



## Review

## A review on thermal and catalytic pyrolysis of plastic solid waste (PSW)

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## ABSTRACT

Plastic plays an important role in our daily lives due to its versatility, light weight and low production cost. Plastics became essential in many sectors such as construction, medical, engineering applications, automotive, aerospace, etc. In addition, economic growth and development also increased our demand and dependency on plastics which leads to its accumulation in landfills imposing risk on human health, animals and cause environmental pollution problems such as ground water contamination, sanitary related issues, etc. Hence, a sustainable and an efficient plastic waste treatment is essential to avoid such issues. Pyrolysis is a thermo-chemical plastic waste treatment technique which can solve such pollution problems, as well as, recover valuable energy and products such as oil and gas. Pyrolysis of plastic solid waste (PSW) has gained importance due to having better advantages towards environmental pollution and reduction of carbon footprint of plastic products by minimizing the emissions of carbon monoxide and carbon dioxide compared to combustion and gasification. This paper presents the existing techniques of pyrolysis, the parameters which affect the products yield and selectivity and identify major research gaps in this technology. The influence of different catalysts on the process as well as review and comparative assessment of pyrolysis with other thermal and catalytic plastic treatment methods, is also presented.

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### List of abbreviations

ABS	Acrylonitrile-Butadiene-Styrene	LLDPE	Linear Low Density Polyethylene
Cl	Chlorine	MAP	Microwave Assisted Pyrolysis
CO <sub>2</sub>	Carbon Dioxide	MSW	Municipal Solid Waste
CSBR	Conical Spouted Bed Reactor	MSWIs	Municipal Solid Waste Incinerators
CV	Calorific Value	PE	Polyethylene
FBCs	Fluidized Bed Combustors	PET	Polyethylene Terephthalate
FBR	Fluidized Bed Reactors	PO	Polyolefin
GHGs	Greenhouse Gases	PP	Polypropylene
HCl	Hydrochloric Acid	PS	Polystyrene
HDPE	High Density Polyethylene	PSW	Plastic Solid Waste
HHV	Higher Heating Value	PU	Polyurethane
HIPS	High Impact Polystyrene	PVA	Polyvinyl Alcohol
ICTAC	International Confederation on Thermal Analysis & Calorimetry	PVC	Polyvinyl Chloride
IRR	Internal Rate of Return	TCT	Thermo-Chemical Treatment
LDPE	Low Density Polyethylene	TGA	Thermogravimetric Analysis
		TPA	Tons per Annum
		VGO	Vacuum Gas Oil
		WEEE	Waste From Electrical and Electronic Equipment

## 1. Introduction

Plastics play a major role in our daily lives and our ever growing dependency on them is justified by their versatility, light weight and low production cost relative to other classical materials such as wood, concrete and metal. Plastics are now considered the key material in numerous sectors such as construction, medical, engineering applications, automotive, aerospace, leisure, electronics, packaging, food and others. In addition, economic growth and increase in population add to the demand on plastic articles and their feedstock chemicals used in their production. This on the other hand has made the demand for plastics grow more rapidly over the last two decades. The global production of plastics was reported to be 299 million tonnes in the year 2013 and an increase of 4% has been reported over the year 2014 reaching a production rate of 311 million tonnes (WI, 2015).

The increase in demand for plastics can only lead to the accumulation of plastic solid waste (PSW) which takes up a large share of the municipal solid waste (MSW) sector in developed and developing countries alike. Recent statistics show that 25.8 million tonnes of plastics ended up in the waste upstream of Europe of which 39% was landfilled (PE, 2014). In addition, developing world countries rely solely on landfilling as a strategy for MSW disposal without realising the advantages that certain recycling schemes might add to their economic chain value (Al-Salem, 2009; Al-Jarallah and Aleisa, 2014; Al-Roumi, 2014). Increase in landfilling without the right means of feedstock or energy recovery, which is what many developing world countries rely upon, has also been associated with major health and environmental concerns namely in causing ground water contamination, increase in greenhouse gases (GHGs) emissions, risk of fire and explosion, human health hazard and sanitary problems (Kumar and Sharma, 2014). Hence, valorising PSW in various treatment methods has been a major area of research and development where emphasis has been on recovering energy and valuable products from waste.

PSW can be managed via a number of treatment methods, categorized as follows (Mastellone, 1999; Al-Salem et al., 2009a, 2010):

- 1) Primary means: where plastic process scrap is re-introduced in the heating cycle of the processing line to increase production;
- 2) Mechanical recycling (secondary methods): where mechanical (physical) means of treatment are used to re-extrude, process and convert PSW typically blended with virgin polymers aiming at reducing overall cost;
- 3) Chemical (tertiary) methods: where a chemical alteration in the polymer structure is performed via chemical, thermo-chemical means, or where PSW is utilized as a monomer feedstock in industrial recycling loops, and finally;
- 4) Energy recovery: which entails recovery of steam, heat and electricity from waste through combustion.

In managing resources and lowering processing costs for converters, these methods present a hierarchy of preference in an ascending order, from primary to quaternary. These methods are categorized based on the nature of the treatment method used and type of products extracted from it. This hierarchy of PSW management fall in the main waste management hierarchy where reducing and reusing are still more favourable than these options (Giroux, 2015). Each PSW treatment method provides a set of advantages that helps orient and utilize PSW for certain applications. Primary methods help reduce the processing costs and the amount of industrial (scrap) waste generated on the part of the plastic converters. It typically subjects the PSW to mechanical means of conversion in a closed loop recycling scheme. However, this method can't resolve the accumulated PSW in urban environments. It is also very sensitive to the age and type of the plastic where scrap from a single industrial plastic conversion line can be re-introduced and used in a similar manner to the virgin resin (Kartalis et al., 1999, 2000). In addition, reprocessing and subjecting the plastic material

to additional heating cycles will result in molecular damage, such as chain scission, cross-linking, or formation of double bonds; which will reduce the integrity of the resulting final product (Herbst et al., 1995; Philip et al., 2004). The same argument can be put forward regarding mechanical treatment methods, where physical techniques (e.g. injection moulding, extrusion, blow filming, rotational moulding, etc) will be employed to produce articles from various converted plastics that are comparable to ones produced from virgin plastic resins. Hence, quality control and final product integrity are of major concerns in this technique. In addition, rigorous requirements and consumer demand for high end products makes investment in this type of recycling schemes non-profitable. Furthermore, sorting and cleaning PSW into a suitable feed for mechanical treatment is not to be overlooked due to the effect that impurities, dyes and pigments have on the quality of the finished product (Masanet et al., 2002; Kang and Schoenung, 2005).

Using PSW as a feed for energy recovery purposes is a matter that has been discussed and reviewed thoroughly in literature (Bani-Hania et al., 2016). Due to their high calorific value (CV) which matches conventional fuels (e.g. gasoline, kerosene, diesel, etc), plastics can be used as a throughput material in incinerators to produce electrical power, steam and heat (Dirks, 1996; Williams and Williams, 1997). However, using PSW or MSW in general presents various challenges that makes this type of treatment very demanding and questions its economical value versus its advantages in reducing volume of waste and energy production. Such encountered problems include non-consistent type of feed resulting from inadequate sorting, fluctuating heating values, combustion instability, complex pollutant emissions in-need of control and unsuitability for plateau areas (Fu et al., 2015).

The main challenge all of the previous treatment methods face, which they are typically criticized for is the high demand of energy and utilities associated with their operation. Moreover, with the increase on plastics demand each year, fossil fuels and especially crude oil depletion and fluctuating prices seems to be a major obstacle for recycling and treatment schemes. It is estimated that 4% of global crude oil being produced is dedicated for the plastics industry (BPF, 2008). In addition, biodegradable plastics production has also increased over the past few decades due to their reputation as an environmentally friendly product. However, biobased products are not considered as a resolution to the PSW accumulation problem. This is due to the fact that biodegradation doesn't degrade the whole plastics product and also ends up in the solid waste main stream. Hence, it is essential to find ways to resolve the accumulated waste originating from the MSW sector and especially PSW to be of more sustainable nature that can self sufficiently help in reducing the dependency on the crude oil industry. This is especially true when considering that the main chemicals that are used to produce plastic materials are all of petrochemical industry sources, i.e. resulting from the crude oil processing and refining industry. Therefore, it would be ideal to find a solution where PSW can be used as a feedstock for producing such chemicals where it would be used as an integrated part of refining and petrochemical complexes or as a standalone recycling schemes. Such a process will also help in designing intelligent energy systems to fully utilize the waste to meet the increased energy demand (Churkunti et al., 2016).

In principle, and being a crude oil derivative, plastics can be converted to their constituting chemicals that are derived from petroleum refining cuts and petrochemicals via thermal or catalytic means of chemical treatment. Hence, the principle of chemical treatment that was mentioned previously was developed to manage the accumulated plastics in the waste sector in a better and more efficient manner. Chemical treatment, as the name implies, is the term used for treatment methods and recycling schemes that

result in changing the chemical structure of the plastic material itself (Al-Salem et al., 2009a). Moreover, it encompasses various treatment methods that result in high end value products from PSW. Such methods include glycolysis (Simon et al., 2014; Sharma and Bansal, 2016), hydrolysis (Campanelli et al., 1993; Evans and Chum, 1991; Panda et al., 2010), pyrolysis (Williams, 2013; Williams and Brindle, 2002; Danon et al., 2015a, 2015b), aminolysis (Goje et al., 2004; Sinha et al., 2010; Sadeghi et al., 2011), gasification (Dou et al., 2016; Wang and Zhao, 2016; Onwudilia and Williams, 2016) and hydrogenation (Bockhorn et al., 1999a; Aznar et al., 2006).

However, advanced thermo-chemical treatment (TCT) methods namely pyrolysis has received renewed attention recently due to the numerous operational and environmental advantages it provides given global energy demand and unstable fuel market. Pyrolysis is defined as the process where thermal degradation in inert atmospheres of long chain organic materials occurs with the presence of a catalyst (catalytic pyrolysis) or without (thermal process). The long chains of the organic materials treated result in smaller and less complex ones by controlling the heat flow and pressure of the operation (Qinglan et al., 2010). Longer residence time of operation is typically required with less intense heat, and products of pyrolysis are typically categorized as tars (a mixture of aromatic hydrocarbons with a molecular weight greater than benzene), gases and char (Figueroa et al., 2013). Pyrolysis requires no flue gas clean up, as the flue gas produced is mostly treated prior to its utilisation (Fodor and Klemes, 2012). It also produces valuable petroleum refining and petrochemical processes comparable products that can reduce the reliability on petroleum processing as previously discussed by Butler et al. (2011) and shown in Table 1.

Pyrolysis is also commonly associated with producing valuable tars (i.e. liquid oils and waxes) at relatively moderate temperatures ranging between 500 and 650 °C, with yields ranging between 75 and 80 wt% (Mastral et al., 2002; Fakhrhoseini and Dastanian, 2013). The residual output of char produced could be easily used as a fuel or a feedstock for other petrochemical processes. Environmentally, pyrolysis provides an alternative solution to land-filling and reduces GHGs, namely carbon dioxide (CO<sub>2</sub>) emissions. Pyrolysis has better environmental advantages compared to other MSW treatment methods. Pyrolysis utilises an inert atmosphere free from oxygen, so it does not form dioxins by reaction of products with oxygen. It also reduces the carbon footprint of processes and products by reducing the emission of carbon monoxide (CO) and CO<sub>2</sub> (Chen et al., 2014; Stanmore, 2004; McKay, 2002; Kanniche et al., 2010; Singh and Ruj, 2016). Financially, pyrolysis produces a high CV fuel that could be easily marketed and used in gas engines to produce electricity and heat (Demirbas, 2001). Along with other TCT methods, namely hydrogenation, pyrolysis has proven to be a very lucrative investment with internal rate of returns (IRR) surpassing 30% in industrial economy of scale schemes (Al-Salem et al., 2014; Arena et al., 2011). Gases (non-condensable fraction) produced from pyrolysis, typically considered as a by-product, are also of a very high CV that can be used to compensate the overall energy requirement of the pyrolysis plant itself (Abnisa and Wan Daud, 2014). Pyrolysis also has economic advantages as it does not require as many feedstock pre-treatment steps as other treatment methods. Pyrolysis comparison will be discussed better in the comparative assessment section with other thermal and catalytic PSW chemical treatment methods later in this review.

Henceforth, pyrolysis has been thoroughly studied over the past years and the process was applied on various types of plastics in thermal and catalytic setups as a mono feedstock (i.e. single plastic) or co-pyrolysis (i.e. mixture feeds) schemes to simulate and mimic PSW treatment in such methods of thermo-chemical recycling. It should be duly notes, as this review paper will reveal, that pyrolysis

**Table 1**  
Summary of main petrochemicals (PCs) produced via pyrolysis of main plastic materials.

Product	Price (€/tonne)	Process	Feedstock	Intermediate/final product
Ethene	692–1084	Thermal cracking	Ethane, propane, naphtha, gas oil	PE manufacture (>50 wt%), antifreeze, polyester fibres, PVC, PS plastic & foam, soaps, plastics, detergents
Propene	692–1279	Thermal cracking	Ethane, propane, naphtha, gas oil	PP, plastics, fibres, foams, cumene (IP), C <sub>4</sub> alcohols, oligomers, soaps, detergents
Butadiene	602–1656	Thermal cracking Dehydration	Ethane, propane, naphtha, gas oil, butane/butenes	SBR (tyres), elastomers, nylon monomers
Benzene	710–922	Catalytic reforming/hydrodealkylation	Naphtha, toluene	Styrene, cumene, cyclohexane, polyurethanes
Toluene	582–828	Catalytic reforming	Naphtha	Gasoline octane enhancer, benzene, TNT (explosive)
Xylenes	597–862	Catalytic reforming	Naphtha	Gasoline, benzene, solvents, PET, textiles fibres, photographic film, bottles, plasticizers, unsaturated polyester resins, alkylated resins

Source: [Butler et al. \(2011\)](#).

is very sensitive to process conditions and type of feeds and catalysts used. This work will present and critically discuss pyrolysis to give the reader a full view of the process and the main influencing factors on its products.

