A Study to Optimise Plastic to Fuel Technology-A Review

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***Abstract*- The global plastic production increased over years due to the vast applications of plastics in many sectors. The continuous demand of plastics caused the plastic wastes accumulation in the landfill consumed a lot of spaces that contributed to the environmental problem. This review showed that many researchers have been done to study the potential of plastic pyrolysis process in order to produce valuable products such as liquid oil and the results were convincing. However, there were some drawbacks of the recycling method as it required high labor cost for the separation process and caused water contamination that reduced the process sustainability. Due to these drawbacks, the researchers have diverted their attentions to the energy recovery method to compensate the high energy demand.**

***Keywords*- Waste plastic, pyrolysis, alternative fuel**

I. INTRODUCTION

Plastic waste in India has become an increasingly pressing problem over the years. With increasing dependence on plastic, the tendency to dispose of plastic casually has also become a part of the mainstream. India's daily generate of over 15,000 tones of plastic daily. The global plastic production was estimated at around 300 million tons per year and is continuously increasing every year (Miandad, *et al.*, 2016; Ratnasari, *et al.*, 2017). Polyethylene and polypropylene, both together accounting for 60 per cent of plastic waste the prospects of conversion to fuel are abundant. Union government's focus on waste management via Swachh Bharat Abhiyan, plastic waste in India could be successfully converted to fuel for both industrial and domestic use that ensure that urban and semi-urban areas become plastic free. The fuel obtained from conversion of plastic is completely environmentally friendly due to absence of any toxic substances (Datta, 2017).

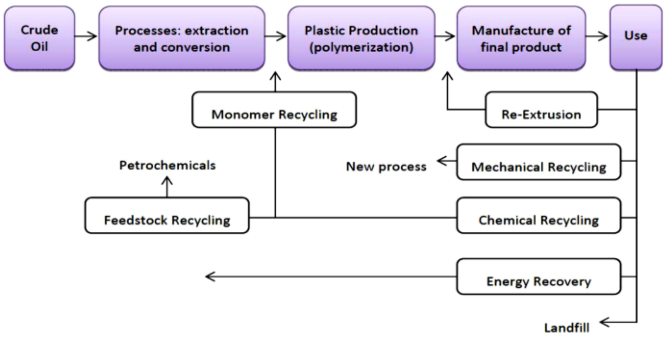
Plastic solid waste (PSW)

Plastic wastes in household waste comprise lots of polymeric materials. In the EU-27, 6.9% polyethylene terephthalate (PET; $(C_{108}O_4)n$), 12.1% high-density polyethylene (HDPE; $(C_2H_4)n$), 10.4% polyvinyl chloride (PVC; $(C_2H_3Cl)n$), 17.5% low-density polyethylene (LDPE; $(C_2H_4)n.$), 18.9% polypropylene (PP; $(C_3H_6)n$), 7.4% polyurethane (PUR, $C_{17}H_{16}N_2O_4$) and 19.7% other polymers are used in the generation of plastic material. Plastics may take up to billions of years to degrade naturally. They degrade gradually since the molecular bonds containing hydrogen, carbon and few other elements such as nitrogen, chlorine and others that make plastic very durable. As petroleum was the main source of plastic manufacturing, the recovery of plastic to liquid oil through pyrolysis process had a great potential since the oil produced had high calorific value comparable with the commercial fuel (Shafferina Dayana, *et al.*, 2016). Pyrolysis (thermochemical conversion) can be successfully applied to polyethylene teraphthalate (PET), polystyrene (PS), polymethyl metacrylate (PMMA), polycarbonate (PC), and certain polyamides such as nylon, efficiently depolymerising them into constitutive monomers (Yoshioka, *et al.*, 2004; Smolders and Baeyens, 2004; Onwudili, *et al.*, 2009 and Brems, *et al.*, 2011).

Polyolefins, and in particular polyethylene (PE), has been targeted as a potential pyrolysis feedstock for fuel (gasoline) production, or to produce waxes as feedstock for synthetic lubricants, albeit with a limited success.

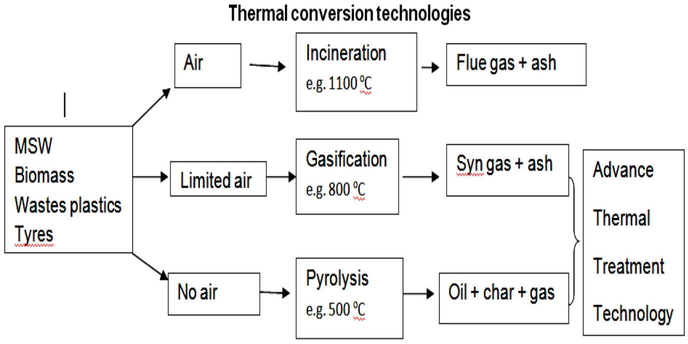
The plastic structure is a long hydrocarbon chain that could contain aromatic cyclic groups or oxygenated groups. From their chemical formula, these polymers except for PET and PVC are only composed of carbon and hydrogen. However, they may also contain low contents of oxygen due to the presence of additives, impurities or moisture. In addition, it has been shown that the volatile matter content is very high (at least 94% except for PET). It should be noticed that PET, PE (LDPE and HDPE) and PP, first melt and then decompose; for PVC, degradation and melting temperature are very close; for PS the degradation temperature is clearly lower than the melting temperature (Matsuzawa, *et al.,* 2001). The two most important of the polymers are polystyrene (PS) and low-density polyethylene (LDPE) (Ali, 2017).

Plastic solid waste (PSW) treatment can be divided in four methods (Brems, *et al.,* (2013).



There are four mechanisms by which plastics degrade in the environment: photodegradation, thermo-oxidative degradation, hydrolytic degradation, and biodegradation by microorganisms. The most useful decomposition products can be obtained by understanding the structures of the different types of polymers found in municipal solid waste (MSW), and their mechanisms of degradation can be altered by the presence of catalysts (Beena Sethi, 2016). Thermo-lysis is the treatment of PSW in the presence of heat at controlled temperatures and under a controlled environment. Thermo-lysis processes can be divided into pyrolysis (thermal cracking in an inert atmosphere), gasification (in the sub-stoichiometric presence of air usually leading to CO and CO_2 production) and hydrogenation (hydrocracking) (Ahrenfeldt, 2007).

There are two types of recycling: mechanical and chemical (Konarova, 2018). Mechanical recycling involves sorting, cleaning and shredding plastic to make pellets, which can then be fashioned into other products. This approach works very well if plastic wastes are sorted according to their chemical composition. In general, the collected plastic waste is shredded and dumped into a reactor. Post that, a catalyst is added and the plastic is heated at a temperature of 150 degrees. The gases emitted such as methane and propane as stored in a separate gas tank to be used as heating source for the machine to function. The oil obtained is filtered, stored and readied for dispatch. A tonne of plastic can approximately produce 600 to 650 liters of fuel, 20 to 25 per cent synthetic gases and 5 to 10 per cent of residual char, which can be used for road filler with bitumen (Graham, 2015). Conventional recycling methods such as sorting and grinding can recycle only 15–20% of total plastic waste (Khan and Kaneesamkandi, 2013; Siddiqui and Redhwi, 2009).



II. METHODOLOGY

Chemical recycling, in contrast, turns the plastic into an energy carrier or feedstock for fuels. There are two different processes by which this can be done: gasification and pyrolysis and catalytic degradation. The main difference is that they use less oxygen than traditional mass-burn incineration. The pyrolysis process thermally degrades waste in the absence of air (and oxygen). Gasification is a process in which materials are exposed to some oxygen, but not enough to allow combustion to occur.

1. Gasification or partial oxidation of plastic waste is commonly operated at high temperatures (>600°C - 800°C). Air (or oxygen in some applications) is used as a gasification agent, and the air factor is generally 20% - 40% of the amount of air needed for the combustion of the PSW. The process essentially oxidizes the hydrocarbon feed stock in a controlled fashion to generate the endothermic depolymerisation heat. The primary product is a gaseous mixture of carbon monoxide and hydrogen, with minor percentages of gaseous hydrocarbons (CH_4), tar and ash also formed. This gas mixture is known as syngas and can be used as a substitute for natural gas or in the chemical industry as feedstock for the production of numerous chemicals. For most of the PSW components, the ash and char production is limited (Brems, *et al.*, 2013). Co-gasification of biomass with polymers has also been shown to increase the amount of hydrogen produced while the CO content is reduced (Pinto, *et al.*, 2012).

Co-pyrogasification of plastics and biomass mixtures, as opposed to separately converting these waste streams, offers several advantages including an improvement in syngas quality and composition (H_2/CO ratio) in relation to the desired application, and an easier reactor feeding of plastics. Furthermore, many studies have shown that co-pyrogasification promotes the conversion of waste to gas rather than char and tar. However, in order to achieve the desired product distribution or syngas composition, operating parameters such as the reactor temperature, equivalence ratio (air or oxygen), steam/fuel ratio and catalyst, have to be optimized (Augustina, 2019).

Photoreforming. In this process the light-absorbing photo catalyst was added to plastic products, which absorbs sunlight and transforms it into chemical energy. The plastic and catalyst combination was then left in an alkaline solution exposed to sunlight, breaking down the material and producing bubbles of hydrogen gas in the process (Future Power Technology (2018).

Gasification Reaction

Solid-Gas Reactions

$C + \frac{1}{2}O_2 \longrightarrow CO$ (partial combustion) [exothermic]

$C + O_2 \longrightarrow CO_2$ (partial combustion) [exothermic]

$C + 2H_2 \longrightarrow CH_4$ (hydrogasification) [exothermic]

$C + H_2O \longrightarrow CO + H_2$ (Water Gas) [endothermic]

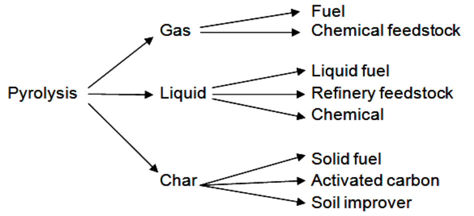
$C + CO_2 \longrightarrow 2CO$ (Boudouord) [endothermic]

Gas-Gas Reaction

$CO + H_2O \longrightarrow CO_2 + H_2$ (shift) [exothermic]

$CO + 3\,H_2 \longrightarrow CH4 + H_2O$ [exothermic]

2. Pyrolysis: Pyrolysis is a thermochemical decomposition using the mechanism of thermo-catalytic depolymerisation (Datta, 2017) of organic material at elevated temperature without the participation of oxygen to produce oil (Rehan, *et al*., 2017) char and gases at high temperatures via thermal decomposition (Chen, *et al*., 2014; Ouda *et al*., 2016; Anjum, *et al*., 2016). In this process long polymer molecules are broken down into shorter chains of hydrocarbons with the help of heat and pressure while inorganic material remains unchanged under the solid fraction (Lopez, *et al*., 2011). Thus, pyrolysis is also known as thermal cracking, thermolysis, depolymerization, molecular vibration, etc. The mechanism of degradation of polymers has generally been described as free radical in the case of a thermal process without catalyst. However, when catalysts are used, it is generally ionic mechanism (Miskolczi, and Nagy (2012).



Pyrolysis

Pyrolysis – The thermal degradation of organic waste in the absence of oxygen to produce a carbonaceous char, oil and combustible gases

Slow pyrolysis also called carbonization, is the slow heating of organic material in absence of oxygen (long isothermal holding time). Slow pyrolysis is emphasizes the solid charcoal as main product, instead of fast pyrolysis which emphasizes the liquid product. In some methods plastic waste pyrolyzed in a semi-batch reactor at a very low heating rate of 1°C min^{-1}.

Fast pyrolysis is a process in which organic materials are rapidly heated in a high-temperature range of 300–700°C in the absence of air at a faster heating rate of 10–200°C/s, with a short solid resistance time of 0.5–10 s and with fine particle size (<1 mm) feedstock. Under these conditions, organic vapors, pyrolysis gases and charcoal are produced. The vapors are condensed to bio-oil. Pyrolysis was carried out at temperatures between 500 and 700°C. This gave widely differing product yields of between 9.79 and 88.76% gas and between 18.44 and 57.11% oil. It was found that as temperature was increased the amount of aromatic compounds in the oil increased (Williams and Williams; 1998a). Typically, 60-75 wt.% of the feedstock is converted into oil (Bridgwater and Peacocke, 2000). In both conventional and fast pyrolysis, carbon conversion to gaseous and liquid products was more than 80%. Gas production was maximized in conventional pyrolysis (about 35% by weight of the initial ASR weight), while fast pyrolysis led to an oil yield higher than 55%. Higher heating values (HHV) of both conventional pyrolysis gas and fast pyrolysis oil increased from 8.8 to 25.07 MJ/N m^3 and from 28.8 and 36.27 MJ/kg with increasing pyrolysis temperature (Zolezzi, *et al*., 2004). Fast pyrolysis was preferred toward efficient conversion of waste plastics into gaseous products, consisting primarily of alkanes, alkenes, and aromatics. (Kannan, *et al*., 2014)

TABLE I. PYROLYSIS: TECHNOLOGIES

Technology	Residence time	Heating rate	Temp (^{0}C)	Major Products
Slow pyrolysis	Hours-days	very low	300 – 500	Charcoal
Conventional Pyrolysis	5 – 30 min			Char, liquids, syngas
	5 – 30 min	Medium	700 – 900	Char, syngas
Fast Pyrolysis	0.1 – 2 sec	High	400 – 650	Liquids
	< 1 sec	High	400 – 650	Liquids, syngas
	< 1 sec	Very High	400 – 650	syngas

Biomass can be converted to bio-oil by two main routes: flash pyrolysis and hydrothermal liquefaction (HTL).

Flash pyrolysis involves the rapid thermal decomposition of organic compounds in the absence of oxygen to produce liquids, gases, and char. Flash pyrolysis (sometimes called very *fast pyrolysis*), characterized by rapid heating rates (>1000°C/s) and high reaction temperatures (900–1300°C), has been shown to afford high yields of bio-oil with low resulting water content and conversion efficiencies of up to 70% (Li Lia, *et al*., 2013). The residence times used are even shorter than those of fast pyrolysis, typically less than 0.5 s. To obtain such high heating and heat transfer rates, biomass feedstock particle size must be as small as is practically possible, usually around 105–250 µm (60–140 mesh size) (Ponzio, *et al*., 2006) hydrothermal liquefaction (HTL).

