an effect, vacuum on atmospheric pressure, rise in diesel yield in term of liquid product.

Space/Residence time is an average time that a particle spends in the reactor. It also effects the product distribution after pyrolysis. Longer the particles stay into reactors, the more thermally stable products like higher weight hydrocarbons and non-condensable

gases will be obtained. However, the final product distribution is strongly influenced by temperature [79]. Product distribution for thermal cracking of HDPE in FBR affected by parameter of temperature and residence time was stated by Mastral et al [80]. It was remarked that at 68.5 % pyrolysis yield (wax and oil) was obtained at 640°C with 1.4s residence time whereas 39% at 700°C at 1.3s residence time.

Hence it is noted that both pressure and space/residence time affect the pyrolysis product distribution only at low temperature. This shows the dependence of both these parameters on temperature. Higher pressure results in gaseous product and affects the product dissemination for both gases and liquid products but just in case of high temperature. Literature survey showed that research conducted on pyrolysis of plastic waste was based mainly on temperature at atmospheric pressure also the residence time does not get much attention of researcher because it gets apparent at higher temperature.

2.7.2 Catalyst

A catalyst increases the speed of the chemical reaction, and it remains recoverable after reaction. Many researchers as well as industries utilize catalysts to optimize the product distribution and to improve the selectivity of pyrolysis product. Catalyst lowers the activation energy of process to speed up the reaction rate as a result lowering the optimum temperature required for pyrolysis process. By using catalyst, this cost of energy may reduce. Other advantage of catalyst includes upgrading of products obtained by pyrolysis to get the liquid product by improvement in hydrocarbon distribution [81].

Total surface area, micro-pore area, pore size distribution, pore diameter, basicity or acidity is the basics features that influence the selectivity of product during catalytic pyrolysis [32]. For the catalytic pyrolysis of WEEE plastic waste, several catalysts like zeolites (zeolite-Y, zeolite- β , HUSY, HMOR, HZSM-5, etc), FCC catalyst, silica-alumina, mesoporous catalyst (MCM-41), minerals, silicates and metal-based catalyst (Table 5) are used by researchers [25].

Wang et al [82] investigated pyrolysis of PCBs with Al_2O_3 catalyst at three different temperatures (400, 500, & 600°C). This study is linked with their previous studies [83] in which they concluded that Al_2O_3 catalyst has good efficiency for debromination of oil derived product with maximum selectivity as compared to HZSM-5 and USY catalyst which has lowest and negligible potential for product selectivity, respectively. From their recent study [82] results revealed the potential of activated Al_2O_3 for elimination of bromine and for formation of liquid product having phenolic composition. Debromination of benzene ring during process leads toward inorganic compounds formation (HBr). They found 600°C as best for liquid fraction product with highest debromination capability. Oil formed can further be used as a raw feedstock for further recycling.

Table 6: Pyrolysis of plastic WEEE by using catalyst.

Polymer(s)	Tested BFR	Reactor Type	Temp °C	Catalyst(s)	Pyrolysis product(s)	Ref
ABS and HIPS	TBBPA and DECA-BDE respectively	FBR	400	Zeolite-Y, ZSM-5	Gas	[84]
ABS and HIPS	TBBPA and Deca-BDE respectively	FBR	400	FCC	Oil	[85]
HIPS	DDO	Fixed bed reactor	500	HY, H β , HZSM-5, all-silica MCM-41, and active Al ₂ O ₃	Oil	[86]
PCBs	Not specified	Not specified	600	Activated Al ₂ O ₃	Oil	[82]
PCBs	Not specified	Not specified	500, 600	Activated Al ₂ O ₃ , HZSM-5 and USY	Oil	[83]
PE-ABS and PS-ABS	Not specified	Glass reactor	450	FeOOH, Fe-C, and Ca-C	Oil	[87]
HIPS	Not specified	Fixed bed reactor	550	Natural zeolite, red mud and limestones	Oil	[88]

2.8 Characterization of Products

Pyrolysis liquid or oil, char, and solid are analyzed by GC, FTIR, MS, and HRGC/HRMS depending upon the need. Analysis techniques like FTIR, and MS provides information on the decomposition products of plastic waste, the TG measurements show decomposition behavior and measures the modification in mass of plastic feedstock as a

function of time and temperature while data from FTIR and MS provides structural and concentration evidence about the degraded products and gives the information about the mechanism for the BFR degradation.

Liu et al [102] reported thermal analysis of WEEE at lab-scale and TG, FTIR, MS analysis for pyrolysis product. The pyrolysis of plastic containing BFR was analyzed in TG analyzer at 800°C and -73.15°C/min rate of heating for 5mg plastic sample. The fluidizing medium they applied was helium (100mL/min) and the compounds released was analyzed by combined FTIR and MS techniques where FTIR was operated at range of 4000-400cm⁻¹ after every 2.5 minute and scanning by MS was done at 70 eV. 0<(m/z)<200 specific charge values were set for the analysis of obtained compounds after pyrolysis of BFR while compounds having m/z value more than 200, analysis was done by online GC-MS method. At certain point (350°C or 450°C, DTG peak values) the compounds were moved with high purity helium gas medium toward online GC-MS via heated transporting tube. The scanning range was 0-500 amu for m/z values at 70 eV MS. The structural elucidation of obtained compounds was done by comparison of spectra's with NIST mass spectral library. The char obtained after pyrolysis of BFR containing plastic was examined by SEM and XPS (Xray photoelectron spectroscopy).

By TG, MS evaluation, it was established, the rate at which aromatic hydrocarbons released by the pyrolysis of DBDPE containing plastic at 510°C was greater as compared to the rate of release from TBBPA plastic at 580°C as explained by TG, FTIR analysis as well. From all the aromatic plastics, styrene and benzene (HIPS depolymerized products) exhibit greatest profusion with MS intensities of about 36× 10⁶ and 17× 10⁶, correspondingly. It is well-known that styrene and benzene, also the other aromatic compounds such as toluene, act as an essential feedstock to produce fine chemicals like dyes, pharmaceuticals, and pesticides [07] showed that pyrolysis is conveniently useful for plastics recycling. Moreover, the release of bromine substituted hydrocarbons showed variable trend. Bromoethane and bromobenzene through process of pyrolysis for DBDPE and TBBPA gave similar release trend with maximum evolution at 600°C providing evidence that both compounds were formed in same manner as an aromatic compound. However, in contradict of them, bromomethyl-benzene showed released at 600°C and 700°C for DBDPE and TBBPA plastic pyrolysis respectively suggesting that it followed different way of mechanism for its formation in DBDPE and TBBPA containing plastics. Another important factor revealed after TG, MS investigation is that bromine substituted hydrocarbons were abundant in DBDPE containing plastic as compared to TBBPA showing that DBDPE plastic were enriched with bromine content.

2.9 Challenges for Pyrolysis of Halogenated Plastic Waste

2.9.1 Behavior of halogenated compounds

Most important challenges associated with viable utilization of feedstock recycling is PVC existence into plastic waste. Although PVC is sorted out from the feedstock, but even a minor amount of chlorine (1% PVC = >0.5 wt% Cl) into product composition cause toxicity. The obtained fuels may face not only the corrosion problems but also halogen substituted hydrocarbons which makes it commercially useless [89]. Uddin et al [90] researched on degradation of PVC blends with PP, PE and PS in 2g/8g ratio respectively at temperature from 360°C to 450°C in a batch-reactor. They demonstrated that 91 to 96wt% of chlorine was eliminated during dehydrohalogenation from which liquid fraction of product obtained 3 to 12 wt% of chlorine, 2800 to 12700 ppm chlorine content in oil fraction while less than 0.5 wt% in solid residue.

Bromine containing WEEE plastic behaves differently as compared to chlorine containing plastics. In the absence of FR synergists Sb_2O_3 the decomposition of polymer would not form HBr as compared to chlorinated compounds. However, in presence of FR synergists, decomposition occurs in two distinct regions (low and high temperature). Sb_2O_3 reacts with HBr to initiate the process of decomposition result in removal of FR at low temperature region [16].