## 2. Thermal pyrolysis process

### 2.1. Types of feedstock

Thermoplastics and thermosets are the main types of plastics which are used as daily commodities. About 80% of consumed plastics in Western Europe are thermoplastics due to their susceptibility to change and molecular reformulation with heat exposure. PSW mainly consists of high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET). Polyethylene (PE) makes up about 40% of the PSW in the total waste stream making it a very common type of waste to accumulate in urban environments ([Onwudili et al., 2009](#)). Due to the fact that plastics produce somewhat clean distillates by comparison to other organic feedstock materials that are used in pyrolysis, attention has been made to the optimal processing conditions and types of plastics treated in order to obtain certain desired products ([Sharma et al., 2014](#)).

The products produced from plastic pyrolysis are very similar to fossil fuels. This is because plastics are essentially polymers with chemical additives that are used to orient and engineer their use towards desired applications by customers. It is also due to the fact that majority of the constituting polymers of plastic materials consist of carbon and hydrogen atoms, which is the case for the two major polyolefin (PO) polymers used on the market, i.e. PE and PP, they have been extensively researched in terms of pyrolysis ([Kunwar et al., 2016](#)). PE has been reported to have a carbon content ranging between 83.9 and 86.1%, whilst PP has a range of carbon between 85.5 and 86.1% ([Sorum et al., 2001](#); [Encinar and Gonzalez, 2008](#)). Such a high carbon content present in major polymers constituting PSW makes pyrolysis a favoured treatment and a method of choice in TCT of plastics. Other common types of plastics such as PS, PVC and PVA have a high aromatic content. This is due to the fact that petrochemical (light) naphtha is used to polymerize these materials (termed as polyaromatic plastics) in the chemical industry. Hence, such plastics yield high fractions of aromatics after being pyrolysed. This is something to consider when treating a certain feedstock in pyrolysis, especially aromatics are the desired end product.

PSW consists of various types of plastics, and it is essential to understand that different feedstock materials properties for pyrolysis would yield different products. [Table 2](#) summarizes the

main properties of major plastics taken from various studies conducted in the past on pyrolysis of plastics. The optimal target is usually pyrolysis tar products namely liquid oils. By studying the proximate analysis of the plastic materials, one can establish an understanding between the properties and types of plastic feedstock to the process of pyrolysis and the products yielded by it. Essentially, high volatile matter and ash content are the main factors that influence the production of pyrolysis liquid oil ([Kreith, 1998](#)). The higher the volatile matter, the higher liquid oil production is yielded ([Abnisa and Wan Daud, 2014](#)). It should also be noted that volatile matter is high in majority of plastics ([Table 2](#)), which favours the production of liquid oils from pyrolysis ([Islam and Beg, 2004](#)). Altering the feedstock of pyrolysis units can result in resolving the accumulation of certain types of solid waste in the environment which leads to a sustainable practice. It can also result in a very lucrative production line of chemicals that can substitute the original feedstock materials which are used for the production of commodity plastics and resins (see [Table 1](#)).

### 2.2. Main experimental setups and reactors used in pyrolysis

In order to convert the feedstock treated in a pyrolysis process into high end value products and energy, a number of setups have been implemented and experimented with to reach the maximum potential from PSW using thermal or catalytic processes. Determining the optimal setup for the pyrolysis process will eventually give the investor or the concerned party a full techno-economic view of the potential work to be conducted and the desired scale that certain production lines can cope with respect to the market demand.

Pyrolysis has been investigated on a number of scales, ranging from micro experimental setups that are typically aimed at studying the degradation kinetics and the properties of the materials in thermogravimetry ([Park et al., 2000a, 2000b; 2012](#); [Acevedo et al., 2015](#); [Thumsorn et al., 2012](#); [Al-Salem and Lettieri, 2010](#); [Al-Salem et al., 2009a](#); [Bockhorn et al., 1999a](#)) or in pilot and semi-industrial scales that can handle hefty proportions of solid waste ([Tukker et al., 1999](#); [Müller-Hagedorn and Bockhorn, 2007](#); [Al-Salem et al., 2009b](#); [Mastral et al., 2007a](#); [Undri et al., 2014](#)). Pyrolysis treatment processes typically consist of a feeding section, that normally handles the feedstock material which requires almost no pre-treatment, reactor unit assembly, and product collection vessels that contain separation lines for the products based on their chemical properties.

The type of the setup and unit implemented can have major influence on the interaction and degradation behaviour of the feedstock, residence time, heat and mass transfer, efficiency of the process and reaction and cost effectiveness of the process. There

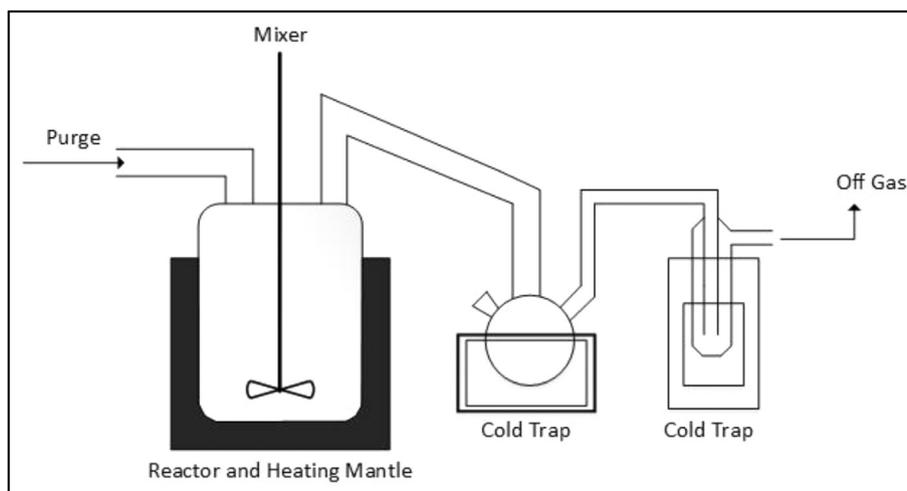
**Table 2**  
Main properties of plastic materials found in plastic solid waste (PSW) stream.

Plastic type	Moisture content	Fixed carbon	Volatile	Ash Content	Higher Heating Value (HHV)	Comments	References
High density polyethylene (HDPE)	0.00	0.01–0.3	98.57–99.81	0.18–1.40	46.4–49.4	Suitable for pyrolysis, however, temperature in thermal pyrolysis is typically greater 500 °C due to its molecular structure. Possibility of conversion to wax and lube products.	Conesa et al. (1996) Sharma et al. (2014) Ahmad et al. (2013) Sorum et al. (2001) Mastral et al. (2002)
Low density polyethylene (LDPE)	0.3	0.0	99.6–99.7	0.0–0.40	46.4	Wax formation occurs on external site of catalyst in catalytic setups while further cracking of wax into gases and liquid occurred in internal site of catalyst.	Sorum et al. (2001) Park et al. (2012) Aboulkas et al. (2012) Miandad et al. (2016)
Polypropylene (PP)	0.15–0.18	0.16–1.22	95.08–97.85	1.99–3.85	46.4	Typically elevated temperatures are require to pyrolyse it.	Sharma et al. (2014) Sorum et al. (2001) Miskolczi et al. (2009a,b) Miandad et al. (2016)
Polyethylene terephthalate (PET)	0.46–0.61	7.77–13.17	86.83–91.75	0.00–0.02	30.20	Pyrolysis is conducted at a temperature around 500 °C	Zannikos et al. (2013) Heikkinen et al. (2004)
Polystyrene (PS)	0.25–0.30	0.12–0.20	99.50–99.63	0.00	41.90	Requires lower temperatures for pyrolysis	Mastellone (1999) Park et al. (2012) Abbas-Abadi et al. (2014)

have been a number of experiments on a lab or pilot scales conducted and reported in open scientific literature, including fluidized bed reactors (FBR), fixed bed reactors including kettle type units, batch and semi-batch reactors, conical spouted bed reactors (CSBR) and microwave assisted reactors. McCaffrey et al. (1995) used a kettle type fixed Pyrex reactor that was aimed at producing synthetic (poly- $\alpha$ -olefin based) lubricants (Fig. 1). Over 20 min of a heat-up time was required for the reactor, and the total liquid yield from the treatment of linear low density polyethylene (LLDPE) varied considerably with the residence time in a proportional relationship, reaching about 70 wt% of liquid products yield with about 55 min of reaction time. The advantage of using this setup by comparison to other works was previously reported (McCaffrey et al., 1996, 1998; 1999). It was possible to produce large liquid products at moderate reaction conditions. In the reactor employed (Fig. 1), products which are volatile at the off-take temperature leave the reactor and enter the condenser whilst higher boiling point ones return to the reactor system to mix and reduce in molecular weight, hence producing desired liquids with low boiling points. Another type of fixed bed reactors (glass assembly) was

used by Hall et al. (2007) where pyrolysis at 430 °C was conducted on polyolefin mixtures with brominated high impact polystyrene (Br-HIPS). The pyrolysis oil yield and the hydrogen abstraction from the polymer chains, were both managed by this type of unit.

Fixed bed reactors are easy to design compared to other types of reactors and are considered very economical due to the manageable maintenance and operation of the unit. Fixed bed reactors have their limitations as well, such as limited surface area of catalysts typically accessed by the reactants and the particle size and shape of the feedstock. Bockhorn et al. (1999b) used a closed loop fixed reactor system with a quadruple mass spectrometer to attain the isothermal kinetics of PVC and PE to ultimately recommend the design of isothermal reactors applied for pyrolysis. The heat transfer limitations were considered carefully which affected the reactor system and are of major importance in such units. In a follow up study, Bockhorn et al. (1999c) reported the reaction kinetics and limitation of the pyrolysis process of a closed loop fixed reactor using a polyamide 6 polymer charge to recover  $\epsilon$ -caprolactam monomer. The implementation of acid base catalyst was possible and was reported to reduced the apparent activation



**Fig. 1.** Pyrolysis setup (kettle type reactor) used in McCaffrey et al. (1995).

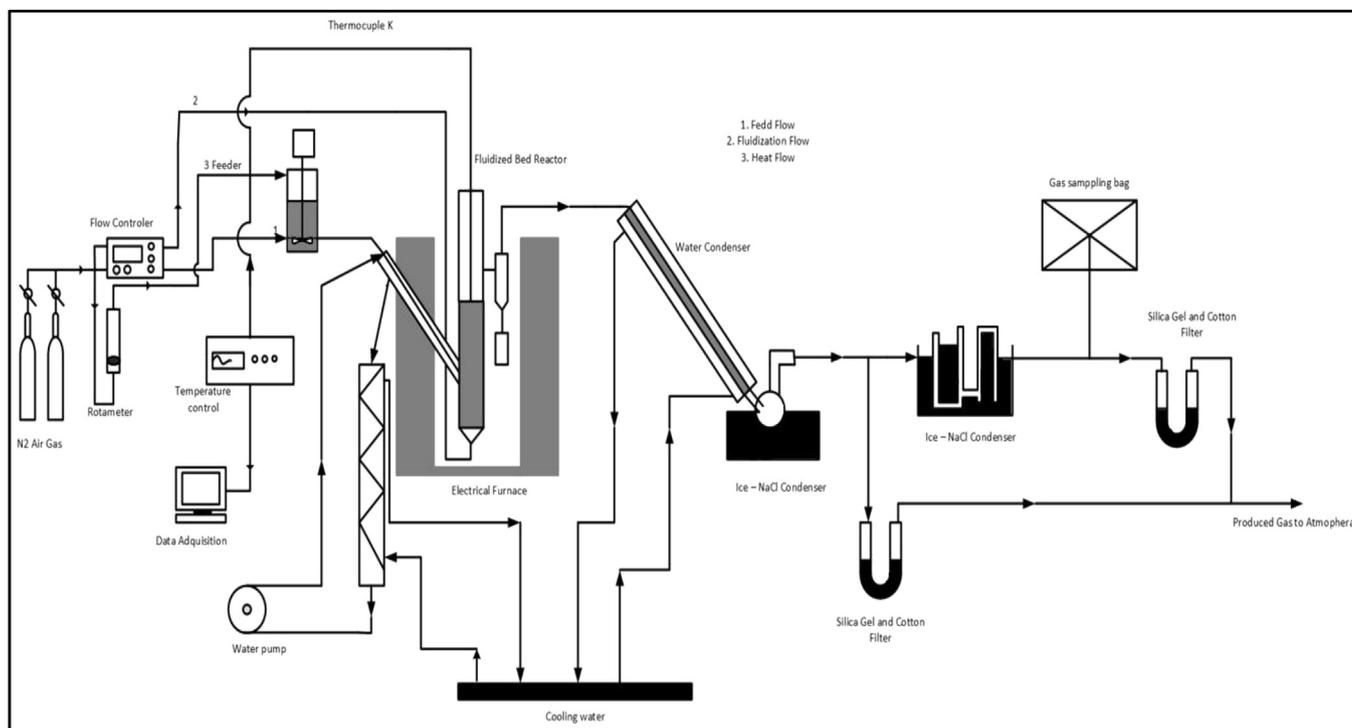


Fig. 2. Fluidized bed reactor (FBR) used by Mastral et al. (2002).

energy ( $E_a$ ). Furthermore, it was noted that catalytic fixed bed reactors are optimally used as a secondary pyrolysis reactors for cracking products evolving from the primary pyrolysis unit (Fogler, 2010; Onu et al., 1998; Vasile et al., 2000). This will be optimal to have a selective product yield that can produce desirable liquids similar to valuable petroleum products due to the selectivity of the catalysts employed.