Hydrothermal treatment, one of the effective methods, is proposed by Motoyuki Sugano, *et al*., (2009) for separation of MW into organic and inorganic substances. The steam-explosion process, based on the sudden decompression of the contents of a hydrothermal reactor down to atmospheric pressure, follows after a preliminary hydrothermal treatment. After this treatment, organic substances become a powder, so that separation of Municipal Waste (MW) into organic and inorganic substances becomes easy. Organic substances from MW mainly consist of plastics; however, waste paper and woody chips are also contained in this feedstock material. Therefore, oil production by liquefaction is considered to be a suitable means of utilizing the organic substances in MW. By means of this hydrothermal pretreatment, including the steam-explosion process, polystyrene and high-density polyethylene can be significantly converted to oil by liquefaction at 300°–400°C. In comparison with liquefaction of hydrothermally pretreated mixed waste (HMW) at 300°–400°C with a batch type reactor, the yield of oil increases significantly on liquefaction using a semi-batch type reactor. It is considered that the radical chain and termination reactions among the radicals from HMW were inhibited in the semi-batch type reactor. On liquefaction of HMW in a semi-batch reactor, the conversion of HMW to oil was enhanced on increasing the liquefaction temperature to 350°C and the holding time to 60 min.

Biodegradation method is considered as the most eco-friendly and cost-effective method of plastic degradation. The collection, isolation, screening, and molecular characterization of plastic (polythene) degrading bacteria from the rhizosphere soil of Avicennia marina from the 12 different ecogeographical sites along the West Coast of India. The results based on the tensile strength were only found reproducible. The most efficient plastic (polythene) degrading bacteria were characterized as Lysinibacillus fusiformis strain VASB14/WL and Bacillus cereus strain VASB1/TS based on 16S rRNA gene sequence homology (Shahnawaz, et al., 2019).

Supercritical water. Polypropylene (PP) can be converted into useful products i.e. oil using supercritical water at 380–500°C and 23 MPa over a reaction time of 0.5–6 h. Up to 91 wt% of model PP was converted into oil at 425°C with a 2–4 h reaction time or at 450°C with a 0.5–1 h reaction time. Higher reaction temperatures (>450°C) or longer reaction times (>4 h) led to more gas products. The oil products consisted of olefins, paraffins, cyclics, and aromatics. About 80–90 wt% of the oil components had the same boiling point range as naphtha (25–200°C) and heating values of 48–49 MJ/kg. This conversion process is net-energy positive and potentially has a higher energy efficiency and lower greenhouse gas emissions than incineration and mechanical recycling. The oil derived from PP has the potential to be used as gasoline blend stocks or feed stocks for other chemicals (Wan-Ting Chen, et al., 2019).

Cold plasma pyrolysis.

It is possible to convert all plastics directly into useful forms of energy and chemicals for industry, using a process called “cold plasma pyrolysis”. Pyrolysis is a method of heating, which decomposes organic materials at temperatures between 400°C and 650°C, in an environment with limited oxygen. The cold plasma, which is used to break chemical bonds, initiate and excite reactions, is generated from two electrodes separated by one or two insulating barriers.

Cold plasma is unique because it mainly produces hot (highly energetic) electrons, these particles are great for breaking down the chemical bonds of plastics. Electricity for generating the cold plasma could be sourced from renewables, with the chemical products derived from the process used as a form of energy storage: where the energy is kept in a different form to be used later.

The advantages of using cold plasma over conventional pyrolysis is that the process can be tightly controlled, making it easier to crack the chemical bonds in HDPE that effectively turn heavy hydrocarbons from plastics into lighter valuable products. This technique is used the plasma to convert plastics into other materials; hydrogen and methane for energy, or ethylene and hydrocarbons for polymers or other chemical processes. The reaction time with cold plasma takes seconds, which makes the process rapid and potentially cheap (Phan, 2018).

Separation is needed since plastics are made of different resin compound, transparency and color. Normally, pigmented or dyed plastics have lower market value. The conversion of plastics to valuable energy is possible as they are derived from petrochemical source, essentially having high calorific value. Hence, pyrolysis is one of the routes to waste minimization that has been gaining interest recently Pyrolysis was chosen by many researchers since the process able to produce high amount of liquid oil up to 80 wt% at moderate temperature around 500ºC (Fakhrhoseini and Dastanian, 2013)

The liquid oil produced can be used in multiple applications such as furnaces, boilers, turbines and diesel engines without the needs of upgrading or treatment Unlike recycling, pyrolysis does not cause water contamination and is considered as green technology when even the pyrolysis byproduct which is gaseous has substantial calorific value that it can be reused to compensate the overall energy requirement of the pyrolysis plant. Abnisa and Daud, (2014) that has been explored together with the main affecting parameters in plastic pyrolysis process that need an attention in order to maximize liquid oil production and enhance the oil quality. The main parameters include temperature, type of reactors, residence time, pressure, different catalysts usage and type of fluidizing gas with its flow rate.

Process parameters condition

Parameters play major role in optimizing the product yield and composition in any processes. Important pyrolysis parameters are heating rate, temperature, type of reactors, residence time, pressure, catalysts, type of fluidizing gas and its flow rate medium and time. The medium may be catalytic, inert, oxidative or reductive. In plastic pyrolysis, the key process parameters may influence the production of final end products such as liquid oil, gaseous and char.

III. PYROLYSIS

The pyrolysis can be carried out via thermal and catalytic routes (Almeida and Marques, (2016).

2.1 Thermal pyrolysis

The non-catalytic or thermal pyrolysis is an endothermic process that does not employ any catalyst. During the pyrolysis, the polymer materials are heated to high temperatures and thus, their macromolecules are broken into smaller molecules, resulting in the formation of wide range hydrocarbons. The thermal pyrolysis proceeds according to the radical chain reactions with hydrogen transfer steps and the gradual breakdown of the main chain. The mechanism involves the stages of initiation, propagation and / or free radical transfer followed by β chain scission and termination (Achilias, *et al.,* 2007; Marcilla, *et al*., 2009; Aguado, *et al*., (2006). This mechanism provides many oligomers by hydrogen transfer from the tertiary carbon atom along the polymer chain to the radical site (Park, *et al.,* 1999). The thermal cracking is more difficult for the high density polyethylene (HDPE), followed by the low density (LDPE) and then by polypropylene (PP) (Achilias, *et al.,* (2007). This is due to high content of tertiary carbons of PP. The initiation step comprises homolytic breaking of carbon-carbon bond, either by random chain scission as by cleavage at the end of the chain, resulting in two radicals. For PP and PE the chain scission occurs at random. This step is followed by hydrogen transfer reactions intra / intermolecular forming more stable radicals secondary. These intermediate radicals can be submitted to break the carbon-carbon bond by β scission to produce compounds saturated or with unsaturated terminal and new radicals. The transfer of intra / intermolecular hydrogen depends on the experimental conditions, the first of which leads to an increase in the production of olefins and diolefins, paraffins results in the second (Marcilla, *et al*., 2009; Achilias, *et al*., 2007; Lee, 2006).

All types of plastic waste show similar degradation behavior with the rapid loss of weight of hydrocarbons within the narrow range of temperature (150–250°C). The maximum degradation for each type of plastic waste was achieved within 420–490°C. PS and PP showed single step decomposition, while PE and PET showed two stage decomposition under controlled conditions. The single step decomposition corresponds to the presence of a carbon-carbon bond that promotes the random scission mechanism with the increase in temperature (Kim, *et al*., 2006). PP degradation started at a very low temperature (240°C) compared to other feed stocks. Half of the carbon present in the chain of PP consists of tertiary carbon, which promotes the formation of carbocation during its thermal degradation process (Jung, *et al*., 2010). This is probably the reason for achieving maximum PP degradation at a lower temperature. The PS initial degradation started at 330°C and maximum degradation was achieved at 470°C. PS has a cyclic structure, and its degradation under the thermal condition involves both random chain and end-chain scission, which enhances its degradation process (Demirbas, 2004; Lee, 2012). PE and PET showed a two-stage decomposition process. PEs initial degradation started at 270°C and propagated slowly but gradually until the temperature reached 385°C. After that temperature, a sharp degradation was observed, and 95% degradation was achieved with a further increase of around 100°C. A similar two-stage degradation pattern was observed for PET plastic and the initial degradation started at 400°C with a sharp decrease in weight loss. However, the second degradation started at a slightly higher temperature (550°C). The initial degradation of PE and PET may be due to the presence of some volatile impurities such as the additive filler used during plastic synthesis (Dimitrov, *et al*., 2013). PS degradation occurred at a lower temperature, compared to other plastics such as PE, due to its cyclic structure (Wu, *et al*., 2014).

Pyrolysis was carried out at temperatures between 500 and 700°C, thermal pyrolysis, where the whole process is temperature-dependent (Sadaf, *et al*., 2015; Tahir. *et al*., 2015). This gave widely differing product yields of between 9.79 and 88.76% gas and between 18.44 and 57.11% oil. The products obtained from the pyrolysis can be divided into non-condensable gas fraction, liquid fraction (consisting of paraffins, olefins, naphthenes and aromatics) and solid waste. From the liquid fraction can be recovered hydrocarbons in the gasoline range (C_4-C_{12}), diesel (C_{12}-C_{23}), kerosene (C_{10}-C_{18}) and motor oil (C_{23}-C_{40}) and high-value ones like benzene, toluene and xylene. (Mastral, *et al*., 2007; Arabiourrutia (2012); Achilias, *et al.,* (2007); Scheirs (2006) and Aguado, *et al*., (2006).

The termination reactions can occur, for example, by disproportionation, which can produce different olefins and alkanes or a combination of radicals can lead to the same products. Branched products can be formed from the interaction between two secondary radicals or between a secondary radical with a primary (Achilias, *et al*., 2007; Lee, 2006). Obtaining this wide range of products is one of the major drawbacks of this technique, which requires temperatures of 500°C to 900°C. These factors severely limit its applicability and increase the cost of recycling raw material of plastic waste (Lin, *et al*., 2010)

2.2 Catalysts

The thermal pyrolysis requires high temperatures due to the low thermal conductivity of polymers, which is not very selective and a possible solution to reduce these reaction conditions is the use of catalyzed pyrolysis. Catalysts have also been employed in the upgrading of pyrolysis products to improve the hydrocarbon distribution and yield similar properties to the conventional fuels such as diesel and gasoline (Sharuddin, *et al.,* 2016).

Catalytic pyrolysis is an alternative to the recycling of pure or mixed plastics waste (Achililas, *et al*., 2007). Moreover, the thermal pyrolysis of PE type plastics such as HDPE and LDPE along with PP are difficult to conduct due to their crossed chain hydrocarbon structures (Achilias *et al.*, 2007). Therefore, catalytic pyrolysis is being developed to overcome the problems of thermal pyrolysis (Lopez. *et al.*, 2011[a]). Over the past two decades, a large number of results on catalytic pyrolysis process for plastic have been reported. A wide range of catalysts such as ZnO, MgO, CaC_2, SiO_2, Al_2O_3, SiO_2–Al_2O_3, ZSM-5 (Si:Al ratio, 20) (Shah, *et al.*, 2010); $CaCO_3$, (Jan, *et al.*, 2013); zeolite, (Mastral, *et al.*, 2006; Miskolczi, *et al.*, 2009); kaolin, (Panda and Singh 2011; Kumar *and Singh,* 2011); red mud, (López, *et al.*, 2011; Adrados, *et al.*, 2012); $CuCO_3$, (Singh, *et al.*, 2018); and FCC, (Lee, *et al.*, 2002; Abbas-Abadi, *et al.*, 2014); Bentonite (SiO_2 46 wt%, Al_2O_3 17 wt%, Fe_2O_3 6 wt%, Na_2O 1.5 wt%, CaO 2.5 wt% and TiO_2 0.2 wt%) (Budsaereechai, *et al.*, 2019) have been used.

Catalyst speeds up chemical reaction at lower temperatures and shorter times but remains unchanged towards the end of the process. Efficiency of these catalysts depends both on its chemical and physical characteristics. These particular properties, promote the breaking of C-C bonds and determine the length of the chains of the products obtained (López, 2011; Serrano, *et al.*, 2012). When catalysts are utilized in the pyrolysis occurs two kinds of decomposition mechanisms simultaneously: thermal cracking, which in turn can follow different mechanisms (random chain scission, scission the end of the chain and / or elimination of side groups) and catalytic cracking (carbenium ions adsorbed on the catalyst surface, beta scission and desorption). As a result, a wide variety of products is generated, which in turn will react with each other resulting in a countless number of possible reaction mechanisms (Lopez, *et al.*, (2012).

Catalytic degradation is particularly interesting to obtain product of great commercial interest such as automotive fuel (diesel and gasoline) and C_2–C_4 olefins. For the pyrolysis of polyolefins, the degradation mechanism occurs by random chain scission, where free radicals are generated propagating chain reactions and thus resulting in the cracking of polymers in a wide range of hydrocarbons that make up liquid and gaseous fractions (Donaj, *et al.*, 2012). When catalyst is used, the activation energy of the process is lowered down, thus speeds up the rate of reaction. Therefore, catalyst reduces the optimum temperature required and this is very crucial since the pyrolysis process requires high energy (highly endothermic) that hinders its commercial application. The usage of catalyst may help in saving energy as heat is one of the most expensive costs in industry. Thermal pyrolysis produces low quality liquid oil and requires both a high temperature and retention time. In order to overcome these issues, catalytic pyrolysis of plastic waste has emerged with the use of a catalyst. It has the potential to convert 70–80% of plastic waste into liquid oil that has similar characteristics to conventional diesel fuel; such as the high heating value (HHV) of 38–45.86 MJ/kg, a density of 0.77–0.84 g/cm^3, a viscosity of 1.74–2.5 mm^2/s, a kinematic viscosity of 1.1–2.27 cSt, a pour point of (−9) to (−67)°C, a boiling point of 68–352°C, and a flash point of 26.1–48°C. Thus the liquid oil from catalytic pyrolysis is of higher quality and can be used in several energy-related applications such as electricity generation, transport fuel and heating source. Moreover, process by-products such as char has the potential to be used as an adsorbent material for the removal of heavy metals, pollutants and odor from waste water and polluted air, while the produced gases have the potential to be used as energy carriers. The produced liquid oil composition is affected by different types of feedstock and catalysts used in the pyrolysis process (Miandad, *et al.*, 2016[a,b,c]). The liquid oil produced from the catalytic pyrolysis of PE, when using both catalysts, produced mainly Naphthalene, Phenanthrene, Naphthalene, 2-ethenyl-, 1-Pentadecene, Anthracene, 2-methyl-, Hexadecane and so on. These results agree with several other studies (Lee, 2012; Miandad, *et al.*, 2019; Xue, *et al.*, 2017). The liquid oil produced from catalytic pyrolysis of PS with TA-NZ and AA-NZ, contains different kinds of compounds. Alpha-Methylstyrene, Benzene, 1,1′-(2-butene-1,4-diyl)bis-, Bibenzyl, Benzene, (1,3-propanediyl), Phenanthrene, 2-Phenylnaphthalene and so on were the major compounds found in the produced liquid oil. The liquid oil produced from catalytic pyrolysis of PS, with both activated catalysts, mainly contains aromatic hydrocarbons with some paraffins, naphthalene and olefin compounds (Rehan, *et al.*, 2017). However, in the presence of a catalyst, the maximum production of aromatic compounds was achieved (Xue, *et al.*, 2017).