The knowledge about reaction between FR synergists and BFR used in WEEE plastics is necessary during pyrolysis because metals and fuel obtained after recycling of pyrolysis products may contain halogenated compounds or Sb which decreases its efficiency. Marongiu et al [91] gave detailed decomposition of TBBPA kinetic model during pyrolysis. They divided the reactions in four classes' i-e initiation, propagation, molecular and termination. An increase in reaction time and temperature leads towards increased removal of bromine by elimination of Bisphenol A and dehydrobromination followed by phenol removal. However further increase in reaction time and temperatures resulted in formation of char from macro-organic compounds with removal of CO and CH_4 . Grause et al [92] performed other studies based on pyrolysis of TBBPA containing paper laminated PCBs. The temperature for degradation was set between 50°C to 800°C set as three levels while 40°C to 1000°C for TGA. These different temperature levels allowed easy chemical analysis of bromine containing products. In the first set, decomposition of cellulose at 272°C to 280°C resulted in evaporation of CO_2 and H_2O . Degradation of FR in bromine products occurred at 270°C to 370°C during second step. At 270°C to 500°C decomposition of BFRs produced HBr which is characterized as two single peaks at 305°C and 398°C respectively. In third step, decomposition of phenol resins take place at 370°C and char is also formed during this step [Figure 13]. Aryl bromide products were formed at temperature range of 270°C to 400°C above which bromine products specifically hydrogen bromide was generated hence phenolic products with lowest content of bromine were formed in their studies and they concluded that pyrolysis at 450°C yielded HBr and low quantity aromatic bromide compounds which is

simply separate in water trap and act as pioneer for formation of PBDD/F respectively [91]

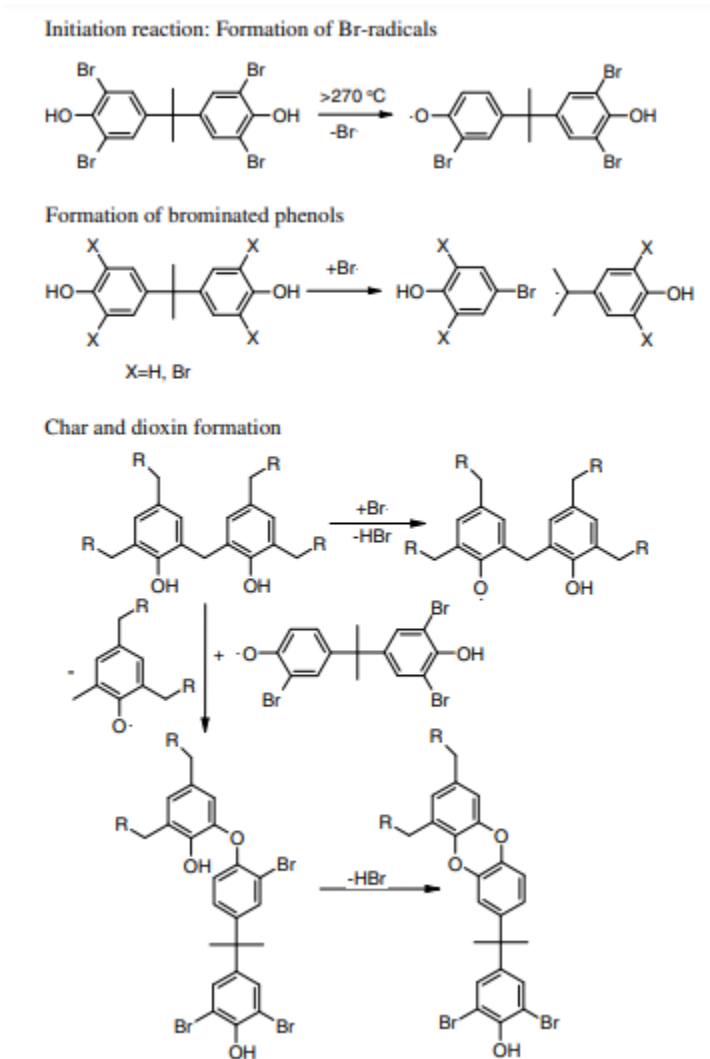


Figure 13: Degradation steps of TBBPA [92]

2.9.2 Behavior of BFR plastic degradation

The application of BFR in plastic ensures its safety for daily life use but they behave separately when thermally degraded during recycling. Grause et al [60] discussed degradation of HIPS and the effect of FR and Sb_2O_3 by TG, MS analysis of pyrolysis products; however, their studies did not cover the area for formation of various pyrolytic products from WEEE under variable reaction conditions. It is considered that BFR containing plastics degradation occurred in two steps based on TGA results. Step-1 involves the degradation of FR additives at lower temperature while step-2 involves

degradation of plastic matrix at higher temperature. Jie et al [93] did comparative studies for single and two step pyrolysis for plastic waste of desktop-computer casings for optimization of product distribution and characterization of pyrolytic liquid/oil product. They performed single-step pyrolysis at temperature ranges from 300°C to 600°C whereas two-step pyrolysis at 350°C to 350°C for initial 15 mins afterward 500°C until process completion. The oil product yielded from single-step pyrolysis contained high content of aromatic, phenolic or nitrogenous compounds comprising 11 to 16% toxic bromine content while comparatively enriched impurities oil product by two-step pyrolysis. The presence of bromine influenced the applications of pyrolysis product as chemical or fuels. WEEE plastic used by them was rich in BFR content which were supposed to produce organo-bromine compounds and inorganic compounds like HBr in larger quantity [15, 25, 84]. The organo-bromine compounds present in waste computer casing plastic were 2,4,6-tribromophenol, dibromo phenol or may be 2-/4-/6-bromophenol with lower content of bromobenzene, 4-methylbenzyl bromide, and 9-bromoanthracene as explained by Jie et al [93]. They determined the thermal decay of plastic not only released brominated analogues by TBBPA degradation but also brominated aromatic compounds by the interaction of plastic matrix and TBBPA. These brominated compounds did not properly discharge during pyrolysis however, utmost of brominated impurities transferred during first step product oil of two-step pyrolysis performed at 350°C to 380°C and smaller quantity of aromatic benzene compounds in step-2 oil product. This showed a strong interaction of BFR additives and plastic matrix and restrain brominated compounds in step 1 oil. Instead of their complete removal in step 1 they evolved at higher temperature in step 2 therefore, it is concluded that for complete degradation of BFR, two-step pyrolysis must be adopted for better use of recycled chemicals or fuels from WEEE.

2.9.3 Formation of by-products

Gas and char are the major by-products and contribute an estimated 10 - 25% and 5 - 10% of the feed treated, respectively depending upon the pyrolysis conditions. The method to provide energy to the pyrolysis by char and gas is to combust it and extract energy. The excess heat generated after combustion of char and gas can be used for drying the feedstock at smaller scale and to support power generation at larger scale [07].

Char could also be used as cracking catalyst; therefore, effective removal of char by-product from the process is advantageous. For the removal of char, cyclone is effective however, as a result of inefficient separation, some fine char particles could entrain into liquid product where they can cause instability and aging problems. Another method for removing char by-product is hot vapor filtration like hot gas cleaning in gasification. [9].

2.10 Toxicity of Halogenated Plastic

Incomplete burning of WEEE, C&DW plastic resulted in formation of PCDD/F and PBDD/F. Both products are highly toxic for human body as well as cause environmental hazardous. Buser et al [60] first discussed the formation of PBDD/Fs during the pyrolysis of PBDEs at 510°C to 630°C. However, prevention of highly toxic by-products emissions like PBDD/F, and dehalogenation are the key challenges for pyrolysis of plastic waste containing halogen atoms. To overcome these problems, temperature should be set in range of 250°C to 450°C to avoid the generation of PBDD/F. At temperature lower than the given range, brominated organic compounds mainly bromophenol is formed which served as precursor for PBDD/F formation so it must be avoided to perform pyrolysis at lower temperature [104].

Table 7: Health risk of some brominated flame retardants

Brominated flame retardants	Health risk	References
PBDE	Cryptorchidism	[61]
HBCD	Thyroid system of fish	[62]
TBBPA	Human health	[111]
PBDE	Diabetes	[71]

3 EXPERIMENTAL WORK

The experimental work was conducted at VTT's pilot-plant in Bioruuki. Different halogenated plastic waste raw materials were tested using fast pyrolysis in a bubbling fluidizing bed reactor.