Thermal and catalytic pyrolysis was also achieved in Bockhorn et al. (2001) work using both a closed loop and a cycled sphere reactor. An extruder was used to feed the cycled sphere reactor which results in optimal mixing of the feed components making pyrolysis an easy process to integrate with conventional mechanical units in plastic processing. Wong and Broadbelt (2001) used a glass ampule reactor to pyrolyse polypropylene (PP), polystyrene (PS) and their mixtures over a temperature range of 350–420 °C. A maximum conversion of about 90% was achieved of feed charge, and it was noted that loading was not affecting the process as much as the temperature used which influenced the evolution of aromatics greatly. Other researchers have used catalysts to similar types of batch reactor setups to improve the evolution of hydrocarbon yields. However, high coke normally results in such setups due to the possibility of reaching elevated temperatures in such a reactor system (Jan et al., 2010; Adrados et al., 2012; Shah et al., 2010; Abbas-Abadi et al., 2014). Vasile et al. (2006) used a batch reactor to pyrolyse various waste from electrical and electronic equipment (WEEE) reaching pyrolysis oil yield of over 70 wt%. Overall, batch reactors have been reported to be non-consistent in pyrolysis products and non-cost effective in terms of labour cost as well (Fogler, 2010), thus it is more convenient and economical to use a continuous pyrolysis process in large scale operations as it avoids frequent charging of the unit and reduces the operating cost.

Fluidized Bed Reactors (FBR) have also been used in past research utilising different feedstock materials for pyrolysis. When catalysts are used in this setup, high mixing is achieved with the fluid providing large surface area for the reaction to occur on

(Fulekar, 2010). This is one of the main advantages of such units. Due to its nature of continuous feeding, it solves the problem of batch reactors because it does not require frequent feedstock charging and does not need to resume often which makes it a very economical design as well. In addition, it is very well documented that such units are heated externally which makes the reactor body very easy to handle and a very operationally attractive option with easily manipulated condensation and product filtration systems as shown by Mastral et al. (2002) in Fig. 2. However, fluidization using a fluidizing media, typically sand, is quite a delicate matter and there is a possibility of bed defluidization when melted plastics stick on the fluidized bed itself which needs to be taken in consideration when applying this process (Wong et al., 2015). Residence time is a major parameter in this setup, where its increase results in cracking conventional polyolefin polymers to aromatics. At moderate cracking conditions (around 650 °C) gas production is typically controlled with ease in this setup (Mastral et al., 2007a, 2007b). Table 3 summarizes the main studies conducted using FBR for the pyrolysis of different feedstock. Jung et al. (2010) also controlled the residence time of polyolefin polymers cracking in a FBR reaching almost a constant temperature with high heat and mass transfer producing a uniform distribution of products. Low to high temperature pyrolysis over a catalyst was conducted by Luo et al. (2000) using a FBR to produce a liquid product from conventional polyolefin polymers reaching 87 wt%. As previously mentioned, FBRs are a common type of reactor that is used in pyrolysis studies. It is worth mentioning that considering a defluidization time suitable for operation is dependable on the pyrolysis temperature and particle agglomeration in the bed (Arena and Mastellone, 2000).

Conical spouted bed reactors (CSBR) (Fig. 3) have also been reported as a pyrolysis unit in literature, which typically results in high gasoline yields over Y-zeolite catalysts at temperatures exceeding 500 °C (Elordi et al., 2012) and wax yields at moderate to low temperatures (around 450 °C, Arabiourrutia et al., 2012).

**Table 3**  
Summary of studies conducted on fluidised bed reactor (FBR).

Reference	Plastic type used as feedstock	Notes
Williams and Williams (1999a)	PS	Over 80 wt% pyrolysis oil was obtained at 700 °C. Maximum yield of wax ( $\approx 20$ wt%) was obtained at 500 °C.
Hall and Williams (2006)	Halogenated WEEE	Pyrolysis at 500 °C was achieved. Over 58 wt% gas yield with benzene concentration 20 wt%. Nitrogen free pyrolysis yielded mainly carbon monoxide gas.
Williams and Brindle (2003a)	Scrap tyres	Semi-continuous FBR was used. Fluidizing gas used at 400 °C, pyrolysis reaction conducted between 450 and 600 °C. 55 wt% of pyrolysis oil was produced at 450 °C.
Williams and Williams (1999b)	LDPE	Pyrolysis carried out between 500 and 700 °C. Maximum pyrolysis oil was produced at 600 °C (51 wt %).
Mastellone et al. (2002)	Recycled PE	Pyrolysis carried out at two different fluidizing temperatures, 0.15 and 0.28 m s <sup>-1</sup> between 550 and 700 °C. Gas production was dominant over liquids at all temperature ranges.
Kaminsky et al. (1995)	1–3 kg h <sup>-1</sup> pyrolysis of mixed PSW (with 0.66% chlorine)	Products contained about 36% C <sub>2</sub> H <sub>4</sub> , 15% C <sub>3</sub> H <sub>6</sub> , 9% C <sub>4</sub> H <sub>8</sub> and butadiene and an additional 15% pyrolysis gasoline
Sodero et al. (1996)	LDPE in pilot scale reactor with a 0.5 g s <sup>-1</sup> flow rate.	75 wt% light olefin gas was obtained at 800 °C.
Conesa et al. (1994)	HDPE	Temperature used was between 500 and 900 °C, yielding maximum gas product at 700 °C (over 95 wt%). HDPE used over sand bed in FBR.

However, at elevated temperatures waxes in CSBR are cracked into gaseous phase products and liquids (Lopez et al., 2010). The main advantage that gears many researchers towards this unit is the ability for it to have good mixing to handle large particle size with different densities and low attrition and bed segregation due to the design configuration of the reactor (Artetxe et al., 2013; Olazar et al., 2009). Aguado et al. (2005) claimed that the CSBR used in their work overcomes the problem of handling sticky solids produced from pyrolysis of plastics which arises in FBRs due to particle agglomeration phenomena that causes de-fluidization. Thus, CSBR avoids the problem of defluidization compared to the fluidized bed and it also has a lower pressure drop by comparison to other experimental setups. However, it is very important to keep a very short residence time to avoid the secondary reactions which lead to the formation of coke (Wong et al., 2015). Polyurethane (PU), a plastic materials typically polymerized and converted for insulation purposes, was studied in a two step reactor system with a platinum coil reaching a temperature of 800 °C (Font et al., 2001).

Microwave-assisted pyrolysis (MAP) is a relatively new pyrolysis technique, thus it has not been studied as well as other reactor setups. It is an attractive method in providing a volumetric heating process at enhanced heating efficiencies (Appleton et al., 2005). The microwave energy is supplied directly to the material through the molecular interaction with the electromagnetic field and no time or energy is wasted to heat the surrounding area of the reactor which means reduced operational costs and low heating time (Fernandez et al., 2011). However, this method has some restrictions, the plastic has low dielectric constant and it has to be mixed with a highly absorbent material such as carbon to absorb the microwave energy and achieve the required temperature, microwave ovens can raise the temperature as high as 1000 °C due to the microwave absorbent materials (Ludlow-Palafax and Chase, 2001; Hussain et al., 2012). Microwave radiation enables high rates of heating and shows excellent efficiencies of 80–85% conversion of electrical energy into heat (Ludlow-Palafax and Chase, 2001). Undri et al. (2014) pyrolysed HDPE and PP using tire and carbon as the microwave absorbers. The temperature in the MAP was reported to be very difficult to identify, so it was not used as a descriptive parameter. Full decomposition of HDPE was achieved after raising the microwave power to 6 kW and the liquid product yield obtained was 37 wt%. In the case of PP, it gave a low density liquid at any condition due to its lower stability using a reaction time of 50 min to achieve complete degradation. Hussain et al. (2012) used the domestic microwave oven with the frequency of 2450 MHz to pyrolyse the waste samples of the polystyrene foam. The temperature was as high as the melting point of aluminium and it was achieved

by the interaction of microwave with closely placed aluminium coil. An 88 wt% of liquid was yielded from the initial PS charge to the reactor, 9–10 wt% into gas and the rest into the residual char. Ludlow-Palafax and Chase (2001) investigated the performance of microwave-induced pyrolysis by studying the degradation of HDPE and toothpaste tubing as aluminium/polymer laminates in a semi-batch apparatus for a mixed feedstock experiment. The pyrolysis was performed in the temperature range of 500–700 °C. The clean aluminium was recovered from the toothpaste tubing together with hydrocarbons and there were no important differences in the products obtained from the pyrolysis of toothpaste tubes compared to HDPE. The molecular weight distribution of the oils/waxes in both cases were similar with a slight increase on the average molecular weights for the toothpaste tubing. The main products (81–93%) from the degradation of oils/waxes were linear hydrocarbons, primarily alkenes, alkanes, and dialkenes, the rest was a complex mixture of cyclic and branched aliphatic and aromatic compounds.

### 2.3. Pyrolysis product yields vs. type of feedstock

As previously mentioned, the ultimate aim is to produce valuable products that are comparable to conventional fuels from pyrolytic processes. Thermal and catalytic pyrolysis have been studied in relation to the type of plastic treated, which was found by many researchers as one of the main crucial parameters in producing certain chemicals for the possibility of chemical processes intensification and thermal recycling of PSW. Alongside other parameters (to be discussed later in this paper), type of feedstock is one of the main elements that controls the product evolution, for it determines the boiling point range of the products, hence, what is to be condensed downstream of the process. Ultimately, it is desired to produce motor engine gasoline and diesel which can be done with the production of hydrocarbons with a boiling point between 35 and 185 °C (gasoline), 180–350 °C (diesel) and 350–538 °C (Vacuum Gas Oil, VGO) (Sharma et al., 2014).

The typical pyrolysis temperature range for thermal processes (non-catalytic) is between 350 and 900 °C, which alongside type of feedstock, reaction time and gas media; controls the products obtained from the process (Panda et al., 2010; Lettieri and Al-Salem, 2011; Kunwar et al., 2016). Thermal pyrolysis typically produces liquid oil that is rich in long carbon chains with low octane number that is comparable to conventional fuels especially from polyolefin polymers (Lopez et al., 2011). This product is typically targeted from pyrolysis process and has the potential to be blended with diesel to be used in engines as well (Frigo et al., 2014; Mukherjee and

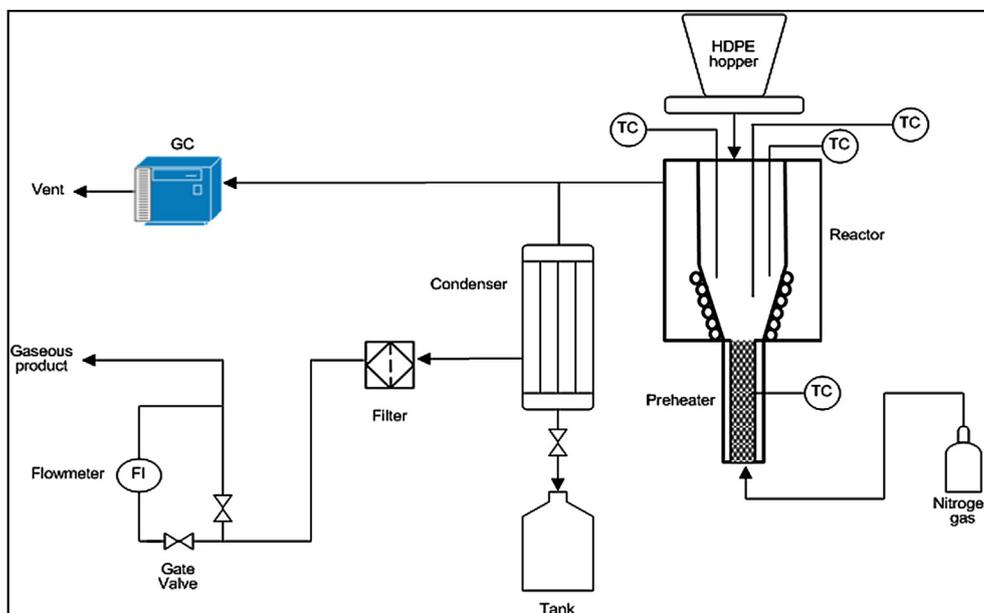


Fig. 3. Conical Spouted Reactor Diagram as shown by Elordi et al. (2012).

Thamotharan, 2014; Miandad et al., 2016). Polyolefin (PO) plastics pyrolysis oil usually contains aliphatic, mono-aromatic and poly-aromatic compounds that results from the degradation of the carbon bonds of their structures (Jung et al., 2010; Williams and Williams, 1998). Readers are referred to Sharuddin et al. (2016) for a more detailed chemical and physical properties description of pyrolysis oil products.

Pyrolysis also produces solid char as a residue from the process which has the potential to be used as a source of energy. Syamsiro et al. (2014) reported a higher heating value (HHV) of pyrolysis char to be in the range of 36.29 and 23.04 MJ kg<sup>-1</sup>. Char can also be used as a substitute to metal adsorbents from MSW and wastewater (Heras et al., 2014). As for the gases produced from pyrolysis, it can be applied in power generation, boiler heating and gas turbine for the generation of electricity (Fernandez et al., 2011). Gases produced by pyrolysis can also be input into the process itself to become more sustainable. Gases produced are very sensitive to the type of feedstock and have the higher heating value (HHV) range of 45–50 MJ kg<sup>-1</sup> (Miskolczi et al., 2009a, 2009b; Jung et al., 2010; Frigo et al., 2014). Gases produced by pyrolysis are typically minimal with the exception of PET and PVC which can produce up to 87 wt% of gas (Sharuddin et al., 2016). Williams and Williams (1997) showed in their work that there is a trend of gases produced when conventional plastics are pyrolysed. There is a tendency for the lighter gases to be formed, in the majority, more ethane is produced than propene and more of this than butane. This is due to smaller gaseous molecules being more stable than larger ones.