The catalytic pyrolysis of PP produced a complex mixture of liquid oil containing aromatics, olefins and naphthalene compounds. Benzene, 1,1′-(2-butene-1,4-diyl)bis-, benzene, 1,1′-(1,3-propanediyl)bis-, anthracene, 9-methyl-, naphthalene, 2-phenyl-, 1,2,3,4-tetrahydro-1-phenyl-, naphthalene, phenanthrene etc. were the major compounds found in the liquid oil (Miandad, *et al.*, 2019). These findings are in line with other studies that carried out catalytic pyrolysis of PP with various catalysts (Marcilla, *et al.*, 2004). Furthermore, degradation of PP with AA-NZ resulted in the maximum production of phenol compounds. The higher production was perhaps due to the presence of high acidic sites, as it favors phenol compound production. Moreover, the presence of a high acidic site on catalysts enhanced the oligomerization, aromatization and deoxygenation mechanism that led to the production of poly-aromatic and naphthalene compounds. Dawood and Miura (2002) also reported the high production of these compounds from the catalytic pyrolysis of PP with a high acidic modified HY-zeolite. Miandad, *et al.*, (2016[b]) reported that feedstock composition also affects the quality and chemical composition of the oil. The produced liquid oil from catalytic pyrolysis of PE/PP contains aromatic, olefin, and naphthalene compounds. The major compounds found were; benzene, 1,1′-(1,3-propanediyl) bis-, mono(2-ethylhexyl) ester, 1,2-benzenedicarboxylic acid, anthracene, pentadecane, phenanthrene, 2-phenylnaphthalene etc. The catalytic pyrolysis of PS produced the highest liquid oil (70 and 60%) compared to PP (40 and 54%) and PE (40 and 42%), using the TA-NZ and AA-NZ catalysts, respectively. On the other hand, the catalytic pyrolysis of PS produced a higher amount of char (24.6%) with AA-NZ catalyst than with TA-NZ (15.8%) catalyst. Ma, *et al.,* (2017) also reported the high production of char from the catalytic pyrolysis of PS with an acidic zeolite (Hβ) catalyst. The high char production were due to the high acidity of the catalyst, which favors char production via intense secondary cross-linking reactions (Serrano, *et al.*, 2000). According to Kim, *et al.,* (2002) catalyst with low acidity and BET surface areas with microporous structures, favor the initial degradation of PP which may lead to the maximum production of gases. Obali, *et al.,* (2012) carried out pyrolysis of PP with an alumina-loaded catalyst and reported the maximum production of gas. Batool, *et al.,* (2016) also reported the maximum production of gas from catalytic pyrolysis of PE, with highly acidic ZSM-5 catalyst. Syamsiro, *et al.,* (2014) reported that catalytic pyrolysis of PP and PS with an acid (HCl) activated natural zeolite catalyst produced more gases than the process with a thermally activated natural zeolite catalyst, due to its high acidity and BET surface area. Various studies also reported the lower production of char from the catalytic pyrolysis of PE (Xue, *et al.*, 2017). Lopez, *et al.,* (2011) reported that catalysts with high acidity enhanced the cracking of polymers during the catalytic pyrolysis. The increase in cracking, in the presence of a high acidic catalyst, promotes the production of gases (Miandad, *et al.*, 2016[b], 2017)

Type of catalysts range of catalysts have been utilized, including Red Mud (Lopez,, *et al.*, 2011[a]), FCC (Lee, 2009), ZSM-5 (Lopez *et al.*, 2011[a]), HZSM-5 (Hernandez, *et al.*, 2007), Y-zeolite (Lee, 2012), Fe_2O_3 (Sarker and Rashid, 2013), Al_2O_3, $Ca(OH)_2$ (Sarker *et al.*,2011) and natural zeolite (Syamsiro, *et al.*, 2014), in catalytic pyrolysis to improve the quality of liquid oil (Wang and Wang, 2011). The catalysts increase the lighter fractions in the liquid oil such as gasoline (Lerici, *et al.*, 2015) and decrease the overall process energy-inputs (Lopez, *et al.*, 2011^a). For instance, the use of ZSM-5 catalyst decreased the impurities such as solid residue, sulphur, nitrogen, and phosphorous in the produced liquid oil (Miskolczi, *et al.,* 2009). It is also reported that the use of catalysts with a high BET surface area allows more contact between reactants and the catalyst surface, resulting in an increased rate of cracking reaction to produce more gases than liquid oil (Syamsiro, *et al.*, 2014).

There are two types of catalyst which are homogeneous (only one phase involve) and heterogeneous (involves more than one phase). Homogeneous catalyst used for polyolefin pyrolysis has mostly been classical Lewis acid such as $AlCl_3$ (Ivanova 1990; Stelmachowski 2010]. ($AlCl_3$, fused metal tetra-chloro aluminates ($M(AlCl_4)_n$), where the metal may be lithium, sodium, potassium, magnesium, calcium or barium and n can be 1 or 2 (Aguado, 2006). However, the most common type of catalyst used is heterogeneous since the fluid product mixture can be easily separated from the solid catalyst. Hence, heterogeneous catalyst is economically preferable because various catalysts are quite costly and their reuse is demanded. Heterogeneous catalyst can be classified as nano-crystalline zeolites, conventional acid solid, meso-structured catalyst, metal supported on carbon and basic oxides (Aguado *et al*., 2006). Some examples of nanocrystalline zeolites are HZSM-5 (microporoous), HUSY, Hb and HMOR which are extensively used in the researches of plastic pyrolysis. Besides, the non-zeolites catalysts such as silica–alumina, MCM-41(Si:AL ratio, 4; mesoporous) and silicate have also received much attention in current researches. Hence, the three types of catalysts that are widely used in plastic pyrolysis which are zeolites, FCC (Fluid Catalytic Cracking) and silica–alumina catalysts.

2.2.1. Zeolite catalyst: Zeolites are described as crystalline aluminosilicate sieves having open pores and ion exchange capabilities International Zeolite Association, 2005; Degnan, 2009. The structure is formed by three-dimensional framework where oxygen atoms link the tetrahedral sides. Each oxygen atom is shared by two silicon or aluminum atoms, thus giving rise to a three-dimensional microporous structure. (Manos, 2006; Tourinho, 2009). The pore size corresponding to two-dimensional opening zeolite is determined by the number of tetrahedral atoms connected in sequence. The three-dimensional interactions lead to the most different geometries, forming from large internal cavities to a series of channels crossing the whole zeolite. (Braga and Morgon, 2007). It is built by different ratio of SiO_2/Al_2O_3 depends on its type. Crystalline microporous structure (textural properties) favor hydrogen transfer reactions and thereby make them suitable for obtaining high conversions of gas at relatively low temperatures, between 350 and 500°C (Shah, *et al*., 2010; Park *et al*., 1999; Serrano *et al*., 2005; Mastral, *et al*., (2006) Miskolczi and Bartha 2008. The ratio of SiO_2/Al_2O_3 determines the zeolite reactivity which affects the final end product of pyrolysis. Artetxe *et al*., (2013) proven that the ratio of SiO_2/Al_2O_3 of the HZSM-5 zeolite highly affected the product fraction yield in HDPE pyrolysis. Low ratio of SiO_2/Al_2O_3 indicated the high acidity of the zeolite. The highest acidic catalyst ($SiO_2/Al_2O_3 = 30$) was more active in cracking waxes, thus producing higher light olefins and lower heavy fraction of C_{12}–C_{20} compared than the lowest acidic catalyst ($SiO_2/Al_2O_3 = 280$). The reduction of SiO_2/Al_2O_3 ratio from 280 to 30 improved the yield of light olefins from 35.5 to 58.0 wt % and decreased the yield of C_{12}–C_{20} from 28.0 to 5.3 wt%. Tae. *et al*., (2004) have investigated the performance of acid treated halloysite clays as catalysts in the degradation of polystyrene. The halloysites showed good catalytic activity for the degradation of polystyrene at 400-450°C with very high selectivity to aromatic liquids, i.e. styrene, ethylbenzene etc.

TABLE II. THERMAL VERSUS CATALYTIC PYROLYSIS.

Catalyst Used	**Amount Of Catalyst**	**Feedstock Used**	**Temp (°C)**	**Thermal Pyrolysis**			**Catalytic Pyrolysis**			**References**
				Liquid	***Gases***	***Char***	***Liquid***	***Gases***	***Char***	
ZSM-5	10%	PE, PP, PS, PET, PVC	450	79.3	17.7	3.0	56.9	40.4	3.2	Lopez, *et al*., (2012)
ZSM-5	10%	PE, PP, PS, PET, PVC	440	79.3	17.7	3.0	56.9	40.4	3.2	Lopez, *et al*., (2011)
Red Mud	10%	PE, PP, PS, PET, PVC	440	79.3	17.7	3.0	76.2	21.6	2.2	Lopez, *et al*., (2011)
ZSM-5	10%	PE PP, PS, PET, PVC,	500	65.2	34.0	0.8	39.8	58.4	1.8	Lopez, *et al*., (2011)
MCM-41, ZSM-5 (1:1)	2	HDPE	500	~80			83.15	25–30		Ratnasari, *et al*., (2017)
Red Mud	10%	PE, PP, PS, PET, PVC	500	65.2	34.0	0.8	57.0	41.3	1.7	Lopez, *et al*., (2011c)
Y-zeolite	50%	Municipal plastic waste	450	58	28	14	52	36	12	Syamsiro, *et al*., (2014)
Y-zeolite $MgCO_3$	0.1–0.2	HDPE	400–475	86–93%			29–84%			Kunwar , *et al*., (2016)
H–Y zeolite	0.5	PS, PP, LDPE, HDPE	500	Wax occur			42–71%			Lerici, *et al*., (2005)
CAT-2 zeolite	-	PP, LDPE, PP + LDPE	460	62–96%			51–68%			Anene, *et al*., (2018)
Natural Zeolite	50%	Municipal plastic waste	450	58	28	14	50	34	16	Syamsiro, *et al*., (2014)
Natural zeolite	0.1	PS,	450	80.8%)	13%)	6.2%)	54%	12.8	33.2	Miandad, *et al*., (2017)
		PP,					14	75.4	10.06	
		PE,					16	71.4	12.7	
		PS + PP,					50	39.8	10.2	
		PS + PE,					34	40.5	25.5	
		PE+PP					18	69.2	12.8	
		PS/PP/PE					38	40.5	21.4	
		PS/PP/PE/PET					22	630.2	17.8	
Synthetic zeolite		PS	450				50%	22.8	27.2	
		PP,					26	61.3	12.7	
		PE,					16	71.4	12.7	
		PS + PP,					40	43.5	16.5	
		PS + PE,					34	49.3	16.7	
		PE+PP					22	40.5	21.4	
		PS/PP/PE					60	25.8	14.2	
		PS/PP/PE/PET					56	26.5	17.4	
bentonite	.05-.2%	PS, PP, LDPE, HDPE	500 °C	85.6-89.5	-	-	86.6-90.5	-	-	Budsaereechai, *et al*., 2019
$CuCO_3$	0.02–0.09	HDPE	400–475	85%			90–94%			Singh, *et al*., (2008)
None		PS	350–550	-			7.11–84.8%			Abdullah, *et al*., (2018)

The catalytic decomposition of the polyethylene occurs at the carbenium ion mechanism. The initial step occurs either by abstraction of the hydride ion (for Lewis acid sites) or by addition of a proton (the Brønsted acid sites) in the C-C bonds of polyethylene molecules (Rizzarelli, *et al*., 2016) or by thermal decomposition of polyolefins. Successive scission of the main chain occurs to produce fragments having lower molecular weights than that of polyethylene. The resulting fragments are cracked or desidrocyclizados in subsequent steps (Park, *et al*., 1999). The acid sites on the catalyst surface are responsible for the initiation of the carbocationic mechanism, which induces the degradation of polyethylene and polypropylene.

As mentioned above, these acid sites are originated the generated load imbalance when AlO_4^- is incorporated in the structure of zeolites. The content of AlO_4^- determines the number of acid sites in the catalyst while topological factors related to its crystalline or amorphous structure influence the strength of these acidic centers. Textural characteristics control the access of molecules that are reacting in the catalytic sites. This accessibility is important in catalyzed reactions involving large molecules such as polymers (Aguado, *et al*., 2007; Hwang, *et al*., 2002).

Besides, the reduction of SiO_2/Al_2O_3 ratio in zeolite also raises the yield of light alkanes and aromatics. Table 3 compares the fuel properties of gasoline fraction obtained with three type of HZSM- 5 zeolite which having different ratio of SiO_2/Al_2O_3. As depicted, the highest acidity catalyst with the lowest ratio of SiO_2/Al_2O_3 led to a higher octane number with high content of aromatics and benzene, but lower concentration of olefins. Even though the octane number was lower and the olefins, aromatics and benzene standard exceeded the specification established by European Union (EU), the absence of sulfur in the gasoline composition made it possible to be blended with refinery stream to achieve the standard outlined by EU. Besides HZSM-5, some more examples of zeolite catalyst are HUSY and HMOR which are widely used in plastic catalytic pyrolysis. Garfoth, *et al*., (1998) investigated the efficiency of different zeolite catalysts to the HDPE pyrolysis which were HZSM-5, HUSY and HMOR with polymer to catalyst ratio of 40 wt%. In their studies, it was found that HZSM-5 had higher catalytic activity than HUSY and HMOR, referring to the very less residue left by HZSM-5 around 4.53 wt% while HUSY and HMOR were leaving about 7.07 wt% and 8.93 wt% residues behind, respectively. This shows that HZSM-5 able to maximize the total product conversion in plastic pyrolysis over other zeolites. In terms of product selectivity, different zeolites may have different product preferences. Marcilla, *et al*., (2008) studied the HZSM-5 and HUSY performance on HDPE and LDPE at constant temperature of 550ºC and 10 wt% polymer to catalyst ratio in a batch reactor.

Higher liquid oil was recovered when using HUSY catalyst (HDPE = 41.0 wt%, LDPE = 61.6 wt%) compared with HZSM-5 catalyst (HDPE = 17.3 wt%, LDPE = 18.3 wt%) Oppositely, higher gaseous product obtained when using HZSM-5 catalyst (HDPE = 72.6 wt%, LDPE = 70.7 wt%). This proves that different catalysts have different product selectivity. The same trend of product selectivity was also reported by Lin and Yen (2005) on PP pyrolysis using the HZSM-5 and HUSY zeolites. It is worth noting that the usage of zeolite catalyst in plastic pyrolysis only maximized the production of volatile hydrocarbon. As for higher efficiency and longer cycle time usage, HZSM was recommended since the deactivation rate of the catalyst was extremely low and thus, more efficient for regeneration.