The principal aim was to understand which products can be obtained by pyrolyzing different kinds of halogenated feedstock under different process conditions. One of the most challenging materials as a feedstock for recycling is halogenated plastic, particularly because of its heterogeneity in composition and formation of toxic products upon pyrolysis. Plastic waste could not only contain toxic compounds but also several different extraneous additives like, paper, dirt, etc. Based on starting material, mode of operation, and other operational conditions, various product phases such as liquid, char, wax, pyrolysis oil and pyrolytic gas are produced. The key objective was the determination of products formed and their composition under varying temperatures and use of additive.

3.1 Unit Description

The experimental work was performed on a bench scale bubbling fluidized bed reactor technology having 1 kg/hr feeding capacity. The procedure for the experiment is discussed in appendix 1. The unit includes feeding-tank, reactor, two cyclones, water cooler, electrostatic precipitator, glycol cooler and two dry ice coolers also non-halogenated plastic waste was pyrolyzed on the same pilot plant in 2019 [73].

The schematic diagram for process description is presented in Figure 14.

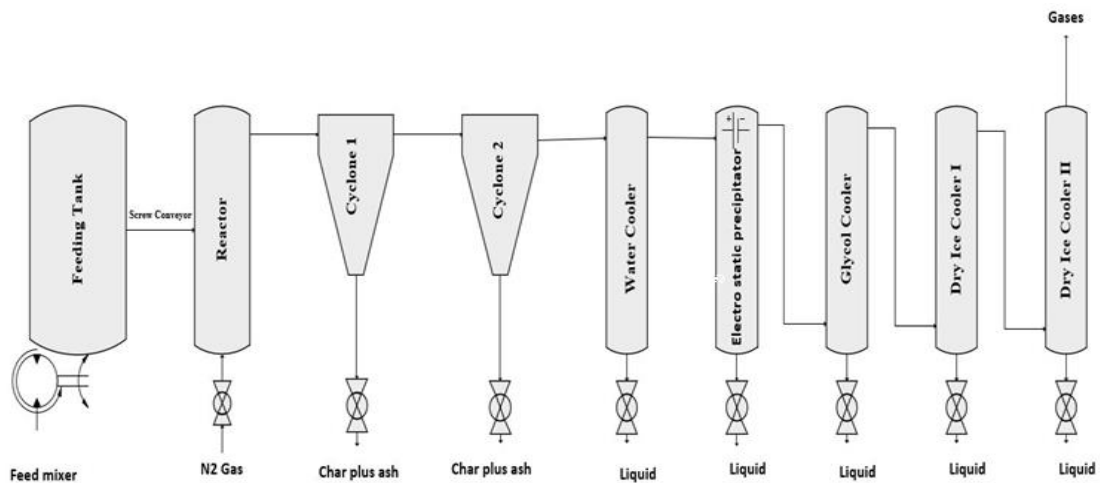


Figure 14: Schematic representation of process plant

3.1.1 Feeding Tank

The feeding-tank constitutes of feeding screw, mixer, and a vibrator for continuous stirring of the feedstock. To get inert atmosphere, nitrogen gas is constantly fed into the tank. Feeding screw controls the feed flow rate to the reactor.

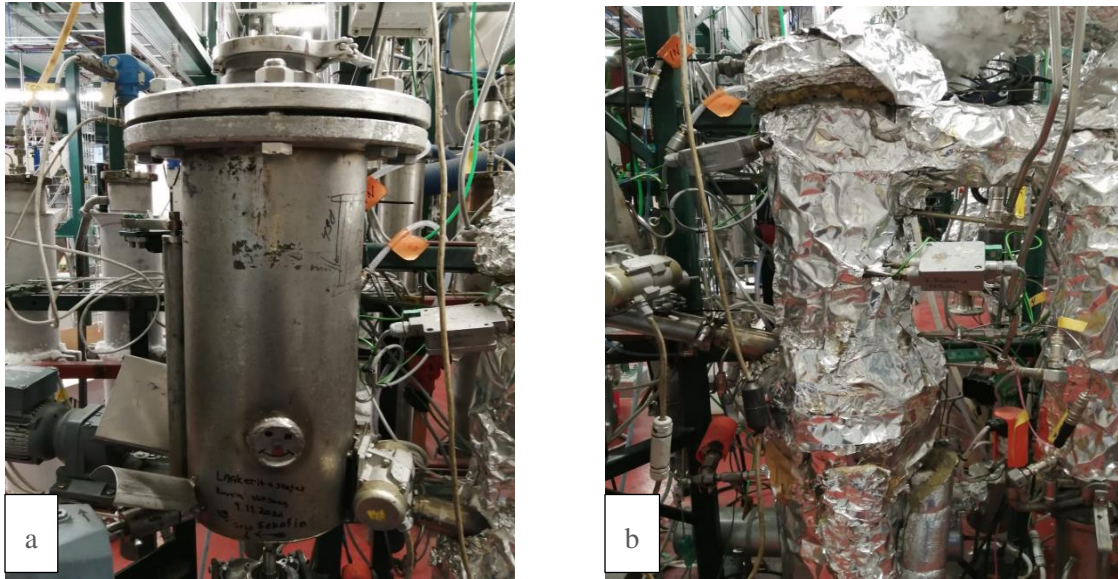


Figure 15: (a) Feeding tank (b) Reactor of KILO's Plant [73]

3.1.2 Reactor

The bubbling fluidized bed reactor used Al_2O_3 as a fluidizing bed material. Fluidization takes place by constant intake of pre-heated nitrogen into reactor. The reactor includes four heaters located on different positions. One at the bottom of reactor, other in the middle of reactor, third known as track heater located at position where feed is entered into the reactor and the last on the above the bed of the reactor.

The residence time of the reactor is varied by altering the temperature and the flow of nitrogen into the reactor. =The space/residence time is calculated as shown in Equation 1.

$$t_{\text{residence}} = \frac{V_{\text{reactor}}}{Q_{\text{N}_2}} \quad \text{Equation 1}$$

Where V is the volume (m^3) and Q is the volumetric flow rate of nitrogen. However, the volumetric flow rate is directly related with temperature and inversely with pressure [Equation 2]

$$t_{residence} = \frac{V_{reactor}}{(V_{n_2} \times 16,666)} \times \frac{1090}{P_{atm}} \times \frac{273}{273 + T_K} \quad \text{Equation 2}$$

For these experiments, the space/residence time is studied from 0.91 to 8s.

3.1.3 Cyclones

After pyrolysis reaction has taken place, gaseous product pass through cyclones where removal of solid particles from gas takes place. These solid materials are accumulated as char. With pure plastic feed, no char is produced while from the waste of plastic having impurities, char is obtained.

3.1.4 Condensing Section

This section contains water cooler, ESP, glycol cooler and two dry ice coolers from A to E [Figure 16]. The hot vapors after solids removal are condensed in the water cooler labeled as A in Fig 18. Water cooling is maintained by normal tap water. At this stage, the cooling of gas takes place at 20 to 30°C. After this step gases enter ESP labeled as B. Here the gas gets condensation on the walls and the oil is collected from the end of ESP. The gas left uncondensed in ESP enters subsequently to glycol cooler labeled as C where cooling of gas takes place at -10°C.

Major portion of the gas is condensed until this unit, is the uncondensed fraction now enters into dry ice coolers (D-E) where the temperature of coolers at is maintained at -40 to -50°C using dry ice-acetone mixture. Non-condensable gases are collected for gas chromatography analysis from exhaust pipe periodically.



Figure 16: Cooling Section of Kilo reactor

3.2 Material and Methodology

Methanol was used for cleaning of apparatus and glassware. The plastic waste samples were sourced from the recycling companies participating in the NONTOX project. Dolomite was used as an additive in some dehalogenation experiments as it is low cost. Many researchers worked on pyrolysis of plastic waste by using dolomite as an additive. Dolomite proves to be effective for cracking of volatile compounds from pyrolysis products [72].

3.2.1 Apparatus and Instruments

Table 8: List of apparatus and instruments used in present study.