Polystyrene (PS) is made of styrene monomers. It is resistant to heat and has high durability, strength and light in weight that make it appropriate to use in food packaging, electronics, construction, medical, appliances etc. In the stepwise pyrolysis conducted by Bockhorn et al. (1999c) at 380 °C PS decomposed into its original monomer styrene (58% by volume), ethylbenzene (35% by volume), styrene dimer, styrene trimer as well as 2-phenylpropene that appear in smaller amounts. Hence, recovery of aromatic products was possible in this process having the potential of scaling up such a process for the development of petrochemical complexes infrastructures. Scott et al. (1990) pyrolysed polystyrene (Dow Styron

<0.5 mm) at three temperatures; 532 °C, 615 °C and 708 °C. The main product in all cases was styrene. Other components identified were toluene, ethylbenzene, propenylbenzene, propynylbenzene, and naphthalene. Fast pyrolysis gave a yield of monomer of 75% or better, with a total yield of aromatic liquids of 83–88% and no char was produced. Kaminsky et al. (1995) achieved 76.8 wt% decomposition of PS to styrene at 520 °C using an indirectly heated FBR. Presence of PS increases the amount of methane in the product gas (Williams and Stanley, 2007). PS pyrolysis oil contained high fraction of benzene, toluene and ethyl benzene especially at elevated temperatures alongside the monomer of styrene which was deemed to form as radicals during the pyrolysis (Onwudili et al., 2009).

Similarly to PS, polyethylene terephthalate (PET) is a common plastic that is extensively used in food packaging especially bottles and containers. PET has the recycling symbol of 1 due to the fact that it is the most common recycled material that is handled by consumers. Cepeliogullar and Putun (2013a) pyrolysed PET using a fixed bed reactor at 500 °C. Gaseous products were mainly obtained ( $\approx 77$  wt%) whilst the balance consisted of pyrolysis liquid with high benzoic acid content (49 wt%). Fakhrooseini and Dastanian (2013) reported 39 wt% liquid yield at similar operating conditions. Hartulistiyo et al. (2015) studied the pyrolysis of reclaimed plastic bottles and modelled the performance of pyrolysis in a fixed reactor to produce liquids at 450 °C, and it was stated that liquid yield was very minimal from the model's results. Thus, it can be concluded that gaseous products from PET is typically the dominant fraction which is a matter noted in past works. This can be attributed to the volatility of its original constituting monomers resulting from condensation polymerization of ethylene glycol and terephthalic acid. PET degrades earlier than other components of the process, so it releases oxygen component early which reacts with the carbon molecules to form CO and CO<sub>2</sub>. The amount of CO and CO<sub>2</sub> produced is based on the amount of the oxygen available which is obtained by the degradation of PET available in PSW. The effect of the temperature on formation of CO and CO<sub>2</sub> is minimal, thus the amount of PET present in the process can affect the yield (Lopez et al., 2010; Adrados et al., 2012; Singh and Ruj, 2016). Presence of PET also increases the ethane concentration (Williams and

Stanley, 2007) and the PET pyrolysis oil will yield high amount of benzoic acid due to its presence in the plastic itself (Cepeliogullar and Putun, 2013a).

Conventional PO plastics, namely PE and PP, have been extensively researched in the past since they make up the largest proportion of PSW due to their versatility towards many applications. HDPE is widely used in the manufacturing of milk bottles, detergent bottles, oil containers, toys and more due to its high strength and durability. The various applications of HDPE contribute about 17.6% in plastic waste category which is the third largest plastic type found in MSW (Michael, 2010). McCaffrey et al. (1998, 1999) treated LLDPE and HDPE pyrolysis in kettle type reactor coupled with reactive distillation, yielding almost solely liquid products from the process. However, volatiles were evolving from LLDPE earlier than HDPE due to its complex chemical structure. Pyrolysis oil obtained from PE, more precisely HDPE, has been compared to conventional fuels, where gasoline, kerosene and diesel have a calorific value (CV) reported to be 43.4–46.5 MJ kg<sup>-1</sup>, 43.0–46.2 MJ kg<sup>-1</sup> and 42.8–45.8 MJ kg<sup>-1</sup>, respectively. HDPE pyrolysis oil has a reported CV of 42.9 MJ kg<sup>-1</sup> (Kumar and Singh, 2011; Boundy et al., 2011; Ahmad et al., 2013, 2014). Sharma et al. (2014) used a batch reactor to pyrolyse HDPE thermally at 440 °C obtaining 74 wt% of pyrolysis oil, whilst Buekens and Huang (1998), Beltrame et al. (1989) and Scott et al. (1990) used PE as a feedstock to thermally pyrolyse it and obtain pyrolysis oil at 760 °C (42.4 wt%), 400 °C (44 wt%) and 515 °C (88 wt%), respectively. Horvat and Ng (1999) obtained high fractions of oil from HDPE at 460 °C (90 wt%) using a semi-batch reactor. The product was reported to be rich in propane (C3, 28%). It can be noted that using PE as a feedstock is a very attractive option for obtaining clean and high CV distillates at moderate temperatures around 500 °C. This presents a very attractive alternative in energy scenarios to develop schemes where conventional fuels could be substituted with PSW feedstock rather than relying on crude oil and its derivatives.

LDPE has also been studied as a feedstock for pyrolysis processes in the past. High CV pyrolysis oil (39.5 MJ kg<sup>-1</sup>) compared to conventional gasoline has also been reported to be obtained from LDPE (Desai and Galage, 2015). Sodero et al. (1996) used a micro batch reactor with a ferromagnetic wire to obtain a majority of olefin gases yield between 800 and 900 °C. High liquid yields have also been obtain from LDPE pyrolysis, reaching 93.1 to 95 wt% with minimal gas products in temperature ranges between 500 and 550 °C (Bagri and Williams, 2001; Marcilla et al., 2009). On the other hand, PP has also been targeted for production of light gases and pyrolysis oil in various experimental setups. The presence of PE (HDPE and LDPE) produces more gaseous components such as ethane, ethene, and n-butane, and the yield of the gaseous fraction also increases along with the increasing temperature up to a certain point (Singh and Ruj, 2016; Miskolczi, 2009b; Williams and Stanley, 2007; Williams and Williams, 1999a, 1999b). The high char content is obtained due to presence of HDPE while LDPE increases the gas percentage in the product (Sharma et al., 2014; Singh and Ruj, 2016). It should also be noted that relating type of plastic to product is a matter that shows great variation in literature due to

the type of additives present in the plastic grade and nature of experimental setup and conditions.

Being the second largest plastic present in MSW after PE, research in PP treatment has received attention in the last decade especially in developed industrial countries (e.g. UK, US, Germany, Canada) due to its various application in plastic film conversion and packaging. Typically PP pyrolysis is carried out at a temperature range between 250 and 400 °C. Although it has a higher melting point than PE, its chemical structure poses a tertiary carbon atom that can be released with moderate heat which leads to the disintegrate of hydrocarbon chains which gives a variety of products from its pyrolysis at moderate temperature ranges. Pyrolysis oil was reported to be produced with a yield of over 69 wt% at such temperature ranges by Ahmad et al. (2014) and Sakata et al. (1999). Williams and Stanley (2007) used a minim bench top reactor to pyrolyse PP and obtained 93 wt% of oil fraction at 500 °C. Fakhrohoseini and Dastanian (2013) used PP as a feedstock to produce oil at 500 °C yielding 82.12 wt% of the total mass balance. Other feedstock materials have also been used in thermal pyrolysis to produce large amounts of products from either virgin or waste plastics (Table 4). Santella et al. (2016) pyrolysed recovered waste from electrical and electronics equipment (WEEE) consisting of 64 wt% (ABS), 33 wt% (HIPS) and 3 wt% (polybutylene terephthalate, PBT) between 400 and 800 °C. Energy released by combustion of the pyrolysis oil was around 39 MJ kg<sup>-1</sup>, thus suggesting the possibility to exploit it as a fuel. In reality, it is very difficult to estimate the yields of the products from pyrolysis in industrial scale units as the proportion of different plastic types constituting the PSW will vary (Lopez et al., 2010).

PVC is a versatile material but during the pyrolysis it tends to yield hydrochloric acid (HCl) which is corrosive to the reactors. Therefore many researchers decided to exclude PVC from the pyrolysis feedstock components. It has always been deemed as a major component to avoid in pilot and industrial scale reactors, with a selected number of technologies able to cope with it in the initial charge of the unit (Tukker et al., 1999). Scott et al. (1990) pyrolysed PVC at 520 °C in a FBR. The main gaseous product of the reaction was HCl, which was absorbed from the gases in aqueous NaOH solution. HCl yield was about 99% (theoretically calculated) and other products were difficult to identify. Because of the corrosive and toxic chlorine component, the experiments with PVC were discontinued. Williams and Williams (1997) conducted their experiments in a FBR at temperatures varying between 500 and 700 °C. They placed a dreschel bottle with de-ionised water to dissolve the HCl gas produced during the process. It was observed that the amount of the HCl decreased with the increase in temperature, since the increase of temperature increases the number of radicals available to react with the HCl molecules. The chlorine molecule contributes more than 56% by weight of the whole polymer and up to 90% of this chlorine is evolved as HCl when pyrolysed. Only 0.51–1.76% HCl gas was trapped in the dreschel bottle, which represented less than one third of that potentially available.

**Table 4**

Product yields of thermal pyrolysis process using common plastic found in municipal solid waste (MSW).

Reference	Temperature range (°C)	Feedstock plastic	Product yields
Buekens and Huang (1998)	740	PP	Pyrolysis oil (48.8 wt%), residue (1.6 wt%) and gases (49.6 wt%)
Williams and Stanley (2007)	500	PS	Pyrolysis oil (71 wt%), residue (27 wt%) and gases (2.0wt%)
Onwudili et al. (2009)	300–500	PS	Pyrolysis liquid product yield (97.0 wt%) at 425 °C, with minimal gas yield (2.5 wt%).
Miranda et al. (2001)	225–520	PVC	Maximum oil obtained was 12.79 wt% and HCl was obtained at a rate over 50 wt%. Vacuum pyrolysis was applied.

Bockhorn et al. (1999c) conducted a step-wise pyrolysis in three reactors connected in series. The first reactor was used for dehydrochlorination to remove chlorine and avoid problems with the incineration. A chlorine content of 0.2 wt% in the residue was achieved which corresponded to a dehydrochlorination of 98%. Lopez-Urionabarrenechea et al. (2012) have conducted a step-wise pyrolysis of a mixture of PE, PP, PS, PET and PVC using a semi-batch reactor. A low temperature 300 °C dechlorination step was carried out with and without the catalyst for 60 min and in both cases it gave a 75 wt% chlorine reduction in the liquid fraction. Demirbas (2004) pyrolysed PVC at 638, 690 and 735 °C in a FBR. At 638 °C over 50 wt% of the pyrolysis product was oil with boiling point less than 265 °C. The experiment at 690 °C yielded about 40 wt% of an oil. At the highest pyrolysis temperature of 735 °C, the main product was highly aromatized oil. PVC is not the best plastic to be used as a feedstock for the pyrolysis process, due to high yield of HCl production which is toxic and corrosive to the equipment. If PVC has to be pyrolysed and is present in the mainstream of the PSW treated, an additional dehydrochlorination step has to be employed such as step-wise pyrolysis or an absorber could be used for chlorine poisoning control.

#### 2.4. Degradation kinetics studies and mechanism of reactions

Understanding the degradation reaction kinetics of plastics pyrolysis is a necessity in determining main kinetics parameters that govern the reaction undergoing in the pyrolytic reactor. Thermogravimetric analysis (TGA) has been the most popular means of conducting this type of work, and is typically done so in non-isothermal (dynamic) conditions utilizing various heating rates to establish the kinetics of the process. The International Confederation for Thermal Analysis and Calorimetry (ICTAC) govern the standards for this type of analysis, in setting the acceptable analytical (model free) and model fitting methods used in kinetics computations (Vyazovkin et al., 2011, 2014). Essentially, weight loss is determined as a function of temperature in the thermal setup to perform further kinetics evaluation. There has been quite a discrepancy in published results when it comes to determining main factor governing the reaction kinetics of plastics pyrolysis due to the various experimental setups and process parameters, heat and mass transfer limitations and type of material studied. Generally, it is quite accepted that plastics degrade in a single order reaction with the exception of PVC (Grammelis et al., 2009).

The mechanism that is acceptable for degradation of plastics consists of three main steps that occur consecutively, initiation, propagation and termination (Simha et al., 1958; Conesa et al., 1996; Horvat and Ng, 1999; Oh et al., 2003). Intermolecular, intramolecular and  $\beta$ -scission are associated with PO degradation and it is typically free radicals and hydrogen transfer that establish the final products from pyrolysis reactions. The first products yielded are usually in the range of C<sub>20</sub> to C<sub>50</sub>. These products are cracked in the gas phase to obtain lighter hydrocarbons, as ethene (ethylene) and propene (propylene), which are unstable at high temperatures and react to form aromatic compounds such as benzene or toluene. If the residence time is long, then coke, methane and hydrogen will form (Westerhout et al., 1998a; 1998b). At temperatures above 800 °C, larger paraffins and olefins produced from the decomposition of plastics are cracked into H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and other light hydrocarbons (Ponzio et al., 2006). As a result of methyl-group abstraction from aromatics and decomposition of paraffins, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> are typically reported to increase with temperature (Ledesma et al., 2000). The abstraction of methyl groups and hydroxyl groups from aromatic structures implies that the aromatic fraction does increase with temperature even though the total amount of tar decreases. H<sub>2</sub>-abstraction from light hydrocarbons

and cross-linking reactions may also produce poly-aromatic hydrocarbons (PAH) in plastics pyrolysis. Kinetic data obtained by previous authors confirms that different molecular structures lead to different mechanisms of decomposition and rates (Bockhorn et al., 1999a; 1999b). Westerhout et al. (1998a) described the pyrolysis of plastics via a three step mechanism, where primary degradation reaction will lead to intermediate products and the secondary ones will lead simultaneously to the production of alkanes and alkenes on one hand whilst on the other it will lead to the evolution of aromatics. Tertiary reactions will result into the development of coke and contribute to the production of aromatics from alkanes and alkenes.