Miandad, *et al.,* (2019) modified natural zeolite (NZ) (Saudi natural zeolite) by thermal activation (TA-NZ) at 550°C and acid activation (AA-NZ) with HNO_3, to enhance its catalytic properties and used for pyrolysis of different types of plastics wastes (PS, PE, PP, and PET) as single or mixed in different ratios. The catalytic pyrolysis of PS produced higher liquid oil (70 and 60%) than PP (40 and 54%) and PE (40 and 42%), using TA-NZ and AA-NZ catalysts, respectively. The TA-NZ and AA-NZ catalysts showed a different effect on the wt% of catalytic pyrolysis products and liquid oil chemical compositions, with AA-NZ showing higher catalytic activity than TA-NZ. FT-IR results showed clear peaks of aromatic compounds in all liquid oil samples with some peaks of alkanes that further confirmed the GC-MS results. The liquid oil has a high heating value (HHV) range of 41.7–44.2 MJ/kg, close to conventional diesel.

2.2.2. Bentonite (SiO_2 46 wt%, Al_2O_3 17 wt%, Fe_2O_3 6 wt%, Na_2O 1.5 wt%, CaO 2.5 wt% and TiO_2 0.2 wt%.; (Budsaereechai, *et al.,* 2019). Bentonite clays have a similar composition to SiO_2 and Al_2O_3 catalyst previously investigated as pyrolysis catalysts. Bentonite also had some compositional similarities to kaoline and red mud. The addition of binder-free bentonite clay pellets successfully yielded liquid based fuels with increased calorific values and lower viscosity for all plastic wastes. The advantages of the proposed pyrolysis system are that no char or wax is formed during the process. This is attributed to the acidic nature of the bentonite catalyst, which enabled the decomposition or cracking of waxes to lighter products. A higher amount of oil is produced from all plastic types. Catalytic oil produced from PS resulted in higher gasoline engine power, while catalytic oils from PP, LDPE and HDPE demonstrated similar values when compare with commercial fuels

TABLE III. COMPONENT IN LIQUID FRACTION OBTAINED FROM PYROLYSIS OF PLASTIC WASTES USING GC-MS

Plastic waste	**Component**	**%Area**			
		No catalyst		**Catalyst**	
		Aromatic	***Non-aromatic***	***Aromatic***	***Non-aromatic***
PS	C_5–C_9	60.22	0.44	61.80	1.74
	C_{10}–C_{13}	1.00	0.00	1.00	0.43
	$>C_{13}$	34.77	3.57	31.53	3.50
PP	C_5–C_9	6.26	18.65	10.94	21.45
	C_{10}–C_{13}	2.20	7.76	1.44	15.05
	$>C_{13}$	13.50	61.63	10.10	40.22
LDPE	C_5–C_9	3.45	8.49	3.59	14.05
	C_{10}–C_{13}	0.00	19.31	0.00	22.28
	$>C_{13}$	0.96	67.79	0.00	62.08
HDPE	C_5–C_9	2.52	13.79	3.12	14.72
	C_{10}–C_{13}	0.00	21.18	0.00	21.43
	$>C_{13}$	0.00	65.45	0.00	62.73
Diesel	C_5–C_9	2.1800		1.1500	
	C_{10}–C_{13}	0.6300		11.1700	
	$>C_{13}$	0.5000		84.3700	
Gasohol 91	C_5–C_9	43.2700		50.5200	
	C_{10}–C_{13}	1.0800		5.1300	
	$>C_{13}$	0.0000		0.0000	

TABLE IV. COMPARISON OF FTIR SPECTRA BETWEEN OIL FROM PLASTIC WASTES AND COMMERCIAL FUEL.

Type of plastic waste	**% Similarity with diesel**		**% Similarity with gasohol 91**	
	No catalyst	***Catalyst***	***No catalyst***	***Catalyst***
PS	17.90	20.75	63.20	66.35
PP	86.18	87.63	58.67	61.01
LDPE	96.89	96.08	56.78	62.80
HDPE	96.75	96.53	56.95	62.75

TABLE V. COMPARISON OF FUEL PROPERTIES OF GASOLINE FRACTION OBTAINED USING THREE TYPES OF HZSM-5 WITH DIFFERENT RATIO OF SIO_2 / AL_2O_3.

SiO_2 / AlO_3	**Octane number**	**Olefins (vol%)**	**Aromatics (vol%)**	**Benzene (vol%)**
30	94.1	33.1	43.3	42
80	86..9	61.2	13.5	1.3
230	85.9	68.9	6.9	0.46
Required	95	<18	<35	<1

2.2.3. FCC catalyst (fluid catalytic cracking). FCC catalyst is made of zeolite crystals and non-zeolite acid matrix known as silica–alumina with the binder (Degnan, 2000; Magee and Mitchell, 1993; Humphries and Wilcox 1989; Rajagopalan and Habib 1992) The main component of FCC catalyst for over 40 years is Zeolite-Y due to its high product selectivity and thermal stability (Marcilly, 2000). FCC catalyst is normally used in the petroleum refining industry to crack heavy oil fractions from crude petroleum into lighter and more desirable gasoline and liquid petroleum gas (LPG) fractions (Marcilly, 2000). Kyong, *et al.*, (2002) investigated the effect of spent FCC catalyst on the pyrolysis of HDPE, LDPE, PP and PS in stirred semi-batch reactor at 400°C. 20 g of catalyst was added into 200 g of reactants and heated up at rate of 7°C/min. As a result, all plastics produced more than 80 wt% liquid oil with PS being the highest (around 90 wt% liquid yield). The liquid yields based on the plastic types were arranged in this order: PS > PP > PE (HDPE, LDPE). The gaseous product yield had a reverse order with that of liquid in this following order: PE > PP > PS. This shows that PS was less cracked to the gaseous product since PS contained benzene ring that created more stable structure. Overall, it is concluded that spent FCC catalyst still has high catalytic performance with the liquid yield obtained above 80 wt% for all plastic samples. Additionally, it is more cost effective since it is a 'reused' catalyst. the usage of spent FCC catalyst in thermal pyrolysis increased the rate of reaction besides improving the overall product conversion. It was found that the best optimum ratio for higher conversion to liquid yield was at 20 wt% catalyst/ polymer ratio. The liquid product obtained was very high at 91.2 wt% with gaseous and coke around 4.1 wt% and 4.7 wt%, respectively. As the catalyst/polymer ratio was increased more than 20 wt%, more coke and gas were produced, thus liquid production was minimized (Kyong, *et al.*, (2003).

2.2.4. Silica–alumina catalyst. Silica–alumina catalyst is an amorphous acid catalyst that contains Bronsted acid sites with an ionizable hydrogen atom and Lewis acid site, an electron accepting sites. The acid concentration of silica alumina catalyst is determined by the mole ratio of SiO_2/Al_2O_3. Unlike zeolite, the acid strength of silica–alumina is determined oppositely in which the high ratio of SiO_2/Al_2O_3 indicates the high strength of acidity. For instance, SA-1 ($SiO_2/Al_2O_3 = 4.99$) has higher acidity than SA-2 ($SiO_2/ Al_2O_3 = 0.27$) and both of them are the commercial silica–alumina available in the market (Sakata, *et al.*, 1997). Different strength of acidity in catalyst has great influence in the final end product of plastic pyrolysis. Sakata, *et al.*, (1997) explored the effect of catalysts acidity (SA-1, SA-2, ZSM-5) on the product distribution of HDPE pyrolysis. The experiment was performed at 430°C in a semi-batch reactor where 1 g of catalyst was mixed with 10 g of HDPE. HDPE and LDPE pyrolysis each produced 77.4 wt% and 80.2 wt% respectively when SA-2 catalyst was used. HDPE structure was stronger than LDPE due to its linear chain, thus the lower amount of liquid yield obtained was expected. HDPE and LDPE pyrolysis each produced 77.4 wt% and 80.2 wt% respectively when SA-2 catalyst was used. HDPE structure was stronger than LDPE due to its linear chain, thus the lower amount of liquid yield obtained was expected. Luo, *et al.*, (2000) performed the HDPE and PP pyrolysis using silica–alumina catalyst at higher temperature of 500°C in fluidized bed reactor. The liquid oil obtained for HDPE was about 85.0 wt% while PP was around 90 wt% which was higher than the studies conducted by Sakata, *et al.*, (1999) and Uddin, *et al.*, (1996). This shows that temperature also plays an important role in maximizing the catalyst performance in order to increase the liquid oil production in plastic pyrolysis process. Thus, FCC is the best catalyst to optimize liquid oil production in plastic pyrolysis. FCC catalyst able to produce high liquid yield above 90 wt% for HDPE and PP pyrolysis while the highest product yield by silica–alumina for HDPE and PP was within the range of 85–87 wt% (Abadi, *et al.*, 2013; Abadi, *et al.*, 2014; Luo, *et al.*, (2000). This shows that these two catalysts were comparable in terms of the liquid oil production but FCC had better catalytic performance. Besides that, the spent FCC catalyst can also be used instead of fresh FCC that made it more economically attractive.

2.2.5. Ni–Mg–Al catalysts. Wu and Willium (2010) conducted gasification at of 800 or 850°C with or without a Ni–Mg–Al catalyst. The results showed that lower gas yield (11.2 wt.% related to the mass of plastic) was obtained for the non-catalytic non-steam pyrolysis–gasification of polystyrene at the gasification temperature of 800°C, compared with the polypropylene (59.6 wt.%) and high density polyethylene (53.5 wt.%) and waste plastic (45.5 wt.%). In addition, the largest oil product was observed for the non-catalytic pyrolysis–gasification of polystyrene. The presence of the Ni–Mg–Al catalyst greatly improved the steam pyrolysis gasification of plastics for hydrogen production. The steam catalytic pyrolysis gasification of polystyrene presented the lowest hydrogen production of 0.155 and 0.196 (g H_2/g polystyrene) at the gasification temperatures of 800 and 850°C, respectively. More coke was deposited on the catalyst for the pyrolysis gasification of polypropylene and waste plastic compared with steam catalytic pyrolysis gasification of polystyrene and high density polyethylene. Filamentous carbons were observed for the used Ni–Mg–Al catalysts from the pyrolysis gasification of polypropylene, high density polyethylene, waste plastic and mixed plastics. However, the formation of filamentous carbons on the coked catalyst from the pyrolysis gasification of polystyrene was low.

III. TEMPERATURE

Temperature is one of the most significant operating parameters in pyrolysis since it controls the cracking reaction of the polymer chain. Molecules are attracted together by Van der Waals force and this prevents the molecules from collapsed. When temperature in the system increases, the vibration of molecules inside the system will be greater and molecules tend to evaporate away from the surface of the object. This happens when the energy induced by Van der Waals force along the polymer chains is greater than the enthalpy of the C–C bond in the chain, resulted in the broken of carbon chain (Sobko, 2008.) In the PET pyrolysis study conducted by Cepeliogullar and Putun[b] (2013), they observed that the main PET degradation started at 400°C with a very small weight change occurred when the temperature was in the range of 200–400°C. The maximum weight loss of the substance happened at temperature of 427.7°C. No significant changes were observed at temperature more than 470°C. Therefore, it is, concluded that the thermal degradation of PET happened at temperature range of 350–520°C. As for the HDPE, Chin, *et al*., (2004) reported the thermal degradation started at 378–404°C and was almost completed at 517– 539°C based on the thermogravimetry analysis (TG) at different heating rates in the range of 10–50°C/min. Higher heating rates speeds up the weight loss, thus increases the rate of reaction. In another thermal behavior study carried out by Marcilla, *et al*., (2005), they found that the maximum degradation rate of HDPE occurred at 467°C. This important temperature needs to put into consideration when running the pyrolysis experiment to ensure the most optimum liquid yield.

In LDPE pyrolysis, Marcilla, *et al*., (2009) observed that small amount of liquid oil formation started at temperature of 360– 385°C. The maximum liquid yield was collected at 469–494°C. Onwudili, *et al*., (2009) observed that the oil conversion of LDPE started at 410°C. A brown waxy material formed at temperature below than 410°C indicated the incomplete conversion of oil. They concluded that the most optimum temperature to obtain the highest liquid was at 425°C for LDPE. In another study done by Marcilla, *et al*., (2009), they concluded that the most optimum temperature to obtain high liquid oil was at 550°C. Further increase in temperature to 600°C only reduced the liquid yield obtained (Williams and Williams,1998[a]). Hence, it can be summarized that the LDPE thermal degradation occurred at temperature range of 360–550°C. PP had lower thermal degradation temperature if compared to HDPE. According to Jung, *et al*., (2010) who studied the effect of temperature on HDPE and PP pyrolysis in a fluidized bed reactor, they found that the main decomposition of HDPE and PP happened within the range of 400–500°C based on derivative thermogravimetry analysis (DTG) curves. However, it was observed that the weight loss of PP fraction started to occur at lower temperature below 400°C in comparison to the HDPE fraction. Marcilla, *et al*., (2005) discovered that the maximum degradation temperature for PP was 447°C while HDPE was 467°C where the major weight loss happened. Theoretically, PP degraded faster than HDPE since half of the carbon in PP chain is tertiary carbon; consequently ease the formation of tertiary carbocation during the pyrolysis (Jung, *et al.,* (2010). Among all plastics, PS degraded at the lowest temperature during pyrolysis process. Onwudili, *et al*., (2009) have investigated the PS pyrolysis in a batch reactor. From their studies, they found that no reaction seems to take place at 300°C. However, they found that PS degraded completely into highly viscous dark-colored oil at lower temperature of 350°C. The highest liquid oil was achieved at 425°C. The increase of temperature to 581°C only reduced the liquid oil production and increased gaseous product (Demirbas 2004). Thus, it is worth noting that the thermal degradation temperature of PS would be in the range of 350–500°C approximately. Miadad, *et al.,* (2016) found that PS in batch reactor at 400°C with a reaction time of 75 min, the gas yield was 8% by mass; the char yield was 16% by mass, while the liquid oil yield was 76% by mass. Raising the temperature to 450°C increased the gas production to 13% by mass, reduced the char production to 6.2% and increased the liquid oil yield to 80.8% by mass. The optimum temperature and reaction time was found to be 450°C and 75 min. Therefore, it was proven that the temperature has the greatest impact on reaction rate that may influence product composition of liquid, gaseous and char for all plastics from the previous discussion. The operating temperature required relies strongly on the product preference. If gaseous or char product was preferred, higher temperature more than 500°C was suggested. If liquid was preferred instead, lower temperature in the range of 300–500°C was recommended and this condition is applicable for all plastics.

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IV. TYPE OF REACTORS

The type of reactors has an important impact in the mixing of the plastics and catalysts, residence time, heat transfer and efficiency of the reaction towards achieving the final desired product. Most plastic pyrolysis in the lab scale were performed in batch, semi-batch or continuous-flow reactors such as fluidized bed, fixed-bed reactor and conical spouted bed reactor (CSBR).

The feasibility of catalytic and non-catalytic pyrolytic conversion of low value post-consumer high density polyethylene (HPDE) plastic into crude oil and subsequent distillation was explored (Kunwar, *et al.*, 2016). Translation of optimized conditions for catalytic and non-catalytic pyrolysis from TGA to a bench-scale system was validated using another kind of plastic (HDPE). The properties of the plastic crude (PC) oil and residue were studied for boiling point distribution; molecular weight distribution; elemental composition; and thermal degradation. The plastic crude oils had properties similar to conventional crude oil. The resulting PC oils were distilled into motor gasoline, diesel #1, diesel #2, and vacuum gas oil fractions.