Sr. #	Apparatus/Instruments	Model #/Company	Location
1.	X-Ray Fluorescence analyzer	SPECTRO XEPOS	Fraunhofer IVV
2.	Thermogravimetric Analyzer	NETZSCH STA 449	IMDEA
3.	Automated Bomb Calorimeter	IKA® C 5000	VTT
4.	Pyrolysis gas chromatography mass spectrometer	GCMS-QP2010/SHIMADZU ultra	VTT
5.	Gas chromatography flame ionization detector	Nexix GC-2030/SHIMADZU	VTT
6.	Elemental Combustion Analyzer	FLASH 2000 CHNS/O	IMDEA
7.	Vario Max Analyzer	25112028	VTT
8.	Trace elemental instruments explorer (TX analyzer)	TE Instruments (USA)	VTT
9.	Bomb + CE	IKA-WERKE CIA 4100	C5012-01, VTT

3.2.2 Analytical Methods

Elemental, proximate analysis and halogen content of feeds were analyzed by IMDEA and Fraunhofer IVV, respectively. While the products formed were analyzed at VTT's laboratories located in Espoo.

XRF is a non-destructive analytical technique used for elemental determination of compounds. It is a type of qualitative analysis which works on the principle of x-rays photon emission from the excitation of atoms by external energy source. The x-ray photon has

characteristic wavelength and energy. The elements present in material can be identified by determining the number of photons of energy emitted from sample.

TGA measures the weight of the sample as the material is volatilized with an increasing temperature in the furnace. The change in the sample mass is recorded as the temperature is varied.

GC/MS is used for the identification of compounds formed by pyrolysis in liquids and gases. This sample is vaporized in the heating chamber and split into different compounds. These compounds travel through a heated capillary and detect at distinct discrete times through a suitable detector.

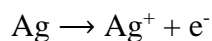
Vario Max analyzer is used for the measuring of elemental composition of the products using ASTM D5291 standard method.

TX analyzer is used for determination of lower halogen contents in the pyrolysis products (gases, wax, char, and liquid). In this method, the sample oxidized rapidly in the existence of a clean O₂ atmosphere at 1000°C (combustion formula) [Equation 3]. Formed fuel gases led through the strong sulphuric acid that helps to remove the contaminants and water from fuel gases. After that, cleaned fuel gases led to titration cell, in which the halogen ions react with silver ions [Equation 4], and the consumed electricity (power) during the titration is measured. The amount of electricity required to react with silver particles is proportional to the halogen contents. Before starting the sample analysis, samples need to be diluted with the selected solvent to reduce halogen contents.

Combustion formula:



Titration cell:



The Capillary Electro Phoresis (CE) based on standard CEN/TS 15289 method is used for the determination of higher contents of halogen in liquid and waxes. From this method both bromine and chlorine can be analyzed accurately. The sample is first reacted with oxygen by combustion in a cylindrical-bomb under pressure. Halogen containing compounds are converted respectively into chlorine and bromine ions which are captured in an absorbing solution like 0.2mol/L water or alkaline KOH. Cl and Br are analyzed by capillary Electro Phoresis (CE), and the detection limit for both elements are 50 to 100 ppm by CE.

Calorific values of the substances are the heat produced by the burning of a unit quantity of substance under specified condition. Composition of substance influences the higher and

lower heating values. Here in the present study, higher and lower calorific heating values of the given feed were calculated by direct formula and Vandralek formula, respectively. The equations for both are given below [108].

Calculation for Lower calorific values (direct formula):

$$LCV = 4.18x(94.19xC-0.5501-52.14xH)$$

Calculation for Higher calorific values (Vandralek formula):

$$HCV = 4.18x(85xC+270xH+26x(S-O))$$

Where C, H, S, and O are the weight percent of carbon, hydrogen, sulfur, and oxygen respectively. Also, both formulas are expressed in KJ/kg.

3.2 Plastic Waste Feedstock

All the plastic waste feedstocks were first homogenized and compacted using MODIX extruder followed by grinding and screening of the material. Modular extruder (MODIX) is a novel extruder consists of comparably short but large diameter cylindrical tube, type screw/rotor and stator. The diameter of screw and cylinder are ten times those of conventional extruders with the same capacity. The larger screw diameter allows feeding heterogeneous input recyclites of different size, density, and shape ratio. This allows feeding of heterogeneous and fluffy film type materials to MODIX. Due to these dimensions, also the inner surface of stator can be machined to a functional geometry notably intensifying the blending, mixing, and heat transfer efficiency. MODIX's hollow screw structure enables also heat transfer from the screw in a techno-economically sound way. This is advantageous especially working at temperature near those of plastic thermolysis [Figure 17].

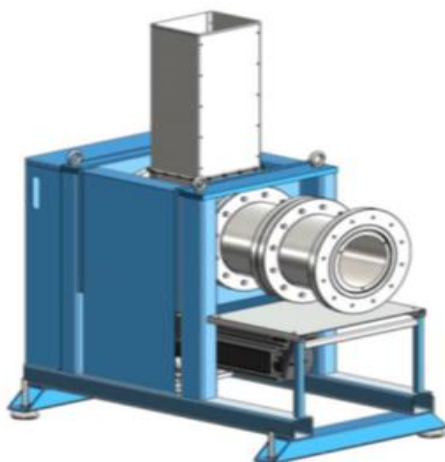


Figure 17: MODIX

3.3.1 Plastic waste sample 1

PWS 1 was expanded polystyrene (EPS). This feedstock is from construction and demolition waste, and it is mainly composed by polystyrene. The feedstock particle size was about 6 mm. The elemental composition and proximate study of plastic waste sample 1 is presented in Table 9 and 10 respectively.



Figure 18: PSW 1 - Expanded polystyrene feedstock.

3.3.2 Plastic waste sample 2

PWS 2 is mainly comprised of polypropylene and polyethylene. This feedstock is originated from SDA (small domestic appliances) and ICT (information and communication technology equipment) waste (type of WEEE) and feed particle size was approximately 3mm. The elemental composition and proximate study of plastic waste sample 2 is presented in table 9 and 10 respectively.



Figure 19: PSW 2 - Polypropylene/Polyethylene feedstock.

3.3.3 Plastic waste sample 3

PWS 3 is comprised of high impact polystyrene (HIPS). This plastic stream is extracted from waste fridges. Feed particle size was approximately 3mm. The elemental composition and proximate study of plastic waste sample 3 is presented in table 9 and 10 respectively.



Figure 20: PSW 3 - High impact polystyrene feedstock.

Table 9: Elemental composition of plastic waste samples 1, 2, and 3

Sample	Elemental Composition (wt%)						
	C	H	N	O	Cl	Br	Cl+Br
PWS 1	89.2	7.7	0.1	0	0.0094	0.002	0.0114
PWS 2	85.6	14.29	0	0	0.0705	0.038	0.108
PWS 3	91.7	8.3	0	0	0.0386	0.0075	0.0461

Table 10: Proximate analysis of plastic samples 1, 2, and 3

Sample	Proximate Analysis (wt%)		
	Volatile Matter	Ash	Fixed Carbon
PWS 1	97.2	2.3	0.3
PWS 2	98.1	1.6	0.3
PWS 3	97.9	2.1	0.0

3.3 Kilo's Experimental Conditions for Plastic Waste Sample 1, 2, and 3

The experimental conditions for each run including feed rate, content of bed material in the reactor, residence time of vapors, temperature, and the duration of the run for plastic waste sample 1, 2, and 3 are mentioned in Table 10. All the runs with dolomite are expressed as grey with steric mark in tabular forms while only steric in figures.

Table 11: Details of the experimental parameters

Sample	PWS 1			PWS 2			PWS 3		
Run number	1	2	3	4	5	6*	7	8	9*
Feed rate (g/h)	300	300	309	300	300	300	300	300	300
Amount of bed material (g)	500	500	500	500	500	500	500	500	500
Residence time (sec)	1	2	1	1	8	8	1	1	1
Temperature (°C)	600	550	600	575	600	600	600	550	550
Time (h)	3	3	3	3	3	3	3	3	3

* Represents experiment with dolomite as an additive.

The space/residence time was calculated based on Equation 1.

4 RESULTS AND DISCUSSION

4.1 Plastic Waste Sample 1

The EPS as plastic waste sample operated at two different temperatures of 550°C and 600°C in run number 2 and 1 respectively. The pyrolysis of EPS at 550°C with 2 second residence time gave maximum liquid yield and less waxes while less total yield whereas at 600°C with 1 second residence, the higher yield was obtained with comparative lower formation of liquid yield and higher wax and gas formation [Table 12].



Figure 21: Liquid, and solid product obtained from EPS feed.

The yield of plastic sample 1 obtained after experiment is listed in Table 12.