Various authors reported the apparent activation energy ( $E_a$ ) of PE pyrolysis after performing kinetics computations on the results obtained which is the main parameters estimated in thermal and catalytic degradation reaction studies. The  $E_a$  for HDPE ranged between 206 and 445 kJ mol<sup>-1</sup> (Mucha, 1976; Urzendowski and Guenther, 1971; Wu et al., 1993; Westerhout et al., 1997a; 1997b, Bockhorn et al., 1999a; 1999b; 1999c; Sorum et al., 2001), while for LDPE the range obtained was reported to be between 163 and 303 kJ mol<sup>-1</sup> (Mucha, 1976; Urzendowski and Guenther, 1971; Westerhout et al., 1997b). The reaction chemistry of PE depolymerisation was reported by Bockhorn et al. (1999a). It can be summarised in three steps starting with an initiation reaction whereby the mechanism is initiated by a random chain scission of the polymer chain producing primary radicals ( $R_p$ ). Propagation then takes over where secondary radicals ( $R_s$ ) are produced due to intramolecular transfer. Two  $\beta$ -scissions reactions are then possible. The first one leads to alkenes, whereas the other leads to the formation of a short  $R_p$  and a polymer with a terminated double bond. The degradation is terminated with a combination reaction which leads to a residual polymer. The number and type of bonds varies considerably in plastics which has been considered as the main reason behind the difference in reported  $E_a$  values by Kunwar et al. (2016). As for PP, the degradation occurs in a three step reaction model as previously described encompassing different reactions for the dissociation of the chemical structures and bonds (Bockhorn et al., 1999a). The initiation step will lead to the evolution of primary and secondary radicals to be rearranged to produce ternary radicals which will lead eventually to the production of the volatile products in the propagation reaction step. PP has been also studied for its degradation kinetics by various authors and the  $E_a$  was reported to be 99–244 kJ mol<sup>-1</sup> depending on the experiments conducted (Dickens, 1982; Bockhorn et al., 1998; Gambiroza-Jukic and Cunko, 1992; Wu et al., 1993; Westerhout et al., 1997b; Dou et al., 2016).

PS is also considered a main component in the PSW load, where studying its degradation reaction kinetics will be of immense importance in determining its optimal thermal treatment and reactor design aspects. The  $E_a$  of PS pyrolysis was reported by various authors over the past forty years and is typically lower than conventional PO polymers, i.e. PE and PP. PS has a complex pyrolysis kinetics scheme which can't be described by a single power law model and involves the production of various products that are yielded from its degradation including its monomer (styrene) (Westerhout et al., 1997b). The  $E_a$  was estimated in the past and determined to be in the range of 83–310 kJ mol<sup>-1</sup> (Westerhout et al., 1997b; Sato and Kaneko, 1983). Bouster et al. (1980) proposed a mechanism of degradation for PS whereby random initiation starts off the pyrolysis to produce radicals that depropagate to radicals and a residual polymer remains after termination in a similar manner to PE and PP. PET was also investigated by various authors in the past to determine the optimal reaction kinetics during pyrolysis. Molto et al. (2007) proposed a degradation mechanism consisting of three reactions occurring simultaneously

to produce the evolved products, volatiles and char from PET pyrolysis. The reported  $E_a$  value for PET has always been a matter of controversy in literature due to the nature of the material and chemical structure, which was reviewed in this work and reported from various papers between 162 and 338 kJ mol<sup>-1</sup> (Cepeliogullar and Putun, 2013a, 2013b; Molto et al., 2007; Saha and Ghoshal, 2005; Andel et al., 2009). Cepeliogullar and Putun (2013b) reported the two temperature ranges of PVC during which the weight loss occurred; the 280–385 °C with the weight loss of 62.25% and 385–520 °C where about 21.74% weight loss occurred. Surpassing these temperature ranges, weight loss was noted to be minimal. Thus the degradation temperature was assumed to be in the range of 220–520 °C and the activation energy for PVC was reported to be in the range of 136–267 kJ/mol (Cepeliogullar and Putun, 2013b; Bockhorn et al., 1998; Wu et al., 1993).

### 3. A note on Co-Pyrolysis of plastics

MSW can be accepted with high fractions of PSW in pyrolytic units and municipal solid waste incinerators (MSWIs). It is a lucrative scenario to have the ability to treat a co-mingled waste stream in one unit, hence co-pyrolysis (the processing of plastic mixtures) have been researched in the past to understand the effect of the presence of different components on eth process. However, for combustion processes to be applicable to PSW a number of issues arise. First, if one wants to produce reusable slags, the heavy metal input into the incinerator should be limited (Kowalska et al., 2002). Furthermore, an important point is the relatively low incineration temperature of MSWIs (around 850 °C). Fluidized bed combustors (FBCs) are increasing in popularity for incineration due to; (i) less complex emissions control systems, (ii) high combustion efficiency with simple operation and a fast response, (iii) reduction in boiler size, and (iv) low corrosion with easier ash removal. Yassin et al. (2009) reviewed FBC technologies in Europe, where the revolving fluid bed developed by Ebara Co. is stated as being very rapidly utilised on the continent. More than 100 units are installed worldwide, including the Madrid plant unit which takes 10% of the city's waste (with 9% commingled PSW) to produce electricity. The main principle for this technology is the mechanism of the internal furnace with no moving parts, which is equipped with a slanted bed floor to produce a revolving sand motion. For pyrolysis in particular to gain public acceptance, many researchers worldwide have studied and developed pyrolysis units that can process co-mingled fractions of plastics. Singh and Ruj (2016) pyrolysed a blend of PSW consisting of PE, PS, PP and PET in a series of experiments between 450 and 600 °C to obtain gaseous products with rich olefin and H<sub>2</sub> content. The residence time effect was evident in increasing hydrocarbon content in gas phase. However, CO and CO<sub>2</sub> content increased with the increase of operating temperatures. Increase in operating temperature increased the concentration of H<sub>2</sub> whereas no effect on formation of products was observed.

The thermolysis of 60/40 (wt/wt%) mixtures of PE and PS was investigated at temperatures below 440 °C as shown previously by McCaffrey et al. (1996), where the liquid yield from the mixture of 84.1% was comparable to the yields obtained with the individual polymers. The yields of styrene monomer, 57.1%, and  $\alpha$ -olefins, 27.7%, increased over those obtained when the polymers were processed individually. A significant interaction was observed between the polymers in which the addition of PS enhanced the rate of thermolysis of PE. Similarly, Wong and Broadbelt (2001) showed that the conversion of a binary mixture of PP and PS was higher than the average conversion obtained for each individual plastic. This shows that results of co-pyrolysis of polyolefin polymers and aromatic base ones (i.e. PS) are typically synergistic and lead to high conversion rates. Red oak and HDPE were pyrolysed in a FBR by Xue

et al. (2015) over a temperature range of 525–675 °C. The increase of temperature resulted in increasing pyrolysis oil reaching 57.6 wt % at 625 °C. The co-pyrolysis of plastics was also studied with other materials such as coal, petroleum waste and waste from motor oil to increase conversion and decreases the viscosity of the product (Oyedun et al., 2014; Yoon et al., 1999; Ali and Siddiqui, 2004; Miranda et al., 2013; Passamonti and Sedran, 2012).

Cepeliogullar and Putun (2013b) performed pyrolysis on a mixture consisting of cotton stalk, hazelnut shell, sunflower residue, and arid land plant *Euphorbia rigida*, after blending in definite ratio (1:1, w/w) with PVC and PET.  $E_a$  required to degrade plastic was higher than the biomass which indicates that kinetic behaviour of biomass/plastic mixture changes significantly from pyrolysing single components. This supports the assumption that biomass can be pyrolysed with plastic to yield products desired by the market due to synergistic effects between the materials. A mixture of HDPE, LDPE and PP with oil shale was pyrolysed for fuel production by Aboulkas et al. (2012) where pyrolysis oil with plastics was produced at higher rates by comparison to pyrolysis without plastics which acted as a promoting materials for degradation. Chattopadhyay et al. (2016) co-pyrolysed biomass in the form of paper with a mixture consisting of HDPE, PP and PET in a catalytic process using a FBR. An optimal gas product evolution was determined in the biomass/plastics ratio of 5:1 with the presence of the catalyst which yielded a hydrogen gas of 47 vol%. Devaraj et al. (2015) tested the performance of single cylinder water cooled engine after mixing waste plastic pyrolysis oil with diethyl ether and found it very suitable substitute for conventional diesel and in certain cases much superior. This also indicated the alternative uses of the pyrolysis products in various applications in blending with other products and co-pyrolysis (Hujuri et al., 2008). There have been previous reports on synergistic effects of plastics among each other in co-pyrolysis in past research. Pyrolysed and liquefied plastics have been reported to be highly interactive in pyrolysis (Williams and Stanley, 2007), and major PO plastics have been reported to degrade differently when pyrolysed together.

PVC has always been a major obstacle in thermal treatment, and more specifically in TCT operations due to chlorine (Cl) poisoning in the reactor's unit. Cl leads to corrosive deterioration with time and reduces process efficiency. PVC will typically yield chlorine in elevated temperatures by pyrolysis and constraints are enforced on a number of reactor systems and setups regarding PVC content. On the other hand, there has been past reports that PVC in the pyrolysis feedstock increases the decomposition rate and results in higher conversion rates of the whole process (Miskolczi et al., 2009a, 2009b; Murata et al., 2004). The British Petroleum (BP) company has developed a fluid bed pyrolysis reactor in a system that was operating in a pilot scale (400 tpa) back in the 1990s called The Polymer Cracking process (Tukker et al., 1999). With minimal pre-treatment, the plastic mix enters the reactor and a typical 85 wt% of pyrolysis liquid is produced from a 80 wt% polyolefin feedstock alongside a 2 wt% PVC feed. The process was superior in Cl removal, where a feed mix that contains up to 10,000 ppm of Cl can be reduced to 10 ppm. Researchers are also considering removal of PVC before entering the pyrolysis reactor by utilizing adsorbents such as FeOOH, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> (Lopez-Urionabarrenechea et al., 2012). The NKT pyrolysis plant was also developed on the basis of PVC treatment and avoiding Cl presence. A pre-treatment plant (capacity: 1 ktpa) is placed to sort the PE, PP and wood fractions for the pyrolysis process which will take place in a separate unit capable of handling PVC waste up to 1800 kg h<sup>-1</sup> in a reactor at low pressures (2–3 bar) and moderate temperatures (maximum 375 °C) (Tukker et al., 1999). HCl is collected from the gas phase by absorption in water and light gases are released after incineration. The liquid phase is separated into an organic condensate and an

aqueous condensate. A non-catalytic (thermal) setup was developed by Chiyoda and implements a thermal pre-treatment step for PVC (HCl) and PET removal. The gases released are the resultant of the plastic melt in the vessel, and it was reported that the light oil produced is a petrochemical feedstock substitute (Scheirs, 2006).

Singh and Ruj (2016) conducted TGA analysis to study the optimum temperature range of degradation of MSW at temperatures ranging 450–600 °C with a sample weight of 200 g. The MSW consisted of 58.8% PE (HDPE and LDPE), 26.9% PP, 8.7% PS and 5.6% PET. PVC was excluded from the experiments to avoid the production of corrosive HCl acid. Synergetic effect was analysed by comparing the MPW mass loss profile with individual plastics like PP, PET, and HDPE. Municipal Plastic Waste (MPW) degradation started at 310 °C as compared to individual plastics which its degradation started at 350 °C. This showed a beneficial synergistic effect of pyrolysing the mixed plastics compared to the individual ones. Cunliffe et al. (2003) pyrolysed thermoset polyester, phenolic resin and epoxy resin in a temperature range between 350 and 800 °C in a static bed reactor. The oil/wax yield obtained was: 47.4–14.5 wt% (thermoset polyester), 12.0–5.1 wt% (phenolic resin) and 18.0–37.1 wt% (epoxy resin). Benzene content in the oil/wax obtained increased as temperature of pyrolysis increased. Williams and Williams (1997) used a fixed bed static-batch reactor pyrolysis of mixed and single HDPE, LDPE, PS, PP, PET and PVC, to conduct their experiments at 700 °C. The following mass balance was obtained: 9.63% gas, 75.11% oil, 2.87% char and 2.31% HCl.

#### 4. Influencing operational factors

Operational factors typically affect the process that is being carried out and these include type of reactor, residence time, temperature and pressure of operation, experimental conditions and type of feedstock material. In pyrolysis, feedstock material affect the product distribution and limits the operation in terms of time required for conversion and anticipated products. The purity of the feedstock material also influences the type and product distribution obtained by the pyrolysis of plastics. It is essential to consider the limitation of the unit being used in the experiment and to understand the governing parameters of the process with respect to feedstock and other factors that may influence the process.

##### 4.1. Residence time

The residence time of the feedstock material in the reactor is one of the main governing factors that affect pyrolysis, and it is defined according to Mastral et al. (2002) as the average amount of time that a particle spends in the reactor which may influence product distribution. The effect of residence time is also something that is subjective and depends on the view undertaken by the researcher depending on the product that is being evolved and monitored at the end of the experimental run. Al-Salem and Lettieri (2010) analyzed the results of isothermal HDPE pyrolysis in TGA setup between 500 and 600 °C. The production rate of both aromatics and residual char was negligible in comparison to non-condensable gases and liquids. A similar observation was made by Ludlow-Palafox and Chase (2001) where non-condensable gases increased with residence time. This can be attributed in both cases to the increase of primary products conversion from PO polymers yielding more thermally stable products, hence favouring production of liquids (Mastral et al., 2003).