TABLE VI. PYROLYSIS REACTORS

Reactor type	**Heating methods**	**Heating rate**
Fluidised Bed	Heated recycle	High
	Fire tubes	Moderate
Entrained flow	Recycles hot sand	High
Fixed bed	Heated recycle gas	Low
Rotary kiln	Wall heating	low

An increase in gasoline and diesel-range fractions was observed with Y-zeolite and $MgCO_3$ catalysts, respectively. Diesel and vacuum gas oil fractions were the major products in the absence of catalyst. The distillate fraction was characterized for fuel properties, elemental composition, boiling point, and molecular weight distribution. The fuel properties of the diesel-range distillate (diesel fraction) were comparable to those of ultra-low sulfur diesel (ULSD) fuel. Market demand, growth, and value of end products will dictate which process, non-catalytic or catalytic (Y-Zeolite/$MgCO_3$) is best suited for providing the product portfolio for a particular scenario.

Details of each type reactors are given as:

4.1. Batch and semi-batch reactor

Batch reactor is basically a closed system with no inflow or outflow of reactants or products while the reaction is being carried out. In contrast, a semi-batch reactor allows reactant addition and product removal at the same time. Pyrolysis in batch reactor or semi-batch reactor normally performed at temperature range of 300–800^{o}C for both thermal and catalytic pyrolysis. In catalytic pyrolysis, the catalyst was mixed together with the plastic sample inside the batch reactor. The drawback of this process would be a high tendency of coke formation on the surface of the catalyst which reduced the catalyst efficiency over time and caused high residue in the process. Besides that, it was also a challenge to separate the residue from the catalyst at the end of the experiment. Sakata, *et al.*, (1999) used batch reactor to study the pyrolysis of PP and HDPE at 380^{o}C and 430^{o}C, accordingly using various catalysts and also without catalyst. It was found that the liquid oil obtained from catalytic pyrolysis was even lower than the thermal pyrolysis for some catalysts. The liquid yield from PP in thermal pyrolysis was 80.1 wt% and from HDPE was 69.3 wt%. With the usage of several catalysts such as silica–alumina (SA-1) and HZSM-5, the liquid yield for both PP and HDPE reduced to 47– 78 wt% and 49.8–67.8 wt% respectively. However, the usage of certain catalysts such as silica–alumina (SA-2) and mesoporous silica catalysts (FSM) improved the liquid yield for both plastics slightly than the thermal pyrolysis with a very small increase of around 1.0–7.0 wt%. Therefore, different catalysts might have different reactivity to the plastic type. However, it has to be noted that the tendency of the coke formation on the catalyst surface also might be one of the reasons that degraded the effectiveness of the catalyst used in batch reactor over time. Nevertheless, the direct contact of the catalyst with the plastics in some cases may also improve the liquid yield. Abadi, *et al.* (2014) conducted the PP pyrolysis in semi-batch reactor using FCC catalyst at 450^{o}C. From the experiment, they found that very high liquid yield of 92.3 wt% was obtained. Some of the batch and semibatch reactors were also equipped with stirrer that running at different speed depends on the required. Seo, *et al.* (2003) studied the pyrolysis of HDPE using batch reactor equipped with stirrer at 450^{o}C. The stirrer speed was 200 RPM. Higher liquid oil was obtained than in thermal pyrolysis which was around 84.0 wt%. Besides that, the amount of liquid product obtained through catalytic pyrolysis using similar catalyst of silica–alumina was also higher than which was 78 wt% while obtained 74.3 wt%. Therefore, it was clearly seen that the stirrer in the batch reactor (Sakata, *et al.*,1999).

Thermal pyrolysis of plastic waste using fluidized bed reactors conducted (Reddy, *et al.*, 2012). Although works on pyrolysis are reported in fixed beds, autoclaves, and fluidized beds, vast majority of them address to the utilization of fluidized bed due to their advantages and large scale adaptability. The pyrolysis temperature and the residence time are reported to have major influence on the product distribution, with the increase in pyrolysis temperature favoring gas production, with significant reduction in the wax and oil. The pyrolysis gas generally contains H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6 while liquid product comprises benzene, toluene, xylene, styrene, light oil, heavy oil, and gasoline with the variations depending on process conditions.

4.2. Fixed and fluidized bed reactor

In fixed-bed reactor, the catalyst is usually in palletized form and packed in a static bed. In certain conditions, the fixed-bed reactors are merely used as the secondary pyrolysis reactor because the product from primary pyrolysis can be easily fed into the fixed-bed reactor which generally consists of liquid and gaseous phase (Fogler 2010). On the other hand, fluidized bed reactor solves some of the problems occur in fixed-bed reactor. In contrast to fixed-bed reactor, the catalyst in fluidized bed reactor sits on a distributer plate where the fluidizing gas passes through it and the particles are carried in a fluid state. Therefore, there is better access to the catalyst since the catalyst is well-mixed with the fluid and thus provides larger surface area for the reaction to occur (Kaminsky and Kim,1999). This reduces the variability of the process conditions with good heat transfer. Besides, it is also more flexible than the batch reactor since frequent feedstock charging can be avoided and the process does not need to resume often. Elordi, *et al*., (2007) used CSBR to conduct HDPE pyrolysis with HY zeolite catalyst at 500°C that resulted in 68.7 wt% gasoline fraction (C_5–C_{10}). The gasoline had an octane number of RON 96.5 which was closed with the standard gasoline quality. On the other hand, Arabiourrutia, *et al*., (2012) explored the waxes yield and characterization from HDPE, LDPE and PP pyrolysis at 450–600°C using the CSBR. According to them, CSBR had the versatility of handling sticky solid that was hard to handle in fluidized bed reactor. The spouted bed design was particularly suitable for low temperature pyrolysis to obtain wax. The authors observed that the amount of waxes yield decreased with the temperature. At higher temperature, more waxes are cracked into liquid or gaseous product. HDPE and LDPE waxes production were very similar around 80 wt% while PP produced higher waxes at lower temperature about 92 wt%.

4.3. Microwave-assisted technology

In this process, a highly microwave absorbent material such as particulate carbon is mixed with the waste materials. The microwave absorbent absorbs microwave energy to create adequate thermal energy in order to achieve the temperatures required for extensive pyrolysis to occur (Lam and Chase, 2012). Microwave radiation offers several advantages over the conventional pyrolysis method such as rapid heating, increased production speed and lower production costs. Unlike conventional methods, microwave energy is supplied directly to the material through the molecular interaction with the electromagnetic field, thus no time is wasted to heat up the surrounding area (Fernandez, *et al*., 2011). The efficiency of microwave heating depends heavily on the dielectric properties of the material. For instance, plastics have low dielectric constant and the mixture with carbon as the microwave absorber during pyrolysis may improve the energy absorbed to be converted into heat in shorter time (Lam and Chase, 2012). In other study, Ludlow-Palafox and Chase (2001) have conducted a microwave induced pyrolysis on two different materials: HDPE pallets and toothpaste packaging which was in combination of aluminum and polyethylene laminates. Carbon was used as the microwave absorber with 5 kW microwave power. This experiment was quite different from others since a quartz vessel reactor with 180 cm in diameter, equipped with 6 RPM impeller was placed inside the microwave. The product yield resulted from HDPE pyrolysis was recorded at temperature of 500–600°C. Liquid oil collected was around 79–81 wt%, gaseous 19–21 wt% and 0 wt% of solid residue formed. In fact, the aluminum did not influence the product yield since it was easily separated by sieving and be seen as a shiny clean surface. During the experiment, they observed a compound known as titanium dioxide which appeared as white powder adhered to the reactor side wall. Titanium oxide clearly presented in the painted surface of the toothpaste tube. This shows that this substance had no influence in the pyrolysis product since it was separated from the organic content of the laminate during pyrolysis.

Microwave assisted co-pyrolysis of mixtures of cellulose, paraffin oil, kitchen waste and garden waste that closely mimic municipal solid wastes (MSW) is conducted at different reaction conditions. Experiments were conducted in a multimode microwave reactor using ten different microwave absorbing materials (or susceptors) such as aluminium, activated carbon, garnet, iron, silica beads, cement, SiO_2, TiO_2, fly ash and graphite. Pyrolysis was conducted up to 600°C. The bio-oil contained oxygenated compounds (furans, phenolics, cyclo-oxygenates), aliphatic and aromatic hydrocarbons (mono and polycyclics). Aromatic hydrocarbons were the key products of interaction among the model components. Highest bio-oil yield of 53 wt% was achieved with an equal composition mixture at 1:1 wt/wt of MSW : graphite. High selectivities of monoaromatics such as benzene, toluene, xylene and styrene, and C_8–C_{20} aliphatic hydrocarbons, and low selectivity of polycyclic aromatics were obtained with a majority of the susceptor–MSW combinations. Methane, ethylene, propylene, isobutylene and hydrogen were the major gaseous products (Suriapparao and Vinu, 2015). Polystyrene was rapidly pyrolyzed under microwave while placing in a batch type reactor containing a cylindrical mesh of iron. The iron mesh generates heat in the range of 1100–1200°C which converts polystyrene into 80% liquid, 15% gas and 5% char residue. The liquid product was analyzed using GC/MS and found that it contains styrene in addition to polycyclic aromatics and condensed ring aromatic compounds (Husain, *et al*., (2010).

V. PRESSURE AND RESIDENCE TIME

The effect of pressure to the HDPE pyrolysis product was studied by Murata, *et al*., (2004) in a continuous stirred tank reactor at elevated temperature of 0.1–0.8 MPa. Based on the studies, they discovered that the gaseous product increased tremendously from around 6 wt% to 13 wt% at 410°C but only a small increase from 4 wt% to 6 wt% at 440°C as the pressure went up from 0.1 to 0.8 MPa. This shows that pressure had high influence to the gaseous product at higher temperature. Pressure also affected the carbon number distribution of the liquid product by shifting to the lower molecular weight side when it was high. Besides, pressure also had a significant effect on the rate of double bond formation. As reported by Murata, *et al*. (2004), the rate of double bond formation decreased when pressure increased and this suggested that pressure directly affected the scission rate of C–C links in polymer. They also discovered that pressure had greater impact on residence time at lower temperature. However, as the temperature increased more than 430°C, the effect of pressure to the residence time became less apparent.

Residence time can be defined as average amount of time that the particle spends in the reactor and it may influence product distribution (Mastral, *et al.*, 2001). Longer residence time increases the conversion of primary product, thus more thermal stable product is yielded such as light molecular weight hydrocarbons and non-condensable gas (Ludlow-Palafox and Chase, 2001) the residence time has not much effect on the product distribution. Mastral, *et al.* (2003) studied the effect of residence time and temperature on product distribution of HDPE thermal cracking in fluidized bed reactor. It was found that higher liquid yield obtained at longer residence time (2.57s) when the temperature was not more than 685°C. However, the residence time had less influence on the liquid and gaseous yield at higher temperature above 685°C. Therefore, it was concluded that pressure and residence time are both temperature dependence factors that may have potential influence on product distribution of the plastic pyrolysis at lower temperature. Higher pressure increased the gaseous product yield and affected the molecular weight distribution for both liquid and gaseous products but only apparent at high temperatures.

VI. TYPE AND RATE OF FLUIDIZING GAS

Fluidizing gas is an inert gas (also known as carrier gas) which only engaged in transportation of vaporized products without taking part in the pyrolysis. There are many types of fluidizing gas that can be used for the plastic pyrolysis such as nitrogen, helium, argon, ethylene, propylene and hydrogen. Each type of fluidizing gas has different reactivity based on its molecular weight. Abadi, *et al.*, (2014) reported that the molecular size of the carrier gas helped in determining the product composition and also dependent on the temperature. The lighter gas able to produced high amount of condensed product which was liquid oil. H_2 produced the highest liquid yield of 96.7 wt% while without any carrier gas only 33.8 wt% liquid was yielded. This proves the importance of carrier gas in enhancing the product yield in pyrolysis process. Besides that, it was also observed that the reactivity of the carrier gas influenced the coke formation. H_2 coke yield was very minimal which was about 0.3 wt%, followed by ethylene, helium and propylene. Ethylene and nitrogen were having the same molecular weight.

However, ethylene seems to produce higher amount of liquid yield and lower coke formation than nitrogen. This is because ethylene is more reactive than nitrogen that it could shift the equilibrium to produce more liquid yield (Abadi, *et al.*, 2014). Nitrogen was commonly used by most researchers as fluidizing gas in plastic pyrolysis since it was easier and safer to handle than the high reactivity gas like hydrogen and propylene due to their flammability hazard. Helium able to produce high liquid yield after hydrogen, it was rarely used since the availability was limited and more expensive than nitrogen. Besides type of fluidizing gas, the fluidizing flow rate also may influence the final product distribution. Lin and Yen (2005) investigated the effect of different fluidizing gas rate on product distribution of PP pyrolysis over HUSY catalyst at 360°C. They found that the rate of degradation dropped instantly at the lowest fluidizing flow rate of 300 ml/min. The contact time for primary product is high at lower flow rate, causing the formation of coke precursor (BTX) to increase with the secondary product obtained even though the overall degradation rate is slower (Lin and Yen, 2007). This was indicated by the high residue left when lower fluidizing flow rate was applied. The gasoline and hydrocarbon gases fraction were also maximized at the highest fluidizing flow rate of 900 ml/min. Hence, the type and rate of fluidizing gas are also very important in plastic pyrolysis.

TABLE VII. THE EFFECT OF CARRIER GAS ON THE PRODUCT YIELD AND THE CONDENSED PRODUCT COMPOSITION (ABADI, *ET AL.*, 2014)

Carrier gas	**Molecular Weight**	**Condensed product yield (%)**	**Non- condensable product yield (%)**	**Coke yield (%)**	**Olefins (%)**	**Paraffins (%)**	**Naphthenes (%)**	**Aromatic (%)**	**Olefin/ Paraffins Ratio**
H_2	2	96.7	3	0.3	30.85	46.53	20.54	2.07	0.66
He	4	94.7	3.2	2.1	43.32	33.41	19.29	3.98	1.3
N_2	28	92.3	4.1	3.6	44.53	32.87	17.23	5.27	1.36
Ethylene	28	93.8	5.1	1.1	41.76	34.76	19.75	3.73	1.2
Propylene	42	87.8	9.7	2.5	42.36	31.85	20.92	4.87	1.33
Air	37	84.8	9.8	5.4	45.21	25.27	21.93	7.59	1.78
No carrier gas	51.3	33.5	14.9	n.d.*	n.d.	n.d.	n.d.	n.d.	n.d.

T: 450°C, stirrer rate; 50 r min^{-1}; catalyst/pp ≠ 1
* not determined
n.d., not available in the literature.
a. Viscosity at 40°C.
b. Viscosity at 30°C.
c. Viscosity at 25°C.
d. Viscosity at 50°C.