Table 12: Product yield (wt%) for plastic waste sample 1

Run Number	Temp °C	Res time sec	Liquid	Wax	Gas	Char	Total	LHV MJ/Kg	HHV MJ/Kg
1	600	1	54	32	3	0	89	33.2	40.5
2	550	2	82	1	1	0	84	33	40.10

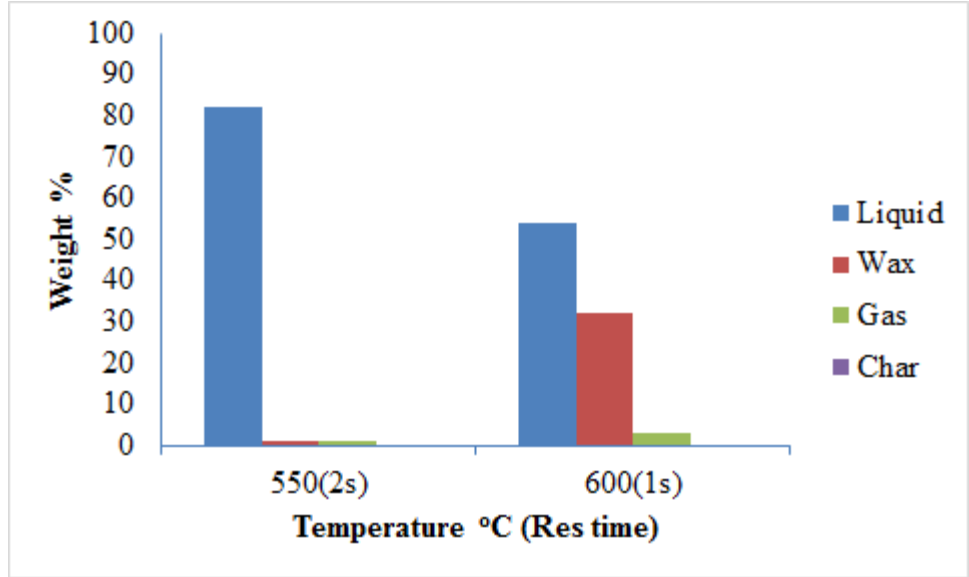


Figure 22: Plastic waste sample 1 product yield as a function of temperature and residence time

The CHN analysis is presented in [Table 13] and it can be seen, carbon content has not been affected by changing the temperature and residence time.

Table 13: CHN analysis of liquid product of PWS 1

Temperature °C	Res time sec	C	H	N	Total
550	2	88.1	7.8	0.1	96
600	1	88.6	7.94	0.1	96.64

The liquid phase of EPS contained 0.00262 wt% of halogen (Cl+Br) content determined by titration method in VTT. The gas phase in a run made at 600°C contained a higher fraction of hydrocarbons than gas phase which made at a lower temperature [Figure 23]. The thermal cracking resulted in formation of methane, ethylene, propylene and hydrogen were observed.

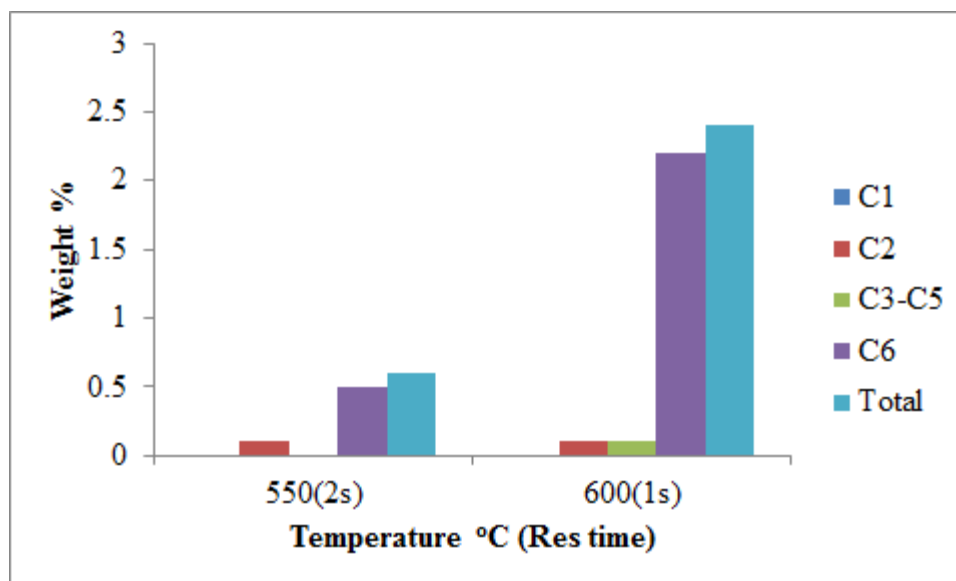


Figure 23: Gas product distribution of PSW 1

The styrene content was analyzed using an Agilent 7890 Gc gas chromatography with flame ionization detector (GC/FID). The recovery of styrene contents in the oil yield of EPS is discussed in Table 14. It has been observed that significant amount of monomer has been recovered in both runs.

Table 14: Styrene content (wt%) of PWS1

Run number	Temperature °C	Styrene wt%
1	600	71
2	550	73

Furthermore, the quantitative analysis of oil fraction of expanded polystyrene is given according to gas chromatography-mass spectrometry measurements of EPS illustrated in Table 15. Formation of single ring aromatic compounds in oil yield with obvious styrene monomer in higher content was investigated by Park et al [109]. The recovery of monomer styrene was observed in both runs.

Table 15: Composition of PWS1 oil

Compound	Area %	
	Run 1	Run 2
Toluene	2.6	1.5
Styrene	69.2	65.8
α -methylstyrene	2.8	1.8

1,2-diphenylethane	3.4	2
Propane-1,2-diylbenzene	1.3	0.7
3-butene-1,3-diylbenzene (dimer)	9	11.4
Hexa-1,5-diene-2,5-diyl dibenzene	2.2	1.6
5-hexene-1,3,5-triyltribenzene (trimer)	1.3	8.7
Other minor compounds	8.3	6.5

4.2 Plastic Waste Sample 2

Plastic waste 2 mainly consisted of PE&PP (information from the recycler). Three experiments were made at 600 °C, of which run 6 was conducted with dolomite as the bed material. Comparing the results from runs 3 and 5, in which residence times of 1 s and 8 s were respectively used, shows that highest total yield was at 600°C with 8 sec residence time with Dolomite while lowest total yield was at 575°C without dolomite. Also, liquid yield was maximum at 600°C with 8 second residence comparatively without dolomite. HHV of liquid phase of plastic waste sample 2 resembled with that of synthetic polypropylene/polyethylene fuel values [112] which illustrate its importance as a fuel while for run 6, calorific values of liquid phase declined considerably which is supposed to be by the reduction in carbon content [Table 16].



Figure 24: Liquid, char and wax of PP/PE feed

The yield of plastic sample 2 obtained after experiment is listed in Table 16.

Table 16: Product yield (wt%) of PWS 2

Run number	Temp °C	Res time sec	Liquid	Wax	Gas	Char	Total	LHV MJ/Kg	HHV MJ/Kg
4	575	1	0	56	18	1	75	30	45.12

3	600	1	1	55	28	0	84	30	44.7
5	600	8	34	16	26	0	76	26.47 (Wax)	38.60 (Wax)
								25.64 (Oil)	37.18 (Oil)
6*	600	8	68	9	36	0	113	23.55	33.18

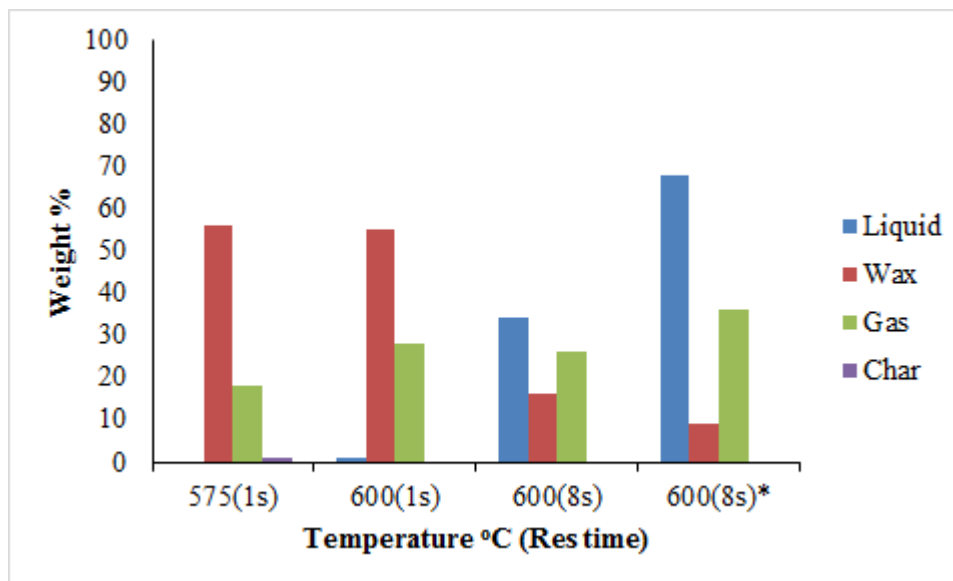


Figure 25: Plastic waste sample 2 product yield as a function of temperature and residence time

The halogen content in wax and oil phase of product is shown in Table 17. It was observed that in the existence of dolomite, the content of chlorine and bromine is remarkably decreased in oil phase from 0.15wt% in run 5 to 0.08wt% in run 6. So, result shows dolomite helps to reduce the halogen contents in oil. There were no wax with runs with dolomite while waxes contain high content of halogen.