The production of pyrolysis oil and liquids fraction is dependent on the retention time and isn't proportional to the increase of

reaction temperature as the work of McCaffrey et al. (1995) on LDPE pyrolysis showed. Secondary reactions in plastics pyrolysis degradation are dependable on the residence time and favours the production of gases (Conesa et al., 1994). Al-Salem et al. (2009b) showed that the condensable liquid fraction increased with residence time in ELTs pyrolysis. PET was also noted to have a higher conversion rate with retention time as Andel et al. (2009) indicated. Mastral et al. (2002) studied the effect of residence time on the product distribution of HDPE thermal cracking in FBR on five different temperatures; 650, 685, 730, 780 and 850 °C with the residence time varying from 0.64 to 2.6 s. The residence time had a great influence on the pyrolysis product distribution. At 640 °C the main product obtained was wax with yields varying from 79.7 wt% at 0.8s to 68.5 wt% at 1.5 s. At these conditions the gas yield varied between 11.4 wt% at 1 s and 31.5 wt% at 1.5 s. The higher gas yields were obtained at 780 °C, with a 86.4 wt% of gas product and 9.6 wt% of oil at 1.34 s. At a higher temperature of 850 °C, the effect of the residence time on the gas composition became more influential. Methane (C<sub>1</sub>) and hydrogen yields increased with the residence time from 11.8 to 22.2 wt% and from 1 to 3.6 wt%, respectively, and the ethene (C<sub>2</sub>H<sub>4</sub>) yield reached a maximum of 40.5 wt% at a residence time of 0.86 s. The most efficient conditions for the pyrolysis were determined to be at temperatures around 750–780 °C with long residence time. Under these conditions, the values of the cold gas efficiency was obtained to be 96% and the CV of the gas produced was the maximum (35900 kJ Nm<sup>-3</sup>). Onwudili et al. (2009) studied the effect of temperature and residence time on the degradation of LDPE and PS. It was observed that long residence time provided opportunity for secondary reactions to occur and crack oil towards gas and char production. LDPE was converted to 91.1 wt% oil and 8.70 wt% gas at zero residence time at a temperature of 450 °C and as the time increased to 120 min the oil yield reduced reaching 61 wt% and the gas increased to 28.5 wt%. PS was completely degraded into liquid products with some char and gas even at zero residence time. Char production remained constant at 1 wt% up to 90 min and increased to 3.4 wt% after 120 min of the process. The gas production went up from 0.6 wt% to 1 wt% after 120 min.

##### 4.2. Temperature

Understanding the behaviour of polymeric materials during their thermal degradation in the presence of inert (i.e. nitrogen, helium, argon, etc.) or partial oxidative atmospheres can aid in the understanding of pyrolysis, combustion and other thermal processes. The thermal decomposition of polymeric and lignocellulosic materials is a complex process which involves a number of chemical reactions as well as physical stages such as heat and mass transfer (Bilbao et al., 1997). However, temperature controls the main decomposition behaviour of the plastic material. Temperature also controls the cracking reaction of the plastics where the Van der Waals force between the molecules collapse due to the increase of the vibration of the molecules which on the other hand tends to make them evaporate away from the surface of the object and results in the breaking of the carbon chain (Lopez et al., 2011). TGA studies conducted in the past reveal the degradation temperature of plastic materials by studying the decomposition curve, conversion curve or the peak point on the derivative curve. Table 5 summarizes main studies found in relation to the effect of temperature and the main degradation temperature of common plastic materials. Westerhout et al. (1998a) reported that at higher temperatures the influence of product concentration, polymer type and residence time on product distribution were insignificant compared to the influence of temperature. Scott et al. (1990) observed in their work that at temperatures lower than 700 °C

**Table 5**  
Summary of common thermal degradation temperature studies of common plastic materials conducted using thermogravimetry.

Reference	Plastic type	Degradation temperature (°C)	Notes
Bockhorn et al. (1999c)	Polyamide 6	200	Heating rates from 1 to 20 K/min between ambient temperature and 800 °C in helium atmosphere.
Bockhorn et al. (1999a)	HDPE	325	Heating rates from 10 K/min between ambient temperature and 600 °C using a 20 mg weight sample.
Bockhorn et al. (2001)	Polyamide 6	290	Heating rates from 10 K/min between ambient temperature and 500 °C using a 20 mg weight sample, two catalysts used which reduced degradation temperature.
	Polyamide 6 + 10% H <sub>3</sub> PO <sub>4</sub>	200	
	Polyamide 6 + KOH/NaOH	200	
Molto et al. (2007)	PET	375	PET fibre cloth pyrolysis at several heating rates (5–20) K/min. Initial loss started around 225 °C.
Cepeliogullar and Putun (2013a)	PET	350	PET fibre cloth pyrolysis at several heating rates (5–20) K/min. Initial loss started around 200 °C.
Chin et al. (2014)	HDPE	378	Heating rates from 10 to 50 °C/min.
Aracil et al. (2005)	PVC	275	PVC powder was used in heating rates between 5 and 20 K/min.
Conesa et al. (1996)	HDPE	400	Heating rates from 5 to 100 °C/min.
Cepeliogullar and Putun (2013a)	PVC	260	A second degradation temperature range was observed between 385 and 520 °C.
Al-Salem and Khan (2014)	Ropet (PET/PMMA)	327	Heating rates between 5 and 20 K/min identifying two onset temperatures in TGA which lead to development of analytical solution model for plastic blends.

the major part of the product yielded was solid, whereas at higher temperatures the main product was a gas.

It can be noted that HDPE starts to degrade at temperatures above 325 °C, and exhibits complete degradation at temperatures of and above 467 °C (Chin et al., 2014; Marcilla et al., 2005). Higher heating rates also speed up the degradation process and consequently increases the rate of reaction. This is unlike LDPE, where the degradation starts at a temperature of 360 °C (Williams and Williams, 1998). Jung et al. (2010) reported the degradation of PP at a temperature below 400 °C, showing that it degrades typically lower than PE. However, PS is known to start to degrade at the lowest temperature among common plastics at around 300 °C (Onwudili et al., 2009), which is even lower than initial degradation of PET. Hence, it can be concluded that the breakage of carbon chains is induced and controlled by temperature of pyrolysis to a great extent. Pyrolytic reactors are also typically designed on the basis of temperature ranges that can cover common feedstock of plastics, which endure the pyrolysis degradation temperature intended for its use.

In the research by Williams and Williams (1997) it was shown that no wax was produced above 600 °C compared to the lower temperatures in the pyrolysis of common PE. That suggests that heavy wax was broken down to lighter components. As the temperature is increased the percentage of gas increases. The high temperature favours increased gas formation as the molecules breakdown and form a wide range of smaller organic molecules. In addition, with the higher amount of energy there is a tendency for an increased number of secondary reactions, so the amount of oil and wax decreases with an increase in temperature. Singh and Ruj (2016) also observed a similar trend where higher temperatures lead to higher gas formation with increase in heavier hydrocarbon components in the products (Adrados et al., 2012). It was found that on increasing the temperature the cracking reduces due to lack of residence time in the reactor and high molecular chain compounds and aromatics were obtained in form of wax in oil product.

Karaduman et al. (2001) pyrolysed PS in a free-fall reactor under vacuum to obtain the monomer. A set of experiments varied the temperature between 700 and 875 °C. The liquid yield was at a maximum at around 750 °C and the styrene yield at 825 °C. Higher temperatures decreased the solid yield and increased the gaseous yield and conversion in total. Up to 750 °C the operating temperature lowered the solid yield but above this temperature, the solid yield continued to decrease at a lower rate. This might be caused by

the partial decomposition of the product styrene. At 750 °C the solid yield was 47% while liquid and gas yields were 32% and 21%, respectively. Mastral et al. (2002) pyrolysed HDPE in a FBR at temperatures between 640 and 850 °C with varying residence times between 0.64 and 2.6s. At low temperatures the main product was wax with yields up to 79.7 wt%. As the pyrolysis temperature increased, gas yields increased along with it; At 685 °C the gas yield reached 64.2 wt% and at 730 °C the gas yield reached 79 wt%. Above 730 °C only gas and oil were obtained. The highest amount of gas was obtained at 780 °C with the 86.4 wt% fraction. Above 850 °C the gas yield declined due to cyclation reactions that formed aromatic hydrocarbons. This suggests that the increase in temperature results in cracking of the wax to oil and gas, which indicated induction of secondary reactions as noted previously. These results show that temperature has a great influence on the process and affects the product yields as well as composition due to the secondary reactions.

#### 4.3. Pressure

Most researchers conducted their experiments at atmospheric pressure (of the unit typically with open vent), so the effect of pressure is not that well reported in literature and needs to be understood fully presenting a major research gap in pyrolysis studies. Murata et al. (2004) studied the effect of the pressure in the range of 0.1–0.8 MPa on HDPE pyrolysis in a continuous stirred tank reactor. It was observed that as the pressure increased the gas production increased along with it from 6 wt% to 13 wt% at 410 °C and from 4wt% to 6wt% at 440 °C. The results show that the pressure has the greatest effect at lower temperatures and its influence diminishes with its increase. This deems the pressure to be a time dependent factor in pyrolysis. Lopez et al. (2010) studied the continuous pyrolysis of waste tyres under vacuum (25 and 50 kPa) and under atmospheric pressure in a pilot plant CSBR operating in the temperature range of 425–500 °C. The main effect of vacuum over the atmospheric pressure is the rise in the diesel fraction yield of the liquid product. In addition, a positive effect on the porous structure properties of the residual carbon black has been reported, a decrease in pore blockage increased the surface areas of the carbon blacks obtained. This effect of the vacuum on the porous structure is caused by the two factors; assistance by the vacuum to the devolatilization and diffusion of the volatiles within the particle; and reduces of the deposition of carbon material on the porous

structure by vacuum (Lopez et al., 2010; Ismadji et al., 2005). Operation under vacuum causes an increase in the gas yield and a decrease in the single ring (C<sub>10</sub>) aromatic hydrocarbons, which is caused by the negative effect of vacuum on the cyclization and aromatization reactions of the pyrolysis products. Increase in the gas yield is due to the attenuation of olefin condensation by Diels-Alder reactions to give aromatic compounds (Lopez et al., 2010).

It was also reported in the past that the average molecular weight of the gaseous products decrease along with the increase in operating pressure (Murata et al., 2004). Also, it was observed that the rate of double bond formation decreases along with the increasing pressure. Since, there is a relationship between the double bond formation and the scission of carbon to carbon (C-C) bonds in polymers, it can be concluded that the reaction pressure takes part in the scission of such bonds in plastics. There are two types of C-C bonds scission in the thermal degradation of polymers; a random chain scission and a chain-end scission towards termination of the reaction, which occur simultaneously. The random scission causes a molecular weight reduction of a polymer and increases the rate of product formation. The chain-end scission causes a dissipation of reactor contents producing volatile products. The chain-end scission is pressure dependant and takes place at a gas/liquid interface producing volatile products and its rate is proportional to the number of molecules. The rate of random scission is proportional to the number of C-C links and it is not affected by the pressure. This is due to the fact that it takes place in the liquid phase. This presents a venue in future work to consider increase in pyrolysis oil production whilst manipulating process pressure. However, a constraint still remains in industrial units where pressure control will need to be economically viable against market value of the products yielded.

## 5. Thermal lag and heat transfer limitations

Previous studies have demonstrated different experimental set-ups used with different inert atmospheres (at different scales), temperature ranges, reactor types, sample amounts, heating rates ( $\beta$ ) and pressures (Conesa et al., 1996; Bilbao et al., 1997; Bockhorn et al., 1998, 1999a; 1999b; Ceamanos et al., 2002; Park et al., 2000a, 2000b; Oh et al., 2003; Berruete et al., 2005). The heat transfer phenomenon (between the experimental system, the sample and inside the sample itself) is a major issue addressed previously by Ceamanos et al. (2002). This could be minimised by using a small amount of sample and low heating rates. Uniform heat distribution is very important for effective mass and energy transfer, and it is integral to obtaining a valuable and narrow range of hydrocarbons (Kunwar et al., 2016). This is something that newly recognised thermal analysis standards set by the ICTAC recommends strongly to avoid mass and heat transfer limitations (Vyazovkin et al., 2011, 2014).

As the pyrolysis temperature increases, the heat demand increases dramatically due to increase of the operating temperature (knowing that the overall pyrolysis reaction is endothermic). Heat transfer problems across the boundary layer into the reacting solid surface (substrate) becomes acute at high heating rates. This was also detailed by Narayan and Antal (1996) who addressed the thermal lag ( $\Delta T_{TL}$ ) problem between the sample's temperature and the temperature of the sample's environment achieved by placing an external thermocouple onto the sample. The difference between these two temperatures is what they have defined as the thermal lag ( $\Delta T_{TL}$ ). There are great variations in the calculated kinetic parameters (namely the kinetic rate constants and activation energy), depending on the approach and the analytical method used (Oh et al., 2003). Consequently, the adequacy of the kinetic model assumed for the complex degradation mechanism is very

important (Ceamanos et al., 2002). Differences due to the reaction mechanisms and kinetic evaluation methods have been reported in the past by various authors (Conesa et al., 1996; Bilbao et al., 1997; Bockhorn et al., 1998, 1999a; Ceamanos et al., 2002; Park et al., 2000a, 2000b; Oh et al., 2003). Conesa et al. (1996) showed that the initial weight of the sample and the surface pan area can affect the displacement of the weight loss curve. Ranzi et al. (1997) stressed the possible presence of mass and heat transfer limitations, generally not taken into account in kinetic data abstraction, which extend the range of variation of kinetics constants. Whilst Dahiya et al. (2008) stated that small errors in temperatures and heating rates cause notable deviations in kinetic parameters. In summary, operating conditions can affect significantly the results obtained by any experimental pyrolysis set-up. FBR systems have been known to reduce energy transfer in pyrolysis and facilitate uniform energy distribution (Marcilla et al., 2007). Plastic with heat will get to be in a molten state, that poses higher viscosity values. Hence, it is paramount to reduce their viscosity by mixing plastics with VGO or lubricants (Kunwar et al., 2016).