VII. PROXIMATE ANALYSIS FOR PYROLYSIS OF PLASTICS

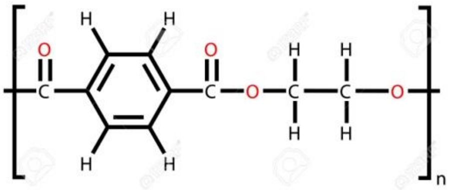
Fundamentally, different types of plastics have different compositions that normally reported in terms of their proximate analysis. Proximate analysis can be defined as a technique to measure the chemical properties of the plastic compound based on four particular elements which are moisture content, fixed carbon, volatile matter and ash content (Kreith,1998).

Volatile matter and ash content are the major factors that influence the liquid oil yield in pyrolysis process. High volatile matter favored the liquid oil production while high ash content decreased the amount of liquid oil, consequently increased the gaseous yield and char formation based on very high while the ash content is considered low. These characteristics indicate that plastics have high potential to produce large amount of liquid oil through pyrolysis process. Since the results of plastics proximate analysis are very convincing, the following discussion would focus more on the process parameters involved during the pyrolysis process that would have major influence in the liquid production. Based on Table 8, it was observed that the volatile matter for all plastics is very high while the ash content is considered low. These characteristics indicate that plastics have high potential to produce large amount of liquid oil through pyrolysis process. Since the results of plastics proximate analysis are very convincing, the following discussion would focus more on the process parameters involved during the pyrolysis process that would have major influence in the liquid production.

TABLE VIII. PROXIMATE ANALYSIS OF PLASTICS(ABNISA, *ET AL.,* 2014)

Type of plastics	**Moisture (wt%)**	**Fixed carbon (wt%)**	**Volatile (wt%)**	**Ash (wt%)**	**References**
Polyethylene terephthalate (PET)	0.46	7.77	91.75	0.02	Zannikos, *et al*., 2013
	0.61	13.17	86.83	0.00	Heikkinen, *et al*., 2004
High-density polyethylene	0.00	0.01	99.81	0.18	Ahmad, *et al*., 2013
	0.00	0.03	98.57	1.40	Hordijk, *et al*., 2004
Polyvinyl chloride (PVC)	0.80	6.30	93.70	0.00	Hong, *et al*., 1999
	0.74	5.19	94.82	0.00	Hordijk, *et al*., 2004
Low-density polyethylene	0.30	0.00	99.70	0.00	Park, *et al*., 2012
	-	-	99.60	0.40	Aboulkas, *et al*., 2010
Polypropylene	0.15	1.22	95.08	3.55	Jung, *et al*., (2010)
	0.18	0.16	97.85	1.99	Hordijk, *et al*., 2004
Polystyrene	0.25	0.12	99.63	0.00	Abnisa, *et al*. 2014
	0.30	0.20	99.50	0.00	Park, *et al*., 2012
Polyethylene (PE)	0.10	0.04	98.87	0.99	Jung, *et al*. 2010;
Acrylonitrile butadiene styrene (ABS)	0.00	1.12	97.88	1.01	Othman, *et al*., 2008.
Polyamide (PA) or Nylons	0.00	0.69	99.78	0.00	Othman, *et al*. 2008.
Polybutylene terephthalate (PBT)	0.16	2.88	97.12	0.00	Hordijk, *et al*., 2004

7.1. Polyethylene terephthalate (PET) ($(C_{108}O_4)$n)



2. PET has become the great choice for plastic packaging for various food products, mainly beverages such as mineral water, soft drink bottle and fruit juice containers. This is due to its intrinsic properties that are very suitable for large-capacity, lightweight and pressure-resistant containers. Other applications of PET include electrical insulation, printing sheets, magnetic tapes, Xrayand other photographic film (Çepeliog˘ullar and Pütün, 2013)[a]. The extensive applications of PET would cause an accumulation of PET waste in the landfill. Recycling PET waste was the current practice of handling accumulated plastic waste. However, the bulkiness of the containers causes high frequency of collections and therefore, increases the transport costs. To ease the recycling process, the PET waste needs to be sorted into different grades and colors that make its recovery inefficient and uneconomical. Hence, other alternative for PET recovery such as pyrolysis process has been explored and the product yield was analyzed by several researchers (Cepeliogullar and Putun, 2013)[b] have explored the potential of PET in pyrolysis process to produce liquid oil using fixed-bed reactor at 500°C. The heating rate was 10°C/min and nitrogen gas was used as the sweeping gas in this experiment. It was observed that the liquid oil yield was lesser than the gaseous product. The liquid oil obtained was 23.1 wt% while the gaseous product was 76.9 wt % with no solid residue left. The low liquid yield could be explained through the proximate analysis based on Table 8, showing the relatively low volatile content of PET around 86.83% in comparison with other plastics in which the volatile contents were all above 90%. Unfortunately, almost half of the oil composition contained benzoic acid which was around 49.93% based on the gas chromatography–mass spectroscopy (GC–MS) analysis. The acidic characteristic in pyrolysis oil was unfavorable due to its corrosiveness that deteriorated the fuel quality (Cepeliogullar and Putun, 2013)[b]. Besides that, benzoic acid was a general sublime that could clog piping and heat exchanger, thus need a serious attention if running in industrial scale (Wan, 2015; Shioya, *et al*., 2005)

On the other hand, Fakhrhoseini and Dastanian (2013) found slightly higher liquid oil yield at the same operating temperature and heating rate. The liquid yield obtained was 39.89 wt%, gaseous was 52.13 wt% and solid residue was 8.98 wt%. Therefore, it can be concluded that the liquid oil production from the PET pyrolysis obtained in the ranges of 23–40 wt% while gaseous yield in the ranges of 52–77 wt%. Based on these results, PET might be the most suitable plastic to be used in pyrolysis if gaseous product became a preference, for instance to provide energy supply to heat up the reactor at the desired temperature.

7.2 High-density polyethylene (HDPE). HDPE $(C_2H_4)n$ is characterized as a long linear polymer chain with high degree of crystallinity and low branching which leads to high strength properties. Due to its high strength properties, HDPE is widely used in manufacturing of milk bottles, detergent bottles, oil containers, toys and more. Ahmad, *et al*. (2014) explored the pyrolysis study of HDPE using micro steel reactor. The pyrolysis temperatures were within 300–400ºC at heating rate of 5–10ºC/min. Nitrogen gas was used as the fluidizing medium. From the experiment, they found that the highest total conversion happened to be at 350ºC with liquid was the dominant product yield (80.88 wt%). The solid residue was very high at 300ºC (33.05 wt%) but the amount was reducing to 0.54 wt% at the highest temperature of 400ºC.

Kumar and Singh (2011) have done the thermal pyrolysis study of HDPE using semi-batch reactor at higher temperature range of 400–550ºC. It was observed that the highest liquid yield (79.08 wt%) and gaseous product (24.75 wt%) obtained at temperature of 550ºC while wax started to dominate in product fraction at higher temperature of 500–550ºC. The dark brownish oil obtained from the pyrolysis had no visible residue and the boiling point was from 82 to 352ºC. This suggested the mixture of different oil component such as gasoline, kerosene and diesel in the oil that matched the properties of conventional fuel as shown in Table 9. Besides, the sulfur content in the HDPE pyrolytic oil was very low (0.019%) that made it cleaner to the environment.

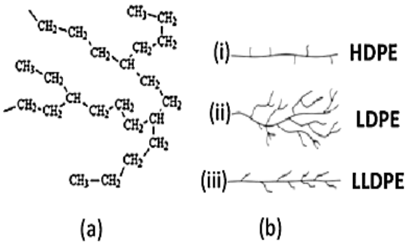
Besides that, Marcilla, *et al.,* (2009) have also studied the HDPE pyrolysis at 550ºC using batch reactor. The liquid oil yield was 84.7 wt% and gaseous product around 16.3 wt%. This, results proven that higher liquid oil could be obtained at higher temperature but there was also a limitation that should be noted. Too high temperature would reduce the liquid oil yield and increased the gaseous product since the process had passed the maximum thermal degradation point. Mastral *et al*., (2001) conducted the HDPE pyrolysis in a fluidized bed reactor at 650ºC and they found that the liquid oil production was around 68.5 wt% and 31.5 wt% gaseous product. This shows that the liquid was cracked to gaseous when further heated up at a very high temperature above 550ºC. Sharma, *et al*., (2014) Pyrolysed HDPE grocery bags followed by distillation resulted in a liquid hydrocarbon mixture with average structure consisting of saturated aliphatic paraffinic hydrogens (96.8%), aliphatic olefinic hydrogens (2.6%) and aromatic hydrogens (0.6%) that corresponded to the boiling range of conventional petroleum diesel fuel (#1 diesel 190–290 °C and #2 diesel 290–340°C). Saturated aliphatic paraffins comprised most of the fuel composition (96.8%). No oxygenated species such as carboxylic acids, aldehydes, ethers, ketones, or alcohols were detected. Comparison of the fuel properties to the petrodiesel fuel standards ASTM D975 and EN 590 revealed that the synthetic product was within all specifications after addition of antioxidants with the exception of density (802 kg/m^3). Notably, the derived cetane number (73.4) and lubricity (198 µm, 60°C, ASTM D6890) represented significant enhancements over those of conventional petroleum diesel fuel. Other fuel properties included a kinematic viscosity (40°C) of 2.96 mm^2/s, cloud point of 4.7°C, flash point of 81.5°C, and energy content of 46.16 MJ/kg. In summary, liquid hydrocarbons with appropriate boiling range produced from pyrolysis of waste plastic appear suitable as blend components for conventional petroleum diesel fuel.

TABLE IX. COMPARISON OF HDPE PYROLYTIC OIL AND CONVENTIONAL FUEL PROPERTIES.

Type of oil	HDPE pyrolytic oil properties (Kumar & Singh, 2011)		Conventional fuel properties (Boundy *et al*, 2011)	
	Boiling point (ºC)	*Cv (MJ/kg)*	*Boiling point (ºC)*	*Cv (MJ/kg)*
Gasoline	82–352	42.9	40–200	43.4–46.5
Kerosene			150–300	43.0–46.2
Diesel			150–390	42.8–45.8

7.3. Low Density Polyethylene (LDP or LDPE) is defined by a density range of 0.910–0.940 g/cm^3. LDPE has a high degree of short and long chain branching, which means that the chains do not pack into the crystal structure as well. It has, therefore, less strong intermolecular forces as the instantaneous-dipole induced-dipole attraction is less. This results in a lower tensile strength and increased ductility. LDPE is created by free radical polymerization. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties. The process is used to convert these waste plastics into liquid fuel creates no harmful emissions and can be produced at a very little overall cost. The thermal process utilized to break down the hydrocarbon chains of the polymers and convert them into liquid fuel. A Steel reactor with temperature range from 100ºC to 400ºC is utilized for the plastic thermal degradation process. Liquid product yield is about 80-90% by this process. Polyethylene contains high Volatile Hydrocarbon Compounds (Kalpana, *et al*., 2013).

Low-density polyethylene (LDPE) $(C_2H_4)n$. In contrast to HDPE, LDPE has more branching that results in weaker intermolecular force, thus lower tensile strength and hardness.



However, LDPE has better ductility than HDPE since the side branching causes the structure to be less crystalline and easy to be molded. It has an excellent resistance to water, thus widely applied as plastic bags, wrapping foils for packaging, trash bags and much more.

Bagri and Williams (2001) have investigated the LDPE pyrolysis in fixed-bed reactor at 500ºC with heating rate of 10ºC/min. The experiment was done for duration of 20 min and nitrogen was used as fluidizing gas. It was observed that high liquid yield of 95 wt% was obtained with low gas yield and negligible char. High liquid oil yield of 93.1 wt% has also been obtained by Marcilla, *et al*., (2009) when the experiment was carried out in a batch reactor at 550ºC, but this time with lower heating rate of 5ºC/min. There are also some researchers who studied the LDPE pyrolysis at lower operating temperature less than 500ºC. From the research conducted by Uddin *et al*. (1996) using batch reactor at 430ºC, the liquid yield obtained was around 75.6 wt%. Aguado *et al*. (2007) have obtained a closer yield with Uddin *et al*. (1996) which was 74.7 wt% when using the same type of reactor at 450ºC. However, the liquid oil yield could be increased when pressure was applied in the reactor during the process, even though at lower temperature. This was proven by Onwudili *et al*. (2009) who used pressurized batch reactor (0.8–4.3 MPa) in LDPE pyrolysis at 425ºC. From the experiment, they have obtained 89.5% liquid oil, 10 wt% gaseous and 0.5 wt% char. This indicates that pressure may have an influence on the composition of pyrolysis product. LDPE polymeric wastes were put to thermal degradation with vacuum gas oil (VGO) as a solvent to get LDPE/VGO:1/1(Ali, 2002). the content amount in the reactor was determined as being separated into liquid and solid, 85.94% liquid, 5.76% solid, 8.3% gas and 94.24% total transformation (liquid + gas) were found.

TABLE 9: COMPOUNDS OF LDPE/VGO:1/1 THERMAL DEGRADATION LIQUID PRODUCTS AT 400°C.