Table 17: Halogen content (wt%) of PWS2

Product Phase	Run Number	Cl + Br
Wax	3	0.3948
	4	0.5424
	5	1.5699
	6*	-
Oil	3	-
	4	-
	5	0.1495
	6*	.0882

CHN of the product made by Vario max analyzer, and it shows CHN content of the oil reduced considerably with dolomite because of its cracking property while without dolomite CHN contents of the liquid and waxes were not affected a lot. Also, it was observed that Carbon and Hydrogen content reduced at higher temperature and higher residence time [Table 18, 19].

Table 18: CHN analysis of liquid derived from PWS2.

Temperature °C	Res time sec	C	H	N	Total
600	8	71	10.6	0.1	81.1
600*	8	64.8	9	0.1	73.9

Table 19: CHN analysis of wax of PWS2

Temperature °C	Res time sec	C	H	N	Total
575	1	82.8	13.5	0.03	96.33
600	1	83.5	13.5	0.05	97.05
600	8	73.4	11.1	0.2	84.7

In absence of dolomite, the distribution of gas yield at 575°C and 600°C with 1 second residence time showed increase in C1 to C6 hydrocarbon whereas, with 8 second residence time at 600°C heavier hydrocarbons declined considerably. In presence of dolomite, distribution of gas yield at 600°C with 8 second residence time, the C6 hydrocarbons concentration was low because it enhanced the yield of light hydrocarbon compounds. [Figure 26].

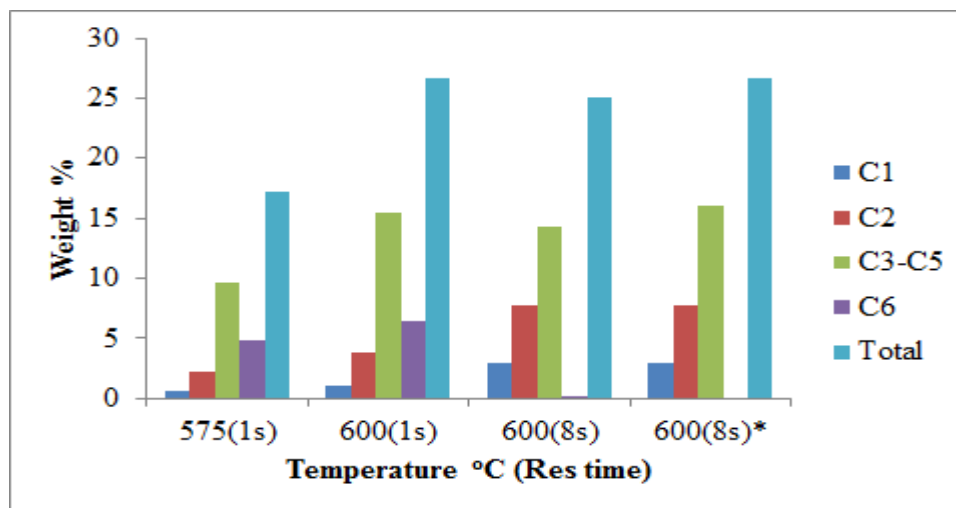


Figure 26: Gas product distribution of PWS2

It can be seen that heavier compounds C37+ were decreased by increasing the temperature while light hydrocarbon compounds were increased. At higher temperatures, with higher residence time liquid yield was almost double than waxes, and it contains a higher quantity of C6-C17 organic compounds. Also, it was observed; waxes were disappeared with the use of dolomite, and it produced a higher amount of liquid that contain C6-C17 hydrocarbon compounds. [Figure 27].

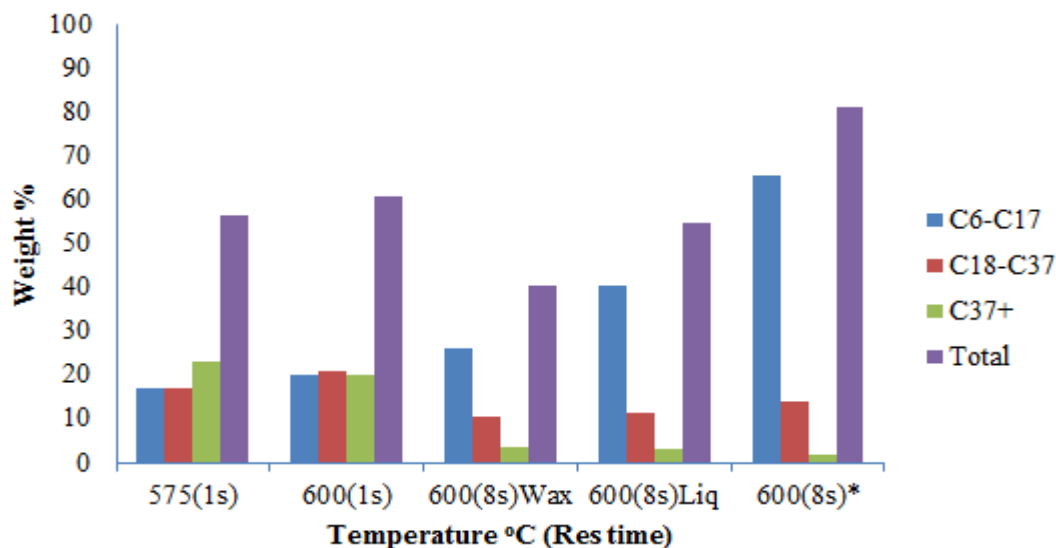


Figure 27: Oil and wax characterization of PWS2

4.2 Plastic Waste Sample 3

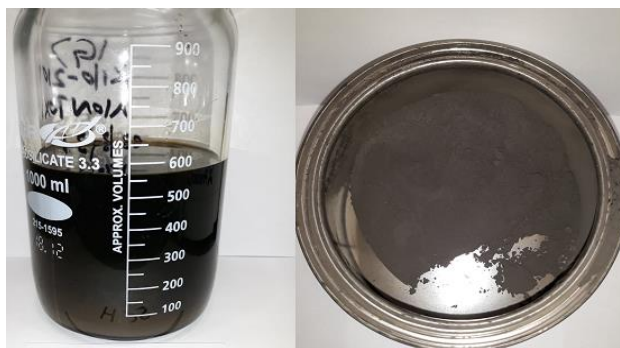


Figure 28: Liquid & char obtained from PSW3.

The product obtained from plastic sample 3 is listed in Table 20. Product yield from run number 9 seems too low comparatively other runs 7 and 8 because of scrubbing unit. During run number 9, CO₂ II condensing column was replaced with the scrubbing unit to absorb halogen gases. During scrubbing, scrubbing liquid formed a complex mixture with liquid oil, and it was hard to measure the exact quantity of oil from the scrubbing solution.

Quantitative analysis for the pyrolysis yield of HIPS showed higher formation of liquid with almost negligible char formation. The heating values for all the runs remain same [Table 20].