## 6. Presence of catalysts and effect on pyrolysis

Catalysts have been employed in PSW pyrolysis due to the numerous advantages it provides the process as a whole. Catalytic cracking is more appealing than thermal degradation on its own as it is faster and requires lower temperatures which significantly reduces the energy demand. Moreover, catalytic cracking using catalysts such as zeolites results in high quality products in the range of motor engine fuels, therefore reducing the need for any further upgrade. Thermal pyrolysis is more restricted to areas of existing oil refineries as its products require more upgrading. Using catalysts lowers the required pyrolysis temperature, reduces time of reaction, produces diesel components around the optimal boiling point range of 390–425 °C, enhances the selectivity to gasoline and stimulates the occurrence of isomerisation (Butler et al., 2011; Lee, 2006). However, catalyst regeneration is required due to coke formation. Pyrolysis reactions are endothermic in nature and the use of catalysts typically reduces energy requirements by reducing the pyrolytic temperature. In this section, the catalyst types and their influence on the pyrolysis of plastics will be discussed to point out the main advantages and disadvantages of their application.

Generally, catalysts are classified either as homogeneous or heterogeneous. The former involves a single phase (usually a liquid solution), whilst in the latter the catalyst is solid. Aluminium chloride (AlCl<sub>3</sub>) catalysts are the most commonly used type of homogeneous catalyst in PSW pyrolysis (Westerhout et al., 1998a, 1998b). Nonetheless, the most common type of catalysts used in pyrolysis of PSW are heterogeneous ones due to the fact that the fluid product can be easily separated from the solid catalyst which can be easily regenerated and reused. Most common examples of such are nanocrystalline zeolites which are the most commonly applied ones (Shah et al., 2010), conventional acid solid, meso-structured catalyst, metal supported on carbon and basic oxides (Aguado et al., 2005). Heterogeneous catalysts have also been reported to withstand severe reaction conditions up to 1,300 °C and 35 MPa and can generally be easily separated from the gas and/or liquid reactants and products (Butler et al., 2011) (Fig. 4).

Acid base zeolite catalysts (HZSM-5 and H-ultrastable Y-zeolite) are more effective in PSW pyrolysis than less acidic ones, e.g. acidic amorphous silica-alumina and mesoporous MCM-41 (Butler et al., 2011). Garfoth et al. (1998) investigated the effect of zeolite catalysts such as HUSY, HZSM-5 and HMOR on the HDPE pyrolysis with a polymer content of 40 wt%. It was found that HZSM-5 was more effective than other types of catalysts as the residue left (coke content) by HZSM-5 was merely 4.53 wt% compared to 7.07 wt%

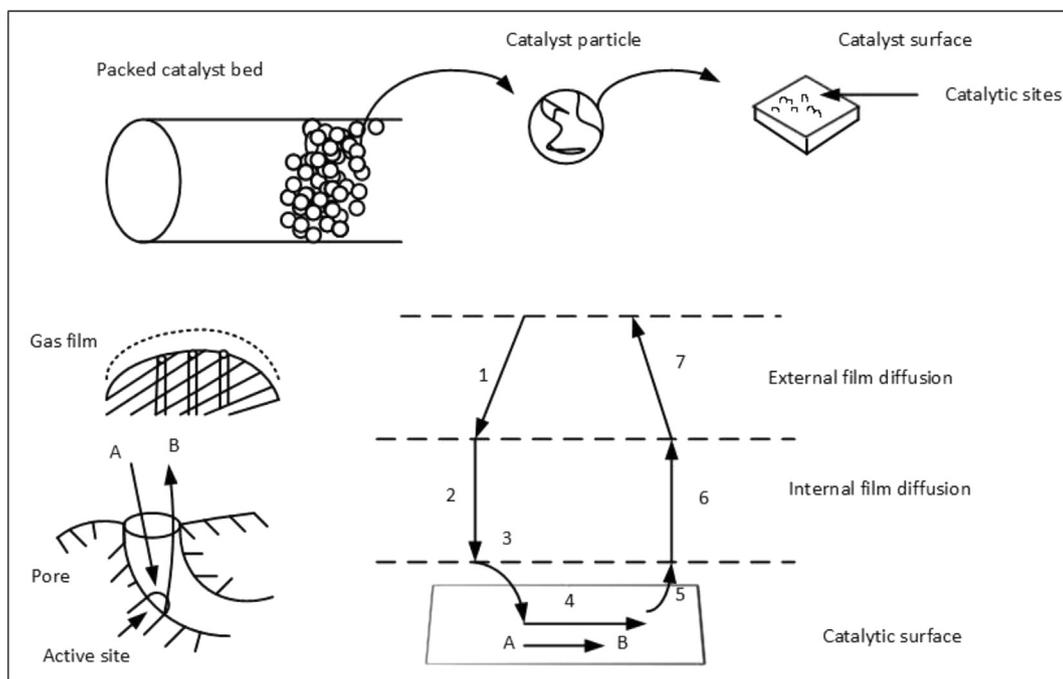


Fig. 4. Reaction of heterogeneous catalysts as reported by Butler et al. (2011).

and 8.93 wt% left by HUSY and HMOR, respectively. Marcilla et al. (2009) observed that different zeolite catalysts have a distinctively different products selectivity. HZSM-5 and HUSY were used to pyrolyse HDPE and LDPE at 550 °C and higher oil recovery was obtained by HUSY while HZSM-5 obtained higher amount of gaseous product. Ateş et al. (2013) also have investigated pyrolysis of MSW and MPW in a batch reactor at 500 °C, 550 °C and 600 °C in absence and presence of catalysts, Y-zeolite,  $\beta$ -zeolite, equilibrium FCC, MoO<sub>3</sub>, Ni–Mo-catalyst, HZSM-5 and Al(OH)<sub>3</sub>. In the presence of catalysts, the yields of gaseous fractions increased, while reaction time required for the total cracking decreased. It was also noted that the catalysts have high selectivity in converting aliphatic hydrocarbons to aromatic and cyclic compounds in oil yield. Seo et al. (2003) observed the effect of HZSM-5 on the pyrolysis of HDPE at 450 °C and obtained a very low liquid yield of only 35 wt%. Other researchers also obtained similar trends (Lin and Yen, 2005; Syamsiro et al., 2014).

Donaj et al. (2012) pyrolysed polyolefins consisting of 46 wt% LDPE, 30 wt% HDPE and 24 wt% PP using commercial Ziegler-Natta catalyst in the fluidized quartz-bed reactor. The gas yield during the thermal pyrolysis at 650 °C was 36.9 wt% and with the catalytic process it increased to 54.3 wt%. In the thermal pyrolysis the liquid yield was reported to be 48.4 wt% and the solid yield 15.7 wt%. However, the use of catalyst decreased these values to 41.9 wt% and 3.8 wt% respectively. Aguado et al. (2007) conducted a conversion of LDPE at the temperature range of 425–475 °C in a two-step reaction process consisting of a pyrolytic furnace and a reactor. In the furnace, the thermal cracking was performed, while in the reactor the nanocrystalline n-HZSM-5 or Al-MCM-41 catalyst was placed in order to upgrade the thermal pyrolysis products. At 450 °C without the catalyst, the gaseous product was only 16.3 wt% and the liquid fraction obtained was 74.7 wt%, the n-HZSM-5 increased the gaseous yield to 73.5 wt% which consisted primarily of olefins, while the Al-MCM-41 due to its weaker acid properties required higher temperatures and produced lower gas yield of 54–58 wt%. The proportion of aromatics produced was less while using Al-MCM-41 catalyst compared to n-HZSM-5, but it produced higher

proportion of isoparaffins and olefins. Aguado et al. (2007) also conducted a thermal gravimetric analysis (TGA) to evaluate the activity of catalysts by determining the degradation temperature shifts. Without the presence of catalyst, the LDPE started degradation at 419 °C. Employing n-HZSM-5 catalyst, reduced the degradation temperature to 396 °C. Muhammad et al. (2015) pyrolysed WEEE in the presence of ZSM-5 and Y-zeolite catalysts using a fixed bed two-stage batch reactor with the plastic pyrolysed in the first stage and the evolved pyrolysis gases catalysed in the second stage reactor for further upgrading and cracking. The main plastics contained in the WEEE were high impact polystyrene (HIPS) and acrylic butadiene styrene (ABS) and were treated in the presence of the zeolite catalysts. Without the catalyst the plastics produced an oil yield of 84.0 wt%, but with the zeolite catalyst the process produced a lower amount of oil evaluated at 80 wt% in the case of Y zeolite and 77.5 wt% using the ZSM-5 catalyst. There was also an increase in the alkene gases, especially ethene and propene. Similar results were found for feedstock reclaimed from fridge plastics. The oils derived from the uncatalysed pyrolysis of WEEE plastics consisted mainly of aromatics with high concentrations of styrene, derived from the HIPS and ABS decomposition. Pyrolysis using zeolite catalyst resulted in large concentrations of benzene, toluene and ethylbenzene in the oil but reduced concentrations of styrene. The oils from thermal and catalysed pyrolysis contained significant concentrations of polycyclic aromatic (PCA) hydrocarbons, e.g. naphthalene, phenanthrene and pyrene.

Garfoth et al. (1998) pyrolysed HDPE and PP over zeolites and silicates as catalysts. Selective yield of aromatics and product distribution were achieved in the FBR. Both the carbon number distribution of the products of HDPE and PP cracking at 360 °C over the various catalysts used in this study and the nature of the product distribution were found to vary with the catalyst used but not significantly with the polymer itself. A fixed bed reactor was used to treat latex by Hall et al. (2009) using Y-zeolite catalyst. The catalyst aided the formation of ethyl-benzene, ethyl-toluenes, tri-methyl-benzenes, and diethyl-benzenes. It was also reported that 3-ethyltoluene was the most abundant ethyl-toluene, with yields of 18.5

and 18.9 mg/g<sub>sample</sub> when the reaction temperature was 380 °C and 480 °C, respectively. Zeolite catalysts have been reported to reduce the yield of limestone (when present in feedstock) and increases the concentration of aromatics (Shen et al., 2007). Williams and Brindle (2002; 2003a; 2003b) have also reported benzene-toluene-xylenes (BTX) production during pyrolysis of tyres in the presence of Y-zeolite. Santella et al. (2016) used two zeolite-based catalysts with high silica content to pyrolyse scrap from WEEE. The mass balance showed that the oil produced by pyrolysis is always the main product with yields ranging from 83% to 93%. A higher yield was obtained when pyrolysis was carried out with HZSM-5 catalyst, and the production of oil was favoured by the catalytic rather than thermal pyrolysis. Mixtures of HZSM5 and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts was also used by Uemichi et al. (1998) in a tubular reactor to pyrolyse LDPE at 425 °C successfully. Eight types of plastics were pyrolysed by Masuda et al. (2001) in a novel design for a continuous flow catalytic bed reactor suitable for degradation and upgrading the pyrolysis products (Fig. 5). The reactor system consisted of three kinds of reactors connected in series. The first was a reactor filled with stirred heat medium particles, which enabled the high heat transfer rate, the high holdup and the good contact of the melted plastics with steam. The second was a tank reactor. The last one was a fixed bed reactor with FeOOH catalyst particles. The plastics used were PE, PP, polycarbonate (PC), PET, poly (butylene terephthalate) (PBT), PS, nylon-6 (N6) and nylon-6,6 (N6,6). Nitrogen and steam were both used in a series of experiments over the catalysts. The degradation mechanism of the polyester plastics investigated changed from the thermal pyrolysis to the hydrolysis by introducing steam into the carrier gas, and it was noted that the resulting oil yield from PE/PET mixture resulted without any sublimate materials.

Zeolite catalysts (ZSM-5) have also been applied on semi-commercial scale in the Fuji process of low pyrolysis treatment of polyolefin waste (Tukker et al., 1999). Catalytic cracking at a temperature around 400 °C would take place after pre-treating the throughput at 250 °C and separating the PVC fraction by using the sink float technique. The unit processes 500 tpa and produced a pyrolysis oil fraction of 80 wt%. Kumar et al. (2013) used a blend of waste HDPE with diesel to estimate the fuel production rate in a catalytic pyrolysis process using Kaolin clay as a catalyst. The performance of the blend was reported to reduce in comparison to conventional diesel fuel. Dual catalytic systems have also been researched in the past to have a pyrolysis process that employs two catalysts in a combination process, which typically involves Zeolite catalysts (ZSM-5) and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (Uemichi et al., 1998; Kunwar et al., 2016). Using such a combination of catalysts have been reported to produce results in a high yield of gasoline with a high octane rating (Syamsiro et al., 2014). Scott et al. (1990) conducted pyrolysis tests using LLDPE manufactured in the temperature range 515–790 °C with Calgon F400 activated carbon (derived from bituminous coal) as a catalyst. At temperatures lower than 700 °C, a major part of the product was solid charred PE. At higher temperatures, the product was mainly a gas containing ethylene, propylene, butylenes, and some other light hydrocarbons. Aliphatic and some aromatics (benzene and toluene) were also detected.