Residence time, min	**wt%**	**Compound**
1.76	5.67	Pentane
1.99	7.46	Hexane
2.58	8.47	Heptane
2.83	1.87	Methylcyclohexane
3.44	3.51	Toluene
3.84	6.55	Octane
4.43	1.71	Ethylcyclohexane
4.7	0.48	Unknown
5.14	3.46	Ethylbenzene
5.88	6.56	Nonane
6.31	0.35	2-Methyl-bicyclo-octane C9
6.58	1.24	7,7-Dimethyl-tetracycloheptane
7.34	0.98	n-Propylbenzene
7.57	1.11	1,3,5-Trimethylbenzene
7.96	1.31	Cyclodecane
8.48	5.03	Decane
8.79	0.50	Cyclodecane C_{10}
9.27	0.84	Cyclodecane C_{10}
10.09	1.44	Undecane C_{11}
11.25	5.60	Undecane
11.65	0.36	Unknown
12.24	0.51	1-Dodecene C_{12}
12.57	0.54	1-Cyclopropyl-1-methyl-benzene C_{12}
12.87	1.06	1-Cyclopropyl-1-methyl-benzene C_{12}
14.04	5.36	Dodecane
15.28	0.46	Dodecane
16.7	4.55	Tridecane
17.04	0.38	Spiro(tricycloundeca-2,4,6-triene),7,1-cyclopropane
17.77	0.43	7-Tetradecene
19.24	3.54	Tetradecane
20.34	0.64	Unknown
21.63	3.10	Pentadecane
22.79	0.71	Unknown
23.92	2.80	Hexadecane
25.15	0.49	Hexadecane
26.07	2.16	Heptadecane
27.01	0.34	2,6,10-Trimethyl tetradecane
27.24	0.33	Unknown
28.12	1.88	Octadecane
29.24	0.41	Unknown
30.08	1.68	Nonadecane
31.93	1.25	Eicosane
32.95	0.41	Docosane C_{22}
33.71	0.95	Docosane
35.39	0.73	Tricosane
37.03	0.47	Pentacosane
38.58	0.33	Pentacosane
1.76	5.67	Pentane
1.99	7.46	Hexane
2.58	8.47	Heptane
2.83	1.87	Methylcyclohexane
3.44	3.51	Toluene
3.84	6.55	Octane
4.43	1.71	Ethylcyclohexane
4.43	1.71	Ethylcyclohexane
4.7	0.48	Unknown
5.14	3.46	Ethylbenzene
5.88	6.56	Nonane
6.31	0.35	2-Methyl-bicyclo-octane C9
6.58	1.24	7,7-Dimethyl-tetracycloheptane
7.34	0.98	n-Propylbenzene
7.57	1.11	1,3,5-Trimethylbenzene
7.96	1.31	Cyclodecane
8.48	5.03	Decane
8.79	0.50	Cyclodecane C_{10}
9.27	0.84	Cyclodecane C_{10}
10.09	1.44	Undecane C_{11}
11.25	5.60	Undecane
11.65	0.36	Unknown
12.24	0.51	1-Dodecene C_{12}
12.57	0.54	1-Cyclopropyl-1-methyl-benzene C_{12}
12.87	1.06	1-Cyclopropyl-1-methyl-benzene C_{12}
14.04	5.36	Dodecane
15.28	0.46	Dodecane
16.7	4.55	Tridecane
17.04	0.38	Spiro(tricycloundeca-2,4,6-triene),7,1-cyclopropane
17.77	0.43	7-Tetradecene
19.24	3.54	Tetradecane
20.34	0.64	Unknown

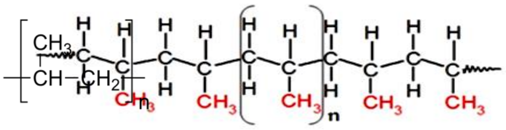
Residence time, min	**wt%**	**Compound**
21.63	3.10	Pentadecane
22.79	0.71	Unknown
23.92	2.80	Hexadecane
25.15	0.49	Hexadecane
26.07	2.16	Heptadecane
27.01	0.34	2,6,10-Trimethyl tetradecane
27.24	0.33	Unknown
28.12	1.88	Octadecane
29.24	0.41	Unknown
30.08	1.68	Nonadecane
31.93	1.25	Eicosane
32.95	0.41	Docosane C_{22}
33.71	0.95	Docosane
35.39	0.73	Tricosane
37.03	0.47	Pentacosane
38.58	0.33	Pentacosane

Liquid products of LDPE/VGO:1/1 at 400°C were examined to evaluate the cetane number of fuel specifications. Cetane number of liquid products from thermal degradation has been found to be nearly 50. This value can be an initiative indicator for this product as it would be used for diesel oil. Consequently, when LDPE is put to thermal degradation in a solvent setting in autoclave, oil like diesel can be obtained.

TABLE X. COMPOUNDS OF LDPE FLASH PYROLYSIS LIQUID PRODUCTS IN FFR AT 825°C. ALI, 2002)

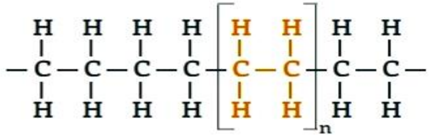
Residence time, min	**wt%**	**Compound**
2.37	2.06	1-Hexane
2.74	0.28	1,3-Pentadiene-2-methyl
3.03	4.15	1-Heptene
3.42	0.77	Cyclohexane-1-methyl
3.99	0.24	Cyclopentane-1-methyl
4.28	1.06	Cyclohexane-1-ethyl
4.91	6.83	1-Octane
5.6	0.79	Cyclohexane-1,2-dimethyl
6.03	0.38	1-Hexadiene-2,5-dimethyl
6.95	0.68	Cyclohexane-1-ethyl
8.18	10.12	Nonane
8.98	0.4	Cyclohexane(1-methylethyldiene)
9.65	0.27	Cyclopentene-1-butyl
11.33	5.49	1-Decane
11.57	3.48	2-Decene
11.69	0.33	Cyclohexene-1-butyl
11.96	0.32	2-Decyne
12.46	0.34	Bicyclo(3,1,1)heptane-2,6,6-trimethyl
14.63	4.88	Undecane
14.87	3.86	Undecyne
16.73	0.51	1,3-Di(1-propyl) cyclopentane
17.67	4.76	Dodecane
17.91	4.23	3-Dodecyne
18.17	0.38	3-Dodecyne
18.83	0.37	1,1,2-Tridecadiene
19.51	0.36	4-Tridecene
20.43	4.83	4-Tridecene
20.71	4.13	Tridecane
20.95	0.39	1,1,2-Tridecadiene
21.73	0.37	4-Nonene-5-butyl
22.2	0.4	1,1,2-Tridecadiene
23.04	5	1-Tetradecene
23.31	4.09	Tetradecane
24.54	0.37	5-Tetradecene
25.74	7.61	Pentadecene
27.95	4.76	Pentadecene
30.02	2.01	Hexadecane
32.01	0.77	1-Octadecene

7.4. Polypropylene (PP) The chemical formula is $(C_3H_6)n$. PP is asaturated polymer with linear hydrocarbon chain that has a good chemical and heat resistance. Unlike HDPE, PP does not melt at temperature below than 160ºC. It has a lower density than HDPE but has higher hardness and rigidity that makes it preferable in plastic industry. PP contributes about 24.3% in plastic wastes category which are the largest amount of plastics found in MSW (Michael, 2010). The diverse applications include flowerpot, office folders, car bumpers, pails, carpets, furniture, storage boxes and more. The high demand of PP in daily life causes the amount of PP wastes to increase each year and therefore, pyrolysis of PP is one of the methods that can be used for energy recovery. Several researchers have investigated the pyrolysis of PP at various parameters to measure the liquid oil yield and properties. In a study conducted by Ahmad *et al.* (2014) on PP pyrolysis within 250–400ºC using micro steel reactor, they summarized that the highest liquid oil was achieved at temperature of 300ºC around 69.82 wt% with total conversion of 98.66%. The increase in temperature to 400ºC only reduced the total product conversion to 94.3% and increased solid residue from 1.34 to 5.7 wt%. This indicates that coke formation started to dominate at higher temperature. However, Sakata *et al.* (1999) have explored the PP pyrolysis at higher temperature of 380ºC. They found higher liquid yield of 80.1 wt%, 6.6 wt% gaseous and 13.3 wt% solid residue left. Whereas Fakhrhoseini and Dastanian, (2013) obtained higher liquid yield about 82.12 wt% when performed PP pyrolysis at 500ºC. Nevertheless, further increase in temperature more than 500ºC only reduced the liquid yield collected. This was proven by Demirbas (2004), who carried out the PP pyrolysis at extreme temperature of 740ºC in a batch reactor which resulted in 48.8 wt% liquid yield, 49.6 wt% gaseous and 1.6 wt% char.

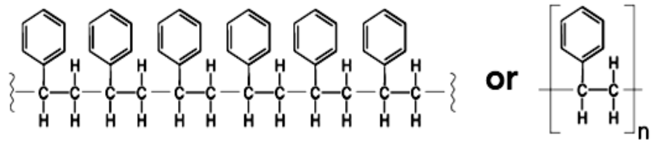


Pyrolysis of polypropylene (PP) and high density polyethylene (HDPE) into fuel like products was investigated over temperature range of 250– 400°C. The product yields as a function of temperature were studied. Total conversion as high as 98.66% (liquid; 69.82%, gas; 28.84%, and residue; 1.34%) was achieved at 300°C in case of PP and 98.12% (liquid; 80.88%, gas; 17.24%, and residue; 1.88%) in case of HDPE at 350°C. The liquid fractions were analyzed by FTIR and GC-MS. The results showed that the liquid fractions consisted of a wide range of hydrocarbons mainly distributed within the C_6–C_{16}. The liquid product obtained in case of PP is enriched in the naphtha range hydrocarbons. Similarly, the liquid product obtained in case of HDPE is also enriched in naphtha range hydrocarbons with preponderance in gasoline and diesel range hydrocarbons. The% distribution of paraffinic, olefinic, and naphthenic hydrocarbons in liquid product derived from PP is 66.55, 25.7, and 7.58%, respectively, whereas in case HDPE, the % distribution is 59.70, 31.90, and 8.40%, respectively. Upon comparing the hydrocarbon group type yields, PP gave high yield of paraffinic hydrocarbons while HDPE gave high yields of olefins and naphthenes. The whole liquid fractions and their corresponding distillates fractions were also analyzed for fuel properties. The results indicated that the derived liquid fractions were fuel-like meeting the fuel grade criteria (Ahmad, *et al.,* 2015)

7.5. Polyethylene (abbreviated PE) or polythene (IUPAC name polyethene or poly(methylene) is the most common plastic (23%). Many kinds of polyethylene are known, with most having the chemical formula $(C_2H_4)nH_2$. Thus PE is usually a mixture of similar organic compounds that differ in terms of the value of n. Low density polyethylene waste plastics are creating environmental problems because plastic are slowly degradable and its can remain long period into environment



7.6. Polystyrene (PS) (C8H8)n chemical formula $C_6H_5CH=CH_2$.



PS is made of styrene monomers obtained from the liquid petrochemical. The structure consists of a long hydrocarbon chain with phenyl group attached to every other carbon atom. PS is naturally colorless but it can be colored by colorants. It is heat resilience and it offers reasonable durability, strength and lightness that make this polymer desirable to be used in variety of sectors such as in food packaging, electronics, construction, medical, appliances and toys. Ali (2017) pyrolysed polystyrene in pressured autoclave surround by a furnace with varied temperature between 350 and 450ºC. The yields were investigated in the experiment at 450°C. Those values were respectively 59.46% liquid, 2.29% solid, 43.46% gas + loss and 92.92% total conversion. According to the results, the majority of the polymer was converted into liquid and gas chemicals. The carbon number ranges of liquid products were found as % 68.8 C_6-C_9, % 4.36 C_{13}-C_{15} and % 26.8 C_{16}-C_{18}.The main products of PS waste pyrolysis were mainly styrene monomer, ethyl benzene, toluene, and α-methyl styrene. The product spectrum can be described as a function of pyrolysis temperature and used organic compounds. The yield styrene of liquid products at various temperatures and at 400°C and 60 min with organic compounds were about from 60 to 74%. The optimum pyrolysis temperature to maximize styrene monomer yield (about 60%) was 400°C, and the maximum styrene yield was obtained with naphthalene as 74% in this study. The amount of styrene was found to increase in the following order: diphenylamine < thermal < phenol < quinone < naphthalene. Solvent addition seems to address the viscosity problem. Heavy oil is the medium utilized in thermal degradation of polystyrene.

Upon thermal-catalytic pyrolysis of polystyrene waste foams in a semi-batch reactor, the highest conversion in catalytic pyrolysis was obtained with Cu/γ-Al_2O_3 catalyst. The components of the liquid are mainly styrene monomer, ethylbenzene, toluene, α-methylstyrene, and 1,3-diphenylpropane. At 500°C the highest styrene yields were obtained with Cu/γ-Al_2O_3 and thermal run. These yields are 63.59 and 63.55%, respectively Çelikgöğüsm and Karaduman, (2015). Williams and Bagri (2004) investigated pyrolysis and catalytic pyrolysis was carried out in a fixed bed reactor. Two catalysts were used, zeolite ZSM-5 and Y-zeolite and the influence of the temperature of the catalyst. The main product from the uncatalysed pyrolysis of polystyrene was oil consisting mostly of styrene and other aromatic hydrocarbons. The gases were found to consist of methane, ethane, ethene, propane, propene, butane and butene. In the presence of either catalyst an increase in the yield of gas and decrease in the amount of oil produced was found, but there was significant formation of carbonaceous coke on the catalyst. Viable operating conditions were identified experimentally for maximizing the production of high value products such as ethylene, propylene, styrene, and benzene, from the ultrapyrolysis of waste plastics. Using both a batch micro-reactor and a pilot-plant-sized reactor, the key operating variables considered were pyrolysis temperature, product reaction time, and quench time. In the micro-reactor experiments, polystyrene (PS), a significant component of waste plastics, was pyrolyzed at temperatures ranging from 800 to 965°C, with total reaction times ranging from 500 to 1000 ms. At a temperature of 965°C and 500 ms, the yields of styrene plus benzene were greater than 95 wt%. In the pilot-plant experiments, our recently patented internally circulating fluidized bed (ICFB) reactor (Milne *et al*., U.S. Patent No. 5,370,789, 1994) was used to ultrapyrolyze low-density polyethylene (LDPE) in addition to LDPE (5% by weight)/heavy oil mixtures at a residence time of 600 ms. Both experiments produced light olefin yields greater than 55 wt% at temperatures above 830°C (Scott Lovett, *et al*, 1997).

TABLE XI. COMPOUNDS OF PS PYROLYSIS LIQUID PRODUCTS AT 450°C.

Residence time, min	**wt%**	**Compound**
2.34	0.08	1-Hexane
2.65	0.07	Bütane-2,3-dimethyl
3.07	0.12	Hexane-3-methyl
4.23	3.62	Benzene methyl
6.03	0.1	1-Heptene-5-methyl
6.9	0.97	Ethylbenzene
8.97	55.52	Styrene
11.35	4.24	Alpha-methylstyrene
24.51	0.1	Diphenylmethane
26.56	0.37	Bibenzyl

Residence time, min	wt%	Compound
28.55	0.12	1,2-Diphenyl cyclopropane
29.7	0.12	Benzene-1,1′(1,3-propanedyl)bis-
31.7	22.98	Naphthalene 1,2,3,4-tetrahydro-2-phenyl
31.91	0.09	Benzene-1,1(1,4-butanedyl)bis
32.34	0.1	Benzene-1,1(1,4-butanedyldiene)bis
32.56	0.16	1,3-Pentadiene-1,1-diphenyl
32.8	0.39	Benzene, 1,1’-(2-pentene-1,5-diyl)bis-
33.29	0.43	3,5-Diphenyl-1-pentene
34.21	0.09	Benzene-1,1(1-methyl-2-butylidiene)bis
34.58	0.1	2,5-Diphenyl-1,5-hexadiene
35.28	0.35	Benzene-1,1(2-pentene-1,5-dyl-bis
36.07	0.09	1,3-Pentadiene-1,1-diphenyl
36.46	0.3	1-Pentadiene-1,5-diphenyl
36.85	0.11	1,5-Diphenyl-1,5-hexadiene
38.87	0.08	5(2-Propylvinyl)dibenzocycloheptane
42.96	0.07	1-Ethyl-2-methyl-3-phenylindane

Flash pyrolysis of household polymeric wastes in free fall reactor (FFR) one of the chemical recycling methods of household polymeric wastes (Ali, 2017). Valuable chemicals can be obtained by flash pyrolysis of household polymeric wastes in FFR at 825ºC.