Table 20: Product yield (wt%) of PWS3

Run Number	Temp °C	Res time sec	Liquid	Wax	Gas	Char	Total	LHV MJ/Kg	HHV MJ/Kg
7	600	1	79	2	3	0	84	32.76	40
8	550	1	84	2	1	1	88	33	40.3
9*	550	1	61	3	3	0	67	33	40.5

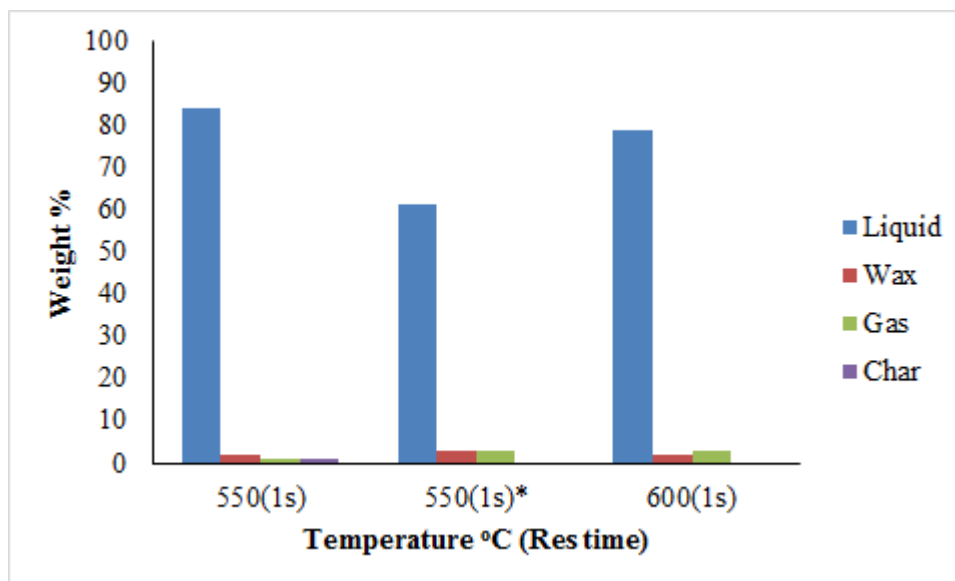


Figure 29: Plastic waste sample 3 product yield as a function of temperature and residence time

There were few precipitations in the liquid phase from run 7, and it could appear because of the reaction between halogenated compound and polystyrene monomers. In run 7, the content of halogens was lower than 8 because it contains oligomer of polystyrene, and maximum halogen content was trapped by solid oligomers due to their higher reactivity. So technically, yields from both runs 7 and 8 had higher amount of halogen contents than run 9. It can be seen in the presence of additive, the halogen content reduced in run 9 [Table 21].

Table 21: Halogen content (wt%) of PWS3

Product Phase	Run Number	Cl + Br
	7	.0483

Oil	8	.0635
	9*	.0496

Table 22 shows that CHN analysis of the liquid yield, and it explains; elemental composition of the compounds has not changed between the all experimental runs.

Table 22: CHN analysis for liquid yield of PWS3

Temperature °C	Res time sec	C	H	N	Total
550	1	87.7	8.1	0.1	95.9
600	1	88.2	8	0.1	96.3
550 *	1	88.4	8.1	0.06	96.56

It can be seen the amount of gas increased by increasing the temperature between 550 to 600°C but C6+ were lower than C3-C5. While C6+ quantity rose with additive at 550°C [Figure 30]. This could indicate that dolomite enhanced C6+ compounds in the produced gaseous mixture.

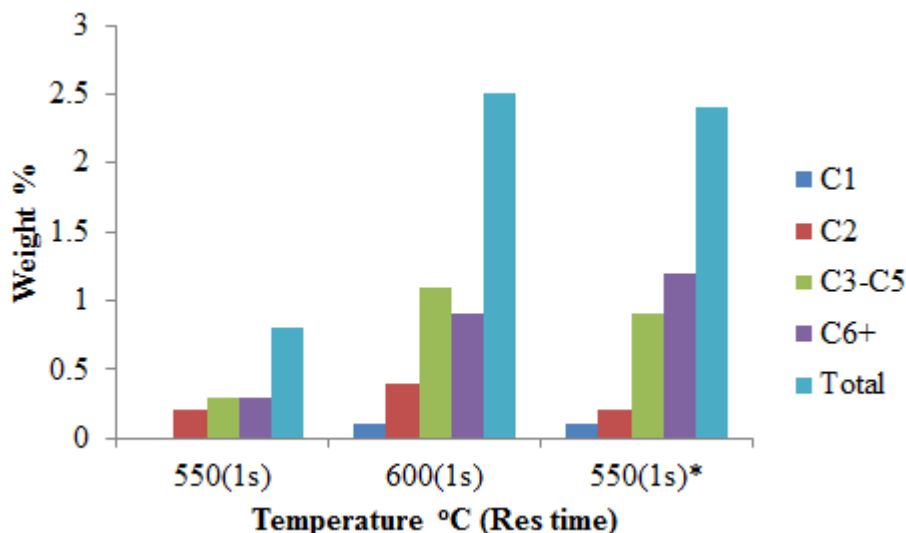


Figure 30: Gas composition of PWS3

The styrene content was analyzed using an Agilent 7890 Gc gas chromatography with flame ionization detector (GC/FID). Table 23 represents the recovery of styrene content from plastic waste sample 3 and it is observed that significant monomer has been recovered from the sample at variable temperatures.

Table 23: Styrene content (wt%) of PWS3

Run number	Temperature °C	Styrene wt%
7	600	76
8	550	72
9*	550	73

The characterization of oil for qualitative analysis was performed by gas chromatography-mass spectrometry (GC-MS) [Table 24]. The presence of dolomite reduced the liquid yield; the volatile products from the catalytic pyrolysis lessen the hydrocarbons yield as compared to the thermal degradation [110].

Table 24: Composition of PWS3 oil

Compound	Area %		
	Run 7	Run 8	Run 9*
Toluene	3.4	2.97	3.73
Styrene	66.7	67.43	66.50
Alpha-methylstyrene	4.1	3.14	4.51
Ethylbenzene	1.3	-	1.25
Unidentified not polystyrene	1.1	1.1	-
Bibenzyl 1,2-diphenylethane	2.5	1.44	1.46
3-butene-1,3-diylbenzene (dimer)	7.5	7.46	6.58
Hexa-1,5-diene-2,5-diyl dibenzene	1.3	1.32	1.57
5-hexene-1,3,5-triyltribenzene (trimer)	7.1	7.07	3.59
Indene	1.2	-	-
Propane-1,2-diyl dibenzene	1.6	-	-
3-butene-1,3-diylbenzene (dimer)	5.6	-	-

4.3 Summary

The experimental was to pyrolyzed three different feedstock namely PSW1, PSW2, PSW3 at different conditions of residence time, temperature, and pressures. Mentioned conditions [Table 11] had been chosen based on the literature survey with the aim to obtain excellent product yield. During the experiments, the pressure was atmospheric while temperature and residence time had been varied to meet the objective.

PWS1 was pyrolyzed at two different temperature and residence time at 600°C, 550°C, 1s and 2s respectively. During the first run, liquid yield was about 54 wt% while the waxes were about 32 wt% at 600°C with 1 second residence time. In the second run by increasing the residence/space time and decreasing the temperature, the liquid yield was increased to 82 wt % whereas yield of waxes decreased from 32 wt% to 1 wt% at 550°C with 2 second residence time. It was noted that the quantity of the liquid phase of the pyrolysis of EPS improved at lower temperature and higher residence time [79].

PWS2 was tested at four different operating conditions by varying the residence time and temperature to obtain the maximum liquid yield in presence as well as in the absence of dolomite additive. First two runs were in absence of dolomite additive with 1 second residence time at 575°C and 600°C gave 0 wt% and 1 wt% liquid yield respectively along with 55 and 56 wt% waxes. During the third run at 600°C with increased residence time (8s) higher phase of liquid (34 wt%) was acquired whereas in existence of additive at same temperature and residence time of run three highest liquid yield of 68 wt% followed by only 9 wt % waxes were attained. The pyrolysis of PWS2 in presence of dolomite additive showed maximum liquid yield in comparison to the experiments done in the absence of dolomite.

Pyrolysis of PSW3 feed was done at three different temperatures, with one in the presence of dolomite at 600 and 550°C respectively. The maximum liquid yield from HIPS pyrolysis was obtained at lower temperature (550°C) with increase in formation of gases by increasing temperature. The liquid composition obtained showed maximum recovery of monomers as well as formation of aromatic compounds, paraffin, and other minor organic matters. The effect of was also discussed during run 9 for PWS3 pyrolysis.