Akpanudoh et al. (2005) studied the effect of acidity on liquid product yields during linear low density polyethylene pyrolysis in the presence of commercial cracking catalysts whose active catalytic ingredient was HUSY zeolite. They varied the system's acidity by varying the acid sites amount in the polymer catalyst system and by varying the catalyst to polymer ratio. They observed an initial steep increase of liquid fuel with acidity content followed by a softer decline beyond a maximum point. They concluded that high acidity leads to over-cracking that leads to formation of much smaller molecules and an increased gas yield. This was also

reflected on liquid fuel quality, as higher acidity shifted the formed liquid boiling point distribution towards lighter liquid hydrocarbons. The same reason is responsible for less acidic catalyst like pillared clays and their original clays (Manos et al., 2001, 2002; Gobin and Manos, 2004), as well as commercial FCC catalysts (Gobin and Manos, 2004) lead to higher liquid yield as well as lower coking than zeolites. Among zeolites, ZSM-5 forms low liquid amounts due to its small pores that influence the production of smaller molecules (Manos et al., 2000a, 2000b). Gulab et al. (2010) studied the effect of conditions on zeolite catalyst performance in pyrolysis of HDPE. The study showed that the degradation can be done at low catalyst content to reduce the economic cost. Decreased catalyst content reduces the activity of the system but this can be compensated by increasing the process temperature. High temperature aids high conversion values and yields higher liquid products due to less over-cracking. Temperature also affected the quality of liquid products, i.e. the product distribution, where higher temperatures favoured middle boiling point components (C<sub>8</sub>-C<sub>9</sub>) while lower temperatures increased the fraction of heavy components (C<sub>14</sub>-C<sub>18</sub>).

## 7. Comparative assessment with other thermal and catalytic PSW chemical treatment methods

Incineration of plastic is a widely used method in waste management. There are four methods for conversion of organic wastes to synthetic fuels: hydrogenation, pyrolysis (thermal and catalytic), gasification and bioconversion (Demirbas, 2001, 2004). As an alternative to combustion and gasification, pyrolysis of plastic waste has gained importance because of having better advantages toward environmental pollution (Singh and Ruj, 2016). Because of an inert atmosphere, free from oxygen, it does not form dioxins by reaction of products with oxygen as stated previously in this work and emphasised by others (Chen et al., 2014; Stanmore, 2004; McKay, 2002; Kanniche et al., 2010).

Other technologies that compete with pyrolysis have also been reviewed in this communication to give a more through assessment of PSW potential in various treatments. Two major elements that drives concerned parties to turn to other technologies for treating plastics, the commercial value of the technology and the performance of it at desired scale. The type of waste and degree of contamination are also major elements that cannot be neglected when considering the type of treatment that is chosen for plastic waste. The two main competing technologies to pyrolysis are gasification and hydrocracking (i.e. hydrogenation) which both make the other two types of thermo-chemical treatment (TCT) technologies that are typically applied for PSW. The gasification process received attention from the early 70s due to its application in various fields including petroleum refining processes and heavy crude treatment, hence its availability on commercial and industrial scale is more noted than pyrolysis. Gasification is defined as the thermal treatment of plastics in low levels of oxygen to produce a syngas, which can be refined for various applications or directly combusted (Robinson, 2009). Ideally, gasification would produce a high CV gas with a completely combusted residual char. The gasification into high CV fuel gas obtained from PSW was demonstrated in research stages and results were reported and published in the literature for PVC (Borgianni et al., 2002), PP (Xiao et al., 2009) and PET (Matsunami et al., 1999). The petrochemical and power industries have several hundred installations of large scale gasification units worldwide. These systems operate at very high temperatures (1100°C or higher), short residence times, and have been reported to obtain fast conversion of feeds. Though, careful feedstock preparation by crushing, shredding and sieving with controlled moisture content has to be achieved. Generally, MSW

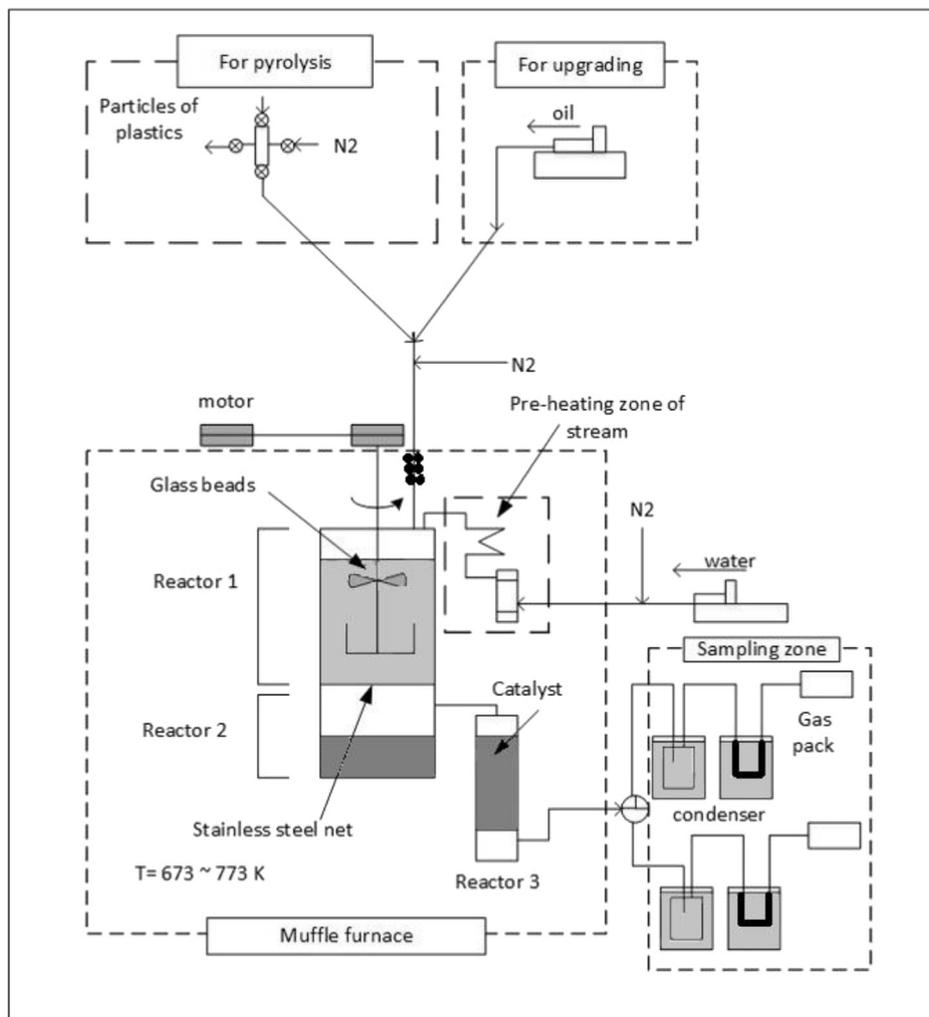


Fig. 5. Novel three reactor system setup used by Masuda et al. (2001) to pyrolyse polyolefin and polyester plastics.

has varying size, moisture content and CV so it does not fit into the gasification feed criteria and has to be pre-treated before the process. This creates additional operational costs. Gasification also requires large operational costs due to feed pre-treatment, consumption of pure oxygen as well as syngas cleaning costs (Panepinto et al., 2015). Gasification of MSW also produces large amounts of tars between 0.1 and 10% of the product gas (Milne and Evans, 1998). Compressed tar may cause serious problems to the process and equipment such as deactivation of sulphur removal systems, erosion of compressors, heat exchangers, filters, and damage gas turbines and engines. Thus, additional physical and chemical treatments are required to solve this problem (Panepinto et al., 2015). This presents a prime advantage in favour of pyrolysis.

Gasification is also a flexible process that can either produce large amounts of char and ash (carbonisation) or convert waste to small amounts of char and ash with large amounts of syngas (gasification) (Begum et al., 2014). This flexibility is the reaction vessel of gasification plants is dependent on the type of feedstock and reaction temperature range. The Akzo process developed for steam gasification has been reported to treat 100 wt% PVC waste in a circulating fluidized bed system (two reactors) with subsequent combustion with promising results (Tukker et al., 1999). The process works on a hot circulating sand bed, steam at 700–900 °C with an input of high PVC and polyolefin mixture of feedstock, and a high yield of methane, hydrochloric acid (HCl), carbon monoxide (CO)

and Hydrogen (H<sub>2</sub>) depending on the type of plastic. The Battelle technology has been widely recognized as an established gasification technology that deals with co-mingled PSW, which the Akzo process was actually based on (Tukker et al., 1999). The technology is a high temperature gasification process in a sand FBR (800–1000 °C) that treats PE, PS, PVC and mixed plastics to yield 40% ethylene, 27% methane, 17% H<sub>2</sub> and small amounts of other chemicals. Plasma gasification is also a competing technology nowadays to classical ones where energy is produced by combustion in engines (Morrin et al., 2012).

In addition, a need to utilise as much waste as possible to treat in co-gasification is something that has captured the attention of many researchers. In its industrial application, the feasibility of co-gasification for a number of waste streams (PSW, biomass, RDF, etc.) has been proven. A typical co-gasification scheme will include a two-step process of two adjacent gasification furnaces (Conesa et al., 1996; Ranzi et al., 1997; Zia et al., 2007). After pre-treatment (i.e. shredding), the mixed stream will be introduced to an RDF moulder in which air sorting takes place and steam treatment. Oxygen and steam will be introduced to the first gasifier operating at low temperatures (outlet steam temperature of 1300 °C) with circulating sand at a temperature around 700 °C. In the second-stage high-temperature gasifier, the gas from the low-temperature gasifier is reacted with steam typically at a temperature of 1500 °C to produce a gas composed primarily of carbon

monoxide and hydrogen. At the furnace outlet, the gas is rapidly cooled to below 200 °C to prevent the formation of dioxins and chlorides (based on chlorine content on PSW). A more comprehensive review on gasification is given elsewhere in Al-Salem et al. (2009a).

Another competing technology that has been widely applied in various industries is hydrocracking, which is the treatment of organic materials in hydrogen atmospheres to produce fuel range hydrocarbons at elevated temperatures. Heterogeneous, and namely acid base catalysts, are quite beneficial in such processes to supply the cracking properties (Butler et al., 2011). Hydrocracking, and in broader terms, hydrogenation (use of hydrogen in thermal treatment) is beneficial in finishing processes of products resulting from pyrolysis and the cracking of PSW. A main advantage of the process is the high gaseous product it yields with no char to avoid further clean up as the work of Scott et al. (1990) demonstrated after treating PE at 600 °C. The RWE process in one of the hydrocracking technologies that emerged in the 1990s which involved the depolymerisation of plastic waste (10 kg h<sup>-1</sup>) after removing HCl in a temperature range between 400 and 500 °C. The main outputs were 80% oil, 10% gas and solids (Nishino et al., 2005). In addition, the Veba Combi Cracking (VCC) technology was deemed to be a very highly desirable one, where a depolymerisation section is employed to produce a Cl-free condensate and gas which were mixed with the depolymerisate (Tukker et al., 1999). The main outputs of the process can be summarised as follows: (i) HCl, (ii) Syncrude from the VCC section (chlorine free), (iii) Hydrogenated solid residue, and (iv) Off gas. The input for the depolymerisation section was described by Sas (1994) as follows: (i) Particle size < 1.0 cm, (ii) Bulk density ≥ 300 kg m<sup>-3</sup>, (iii) Water content < 1.0 wt%, (iv) PVC < 4% (≤2 wt% chlorine), (v) Inert content < 4.5 wt% at 650 °C, (vi) Metal content < 1.0 wt%, and (vii) Content of plastic ≥ 90.0 wt%.

## 8. Conclusions and recommendations

An extensive review of pyrolysis as a means of solving PSW accumulation in urban environments was conducted in this communication. Pyrolysis presented itself as a sustainable and an efficient treatment method to treat solid waste accumulation which is an important issue nowadays in overcoming landfilling and pollution control. Pyrolysis is a versatile method which can produce a range of useful hydrocarbons potentially used as a chemical feedstock or as energy. This could minimize the dependency on non-renewable fossil fuels and in addition solve the landfilling problem. Pyrolysis has environmental advantages compared to other PSW treatment methods as it takes place in an atmosphere free of oxygen, thus does not produce dioxins and has reduced carbon monoxide and dioxide emissions. It is a flexible process as the conditions such as temperature, pressure, residence time can be easily varied to achieve the desired product distribution. However, the effect of pressure on the process is not as well documented as the effect of other factors such as temperature. However, it was noted that the pressure of pyrolysis processes can be considered as an influencing factor at low temperatures. There are many reactor types and experimental setups which could be employed for pyrolysis. Batch reactors have been reported to be inconsistent and non-cost effective as the frequent charging of the feedstock is required, increasing labour cost of the process. Thus, for large scale operation a continuous pyrolysis process is recommended. Conical spouted bed reactors (CSPR) are a good choice for handling large particles with different densities, while microwave assisted reactors are a good alternative to minimize the operational costs and the heating time required for the full degradation of feedstock. It is also noted that fixed bed reactors will be ideal as a secondary

pyrolysis units to treat product evolving from the first reactor. This will yield products as desired by consumers with quite an ease. Catalytic pyrolysis has several advantages over the thermal process, as it improves efficiency by decreasing the process's residence time and affects the product selectivity. Moreover, catalytic cracking using the catalysts such as zeolites results in high end quality of products in the range of motor engine fuels, therefore reducing the need for any further upgrade downstream of pyrolysis processes. Despite this fact, catalysts are expensive and the design has to consider the possibility of avoiding catalyst poisoning and deactivation by the impurities in the feedstock. Thermal pyrolysis is recommended to be carried out near the areas of existing oil refineries as its products require more upgrading. One of the main components in the PSW is PVC which produces during its decomposition corrosive hydrochloric acid. To avoid such a problem, the efficient pre-treatment step or addition of the absorber is suggested. It can also be concluded that pyrolysis will be an ideal treatment method in the case of co-mingled plastics or MSW if the feedstock was to be somewhat similar in its acceptance criteria to the process itself.

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