Pyrolysis or thermal cracking encompasses the degradation of polymers in the lack of oxygen mostly under inert environment. Depending upon polymeric material, pyrolysis is proceeded by either chain-end or random scission of macro-molecules. The free radical chain mechanism for EPS begins via random scission and monomer is recovered as mechanism is de-propagated. The maximum recovery of monomers was found during all experiments also the formation of methane, ethylene, propylene, and some of C_x were observed. The range of temperature set for overall pyrolysis of all the feeds with or without additives were between 500°C to 600°C and it was observed that by increasing the temperature the gaseous products also increased. While the formation of pyrolysis oil reduced by reduction in temperature of

pyrolysis. It was also remarked that the formation of char and other residue was not greatly influenced by temperature and the presence of additive.

Mostly liquid yield with low halogen content was obtained with dolomite after the pyrolysis of all the given feeds however the upgrading of pyrolysis products could not be done to obtain completely de-halogenated products.

4.4 Challenges and Recommendations

It was observed there were some practical challenges during the experiments. During the experiments, PSW1 was run 3 times, and it was noticed; electrostatic precipitator was not working appropriately because at those conditions this waste produced higher amount of waxes, which were deposited on the walls of the ESP stopping the charge to pass through. Therefore, ESP was eliminated from the condensing section after few experiments. Run number 1 was problematic because of two prominent reasons. Firstly, there was pressure rise in ESP condenser column because of accumulation of waxes in pipeline. Secondly, feeding screw was broken because feeding particles were not homogeneous, and there was back pressure force which was generated by melted particles in screw conveyor. Consequently, the feed was size reduced, and the conveyor screw was provided with additional cooling using cooling jacket.

Recommendations include improvements and optimizations for the process of pyrolysis. As the products of pyrolysis constitute of waxes and their collection is difficult. It is hard and gets stuck into pipes and cause blockage of the pipelines also the cleaning post experiment is challenging. Formation of waxes during pyrolysis process depends upon the temperature of reaction for a given feedstock so one of the suggestions for the collection of wax is to place a collection tank where the waxes would get collected during the process depending upon operation temperature.

During the pyrolysis of expanded polystyrene, it was observed; a minor part of the product was leaving the system, and it may affect the mass balance of kilo. It not only affects the process but also their collection is problematic. This same problem was noticed during the work done by Joon [73]. By increasing the residence time in the cooling section, the quantity of lost products could be recovered.

5. CONCLUSION AND FUTURE PERSPECTIVE

The objective of the thesis was to treat hazardous plastic waste samples Therefore i-e expanded polystyrene, polypropylene/polyethylene, and high impact polystyrene from WEEE, and CDW was tested at variable temperature, and residence time. The experiments

were performed with or without dolomite to study its effect on liquid phase and halogen contents.

Overall, nine runs were carried out at temperature ranges from 500°C to 600°C by varying the residence time between 1 second to 8 second at constant pressure (1 atm). Out of nine, two runs (6, 9) were done with dolomite at 600°C with 8 second residence time and 550°C with 1 second residence time, respectively.

EPS was pyrolyzed at 550°C and 600°C with 2 and 1 second residence time, respectively. PP/PE was pyrolyzed with or without dolomite at 575 – 600 °C with 1 and 8 second residence time, to produce oil and wax with lower halogen contents. Halogen contents in oil obtained were lower than that obtained without dolomite. HIPS was also pyrolyzed with or without dolomite using same reactor at 600°C, 550°C, and 550°C with 1 second residence time to produce oil and wax with lower halogen contents. The oil yield in the product decreased, also halogen contents declined. Thus, halogen contents in oil obtained were lower than that obtained without dolomite.

Research on the thermolysis(pyrolysis) of halogenated plastic waste is still ongoing, and thermolysis has a worthwhile role to convert plastic-waste into plastic-based liquid fuel oil. Liquid oil fuel obtained from thermolysis is like crude oil and thus, this cannot be used straight as an energy source until it fulfills certain standard specifications to certify the quality and performance of the oil fuel. The upgradation of the oil produced from pyrolysis will be considered in future work to obtain refined and high-quality fuel oil by using post-treatment. While post-treatment involves catalytic cracking, dehydrohalogenation (on-line and off-line cracking), hydrocracking, and hydrogenation.

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Appendix 1

Starting Procedure

- Turn ON the glycol cooling device as it takes too long duration to get cooled. After started by weighing the raw material and transfer it to the feed tank (remember to determine the weight of the bucket first).
- Calibrated the frequency for the feeding screw by observing 125g material per 15 minutes at different frequencies (e.g., 11.25 for EPS).
- After adjusting the appropriate frequency for feed, feeding tank need to be filled by 3000g raw material (feed).
- Dry ice cooler (D-E in figure 6-4) should be filled by acetone respectively 1L and 0.5L followed by filling dry ice. The purpose of adding acetone is to improve the heat transfer rate.
- Weigh the bed material (Al_2O_3) approximately 500 g and attach the feeding tank and reactor with feeding screw conveyer to fix the bed material. The fluidizing gas should be float at 10L/min before inserting 500g bed material into the reactor. Simultaneously check all the valves, and nuts to make sure that pipelines are open.
- Before the start of experiment, reactor temperature should be above 50°C than the target temperature. That's why turn on the heater at the beginning of experiment.
- Do the pressure test to check any leakage in plant.
- Open the water cooler valve and adjust 1 sec reactor residence time.
- Switch ON the mixer and screw conveyer (to push raw material toward reactor).
- Begin data collection on computer and turn ON the timer and feed at the same time.
- To observe the smoke in sample bottle (attach with ESP unit) after starting the experiment.
- No need of cyclone cleaning is required for pure plastic sample because it does not form any ash

Process Operation

- GC gas sample is taken twice, during the three hours based experimental run. First sample can be taken after one hour and second after two hours.
- Reactor temperature adjustments depends mainly on '1-KG Arina Laippa'. Shown by controller 2 on the control panel. Other temperature controllers are used to tune reactor temperature during the process.
- Monitor temperature and pressure changes via panel all over the plant. Because sudden change in pressure (increase in pressure) indicates clog formation in pipelines because

of wax (pipe can be unclogged by gently hitting the pipelines with hammer). While temperature rise may indicate feed is not properly inserting to the reactor (For this purpose, combine the feed in feed tank or gently hitting the feeding screw with hammer)

- Timely add dry ice to the dry-ice cooling units during the experiment.

Shutdown Procedure

- Switch OFF the mixer, stop-watch and feeding-screw.
- Turn OFF the glycol cooler also all heaters.
- Let the transfer all the feed to reactor from screw conveyer before it turns off.
- Open all valves toward the combustion pipeline and closed the product pipelines valves.
- Close the cooling water valve after it cools down the screw conveyer line below 100°C.
- Screw conveyor and feeding tank can be disconnected and close the reactor hole with seal.
- Reduce the Nitrogen flow rate to 10 L/min, and turn-off data collecting option from computer.
- At the end, open all sample valves.

Cleaning Process

- During the entire cleaning process, PPE (Mask, safety helmet and gloves), HCN and CO gas detectors should wear.
- Right after the experiment, screw conveyer is needed to be cleaning after its removal because it's easy to peel off melted plastic from the screw by using metallic spatula and wire brush. Plastic from the screw conveyor weighted out because it is needed for the material balance.
- Remove and weigh the all vessels, sample bottles and pipelines from water condenser (A) to dry-ice condenser (D-E). After cleaning the whole vessels and pipelines carefully.
- Carefully label the plastic boxes as per experimental run and date.
- Sink the acetone from dry ice cooler to a bucket.
- Vacant both cyclones and weigh them.
- Empty the feeding tank into bucket via feeding screw and remaining feed can be vacuum and weighted for the material balance (before vacuuming, bag weight must be measured).
- Reactor bed material can be vacuumed (bag weight must be measured before) after its cooling. Mostly it is done one the second day of experiment.

- After removing the bed material, remaining things can be burn in reactor in the presence of 20 l/min flow of air at high temperature (600 °C) for 15 minutes.
- After burning, turn off the whole heater and air flow.
- At the end, reattached all vessels, pipelines and new weighted glass sample bottles.