TABLE XII. COMPOUNDS OF PS FLASH PYROLYSIS LIQUID PRODUCTS IN FFR AT 825°C

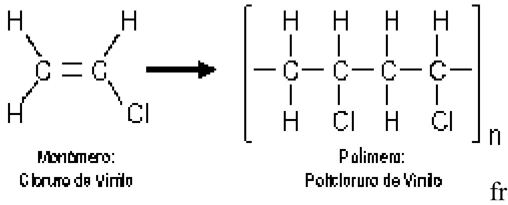
Residence time, min	wt%	Compound
4.26	1.29	Toluene
6.85	1.05	Ethylbenzene
8.27	53.60	Styrene
11.07	1.41	α-methylstyrene
29.43	0.79	1,3-Diphenyl propane
31.24	12.73	1,1-Diphenyl-2-methyl propane
32.65	0.34	1,3-Diphenyl-butane
33.23	0.21	1,1-Diphenyl-2-methyl propane
42.87	0.14	Dimer
44.44	16.84	Trimer (2,4,6-triphenyl-1-hexane)
45.78	0.52	Trimer
	11.60	Others

Flash pyrolysis of polystyrene in FFR showed that it can obtain important liquid chemicals such as toluene, ethylbenzene, α-methyl styrene and others besides styrene monomer.

Onwudili *et al.* (2009) have investigated the pyrolysis of PS in a batch pressurized autoclave reactor at 300–500ºC for one hour duration. The heating rate used was 10ºC/min and the experimental pressure given was 0.31 MPa up to 1.6 MPa. From the experiment, they found that the PS pyrolysis produced a very high liquid oil yield around 97.0 wt% at optimum temperature of 425ºC. The maximum amount of gas produced was only 2.5 wt%. The high yield of liquid oil product was also supported by Liu *et al.* (2009). The difference was during this time, the pyrolysis of PS was conducted using fluidized bed reactor at temperature of 450–700ºC. The highest liquid oil obtained was 98.7 wt% at 600ºC. Nevertheless, the amount of liquid oil produced was also considered high at lower temperature of 450ºC which was around 97.6 wt% and it differed by only 1.1 wt%. Demirbas (2004), the liquid oil reduced to 89.5 wt% when the PS pyrolysis was running at 581ºC in a batch reactor. Therefore, the PS pyrolysis was not recommended to run at temperature more than 500ºC to optimize the liquid oil production. Main products of PS chemical recycling were obtained as follows: styrene monomer, toluene, ethylbenzene, α-methyl styrene and other valuable chemicals. When LDPE undergoes thermal degradation in a solvent setting in autoclave, oil like diesel can be obtained.

7.6. Polyvinyl chloride (PVC)

Unlike other thermoplastics such as polyethylene (PE), polystyrene (PS) and polypropylene (PP) which can be softened by heating and solely derived from oil, PVC is exceptional since it is manufactured from the mixture of 57% chlorine (derived from industrial grade salt) and 43% carbon (derived from hydrocarbon feedstock such as ethylene from oil or natural gas) British Plastics Federation (2015). The chlorine property makes PVC an excellent fire resistance, thus very suitable for electrical insulation. The compatibility PVC to be mixed with many additives makes it a versatile plastic. Regular applications of PVC include wire and cable insulation, window frames, boots, food foil, medical devices, blood bags, automotive interiors, packaging, credit cards, synthetic leather, etc. Even though it has wide applications, the research done on the Tertiary recycling of plastic waste containing PVC releases hydrogen chloride, which causes corrosion of the pyrolysis reactor and formation of organochlorine compounds (Lin. *et al.,* 2010). The presence of chlorine is very harmful for use as fuel in the pyrolysis liquid products obtained (Lopez *et al*, 2010). PVC pyrolysis found in the literature was very less due to the dangerous substance that it tends to release when heated at high temperature. Therefore, PET and other special polymers should be removed from municipal waste by mechanical recovery, which is economically viable.



Miranda *et al.* (1998) conducted the pyrolysis of PVC in a batch reactor at temperature range of 225–520ºC and heating rate of 10ºC/min. The experiment was done under vacuum and total pressure of 2 kPa was applied. Liquid oil obtained was not that high and varied from 0.45 wt% to 12.79 wt% as the temperature increased. Tar accumulation was even higher than the liquid oil obtained and the amount kept increasing up to 19.6 wt%. Hydrogen chloride (HCl) was found to be the main product obtained from the experiment with the highest yield of 58.2 wt%. HCl tend to be corrosive and toxic when heated moderately that caused damage to the process equipment. This was one of the main reasons that led to the shutdown of the pyrolysis pilot plant in Ebenhausen, Germany (Miranda *et al.* (1998). Therefore, it can be concluded that PVC was not preferable for pyrolysis since the yield of liquid oil was very minimum. Furthermore, PVC waste accumulated in MSW was very minimal, about less than 3% in plastic waste category which was very limited (Michael, (2010). Additionally, the release of harmful product such as HCl and the presence of chlorinated compound such as chlorobenzene in the pyrolysis liquid could be toxic to the environment. To overcome this, a dechlorination process of PVC was required to reduce the chlorine content in liquid oil. This process could be achieved through several methods such as stepwise pyrolysis, catalytic pyrolysis and pyrolysis with adsorbents added to the PVC sample (López *et al*, 2011). Hence, the pyrolysis of PVC required an additional cost when an extra dechlorination step was needed which was one of the disadvantages to the industry.

7.7. Mixed plastics

As previously mentioned, pyrolysis process has an added advantage over the recycling process since it does not need an intense sorting process. In recycling process, most plastics are not compatible with each other to be processed together during recycling. For instance, a slight amount of PVC contaminant present in PET recycle stream will degrade the whole PET resin by becoming yellowish and brittle that requires reprocessing Hopewell et al. 2009. This shows that recycling process is very sensitive to contaminants that it requires all plastics to be sorted based on type of resins, colors and transparency. However, pyrolysis process seems to be more sustainable since liquid oil still can be produced from the mixed plastics in the feedstock. This has been encountered by several researchers who conducted studies of mixed plastics pyrolysis. Kaminsky *et al.*1996 studied the pyrolysis of mixed plastic wastes collected from German households which was composed approximately 75% of polyolefins (PE, PP) and 25% PS. There was indeed a small amount of PVC content remained in the material after the separation step about less than 1 wt% and this was shown by the presence of the chlorine content in the product yield. The experiment was conducted in a fluidized bed reactor at 730ºC which finally produced 48.4 wt% liquid oil. The amount of liquid oil obtained was very similar to the study conducted by Demirbas (2004) in pyrolysis of polyolefins (PP, PE) and PS mixture collected from landfill which was approximately 46.6 wt%. The gaseous and solid yields were reported to be 35 wt% and 2.2 wt% respectively. In terms of the oil composition, it contained 4 ppm chlorine resulted from the remaining PVC left in the material. However, it did not deteriorate the oil quality since the minimum chlorine limit in petrochemical processing was less than 10 ppm. Furthermore, the rest of the chlorine content was found to be the largest in solid residue. Therefore, the author concluded that the chlorine content in the feedstock could not be more than 1 wt% to ensure high quality oil was produced. The potential of polyolefins mixed plastics in pyrolysis was also explored by Donaj *et al*. (2012). The mixed plastics were composed of 75 wt% LDPE, 30 wt% HDPE and 24 wt% PP. The experiment was operated at high temperatures of 650ºC and 730ºC in a bubbling fluidized bed reactor. The results showed that the liquid obtained was higher at lower temperature of 650ºC which was around 48 wt%. However, this oil fraction consisted of 52% heavy fraction such as heavy oil, wax and carbon black. In contrast, it was up to 70% light fraction of liquid contained in the pyrolysis oil (44 wt%) running at 730ºC. This means that the higher the temperature, the lighter the hydrocarbon liquid or gaseous produced. Therefore, it should be noted that there was a tremendous change in the product distribution when the temperature was further increased. In comparison to the single plastic pyrolysis, it can be seen that the pyrolysis of mixed plastics produced lower liquid yield less than 50 wt%. Nevertheless, the quality of oil produced was comparable to the single plastic pyrolysis in terms of the oil composition that made it ideally suited for further processing in petrochemical refineries.

7.8 Bio-oil is a kind of liquid fuel made from biomass materials such as agricultural crops, algal biomass, municipal wastes, and agricultural and forestry by-products via thermo-chemical processes (Demirbas, 2007). In addition, the characterization of bio-oil is also being focused and got more achievements. Bio-oils are CO_2/GHG neutral.

Plastic diesel can be obtained while untreated polyethylene can be broken down; it requires either a significant amount of heat or reactive, toxic chemicals, and results in the atomic bonds breaking in an unusable way.

7.9 Plastic Oil: Plastic waste types such as polystrene (PS), polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET) on the yield and quality of produced different liquid oil from the pyrolysis process. In order to extract the oil, plastic needs to be heated to over 400°C. At this temperature, the long-chain molecules from the plastic are cracked and produce synthetic crude oil. It is heated to 427°C (800°F) which converts the plastic into a liquid. Oil that produced at lower pyrolysis temperature performed better. It has higher brake thermal efficiency and shorter ignition delay period at all loads (Ioannis et al., 2017)

The machine then transforms the liquid into gaseous state. The gas produced is trapped and allowed to cool. The vapors condense when cooled and form crude oil. In the case of plastic, some of the valuable fuels and solvents that can be extracted through waste plastic pyrolysis are fuels like gasoline, kerosene, diesel, and high-value ones like benzene, toluene and xylene (Technology Review, 2018)

7.9. Characteristics of plastic pyrolysis oil

7.9.1. Physical properties

The pyrolysis oil composition from polystyrene consists of 95% aromatic hydrocarbons, while in contrast, those from polypropylene, low density polyethylene and high density polyethylene, were dominated by aliphatic hydrocarbons. The low density polyethylene and high density polyethylene oils had functional groups that were consistent with those of commercial diesel (96% similarity match). In contrast, pyrolysis-oils from polystyrene demonstrated chemical and physical properties similar to those of gasohol 91. Pyrolysis-oil from the catalytic treatment of polystyrene resulted in greater engine power, comparable engine temperature, and lower carbon monoxide (CO) and carbon dioxide (CO_2) emissions, as compared to those of uncatalysed oils and commercial fuel in a gasoline engine. Pyrolysis-oils from all other polymers demonstrated comparable performance to diesel in engine power tests (Budsaereechai, *et al.,* 2019). The experimental calorific value of HDPE, PP and LDPE are all above 40 MJ/kg and were considered high for energy utilization. According to Ahmad *et al.* (2014), the calculated calorific value for both HDPE and PP were above 45 MJ/kg, and thus very closer to the commercial fuel grade criteria of gasoline and diesel. The calorific value of PS was commonly lower than the polyolefin plastic due to the existence of the aromatic ring in the chemical structure which had lesser combustion energy than the aliphatic hydrocarbon (Onwudili, *et al*., 2009). API gravity was the method used for measuring the density of the petroleum relative to water. The API gravity of HDPE and PP were 27.48 and 33.03 respectively while the densities were 0.89 and 0.86 g/cm3 accordingly Ahmad *et al*. (2014). The API gravity of PVC was very close to the diesel API gravity value which was 38.98. On the other hand, the API gravity of LDPE was approaching the gasoline standard value which was 47.75. Therefore, all of these values were comparable to the commercial diesel fuel except LDPE which was comparable to the standard gasoline. In terms of density, all values seem comparable with the commercial standard value of both gasoline and diesel.

The viscosity on the other hand was defined as a measurement of the fluid resistance to flow. Viscosity is very crucial in petroleum industry since it determines how easy the oil can flow from the reservoir to the well during extraction process and also plays a crucial role in fuel injection process (Ahmad *et al.* (2014); Meyer and Attanasi, 2003). In Table 13, the viscosity values were determined at different temperatures as denoted at the bottom of the table. Based on Table 13, it depicted the value of kinematic viscosity of all plastics were very close with the viscosity of diesel except for PS which the viscosity value was closer to the gasoline viscosity. Miandad *et al.* (2016) reported that the liquid oil obtained from PS at optimum condition had a dynamic viscosity of 1.77 mPa s, kinematic viscosity of 1.92 cSt, a density of 0.92 g/cm 3, a pour point of À60 °C, a freezing point of À64 °C, a flash point of 30.2 °C and a high heating value (HHV) of 41.6 MJ/kg this is similar to conventional diesel. .In terms of ash content, HDPE and PP had negligible ash content and these indicated that the HDPE and PP pyrolysis oil was free from any metal contamination. The ash content in PS was also lower than the standard diesel which was less than 0.01 wt%. LDPE had slightly higher ash content of 0.02 wt% but the value was still tolerable since the difference was very minimal.

TABLE XIII. FUEL PROPERTIES OF PLASTIC PYROLYSIS OIL.

Physical properties	**Type of plastics (experimental typical value)**										**Commercial standard value (ASTIM 1979)**			
	PET	HDPE		PVC	LDPE		PP		PS		Gasoline		Diesel	
References	[5];[9]	[1]	[4]	[5];[7]	[6]	[4]	[4]	[1]	[2] [8]	[4]	[3]	[4]	[1]	[4]
Calorific value (MJ/kg)	28.2	40.5	43 646 g^{-1}	21.1	39.5	43 390 g^{-1}	43 695 g^{-1}	40.8	43.0	43 550 g^{-1}	42.5	45 940 g^{-1}	43.0	46 951 g^{-1}
API gravity @ 60 °F	n.a	27.48		38.98	47.75			33.03	n.a		55		38	
Viscosity (mm2/s)	n.a	5.08a	2.5	6.36b	5.56c	2.5	2.3	4.09a	1.4d	2.0	1.17	1.5	1.9–4.1	2.5
Density @ 15 °C (g/cm3)	0.90	0.89	0.91	0.916	0.78	0.911	0.905	0.86	0.85	0.855	0.780	0.802	0.807	0.875
Ash (wt%)	n.a	0.00		n.a	0.02			0.00	0.006		–	-	0.01	
Octane number MON (min)	n.a	85.3		n.a	n.a			87.6	n.a		81–85	-	–	
Octane number RON (min)	n.a	95.3		n.a	n.a			97.8	90–98		91–95	-	–	
Pour point (°C)	n.a	_5	24	n.a	n.a	24	15	_9	_67	19	–	-	6	3
Flash point (°C)	n.a	48	50	40	41	45	40	30	26.1	48	42	41	52	63
Aniline point (°C)	n.a	45		n.a	n.a			40	n.a		71		77.5	
Diesel index	n.a	31.05		n.a	n.a			34.35	n.a		–		40	

n.a., not available in the literature.
a. Viscosity at 40°C;
b. Viscosity at 30°C;
c. Viscosity at 25°C;
d. Viscosity at 50°C.

References:
[1]. Ahmad, *et al*., 2014;
[2]. Blazso, 2006;
[3]. Boundy., 2011;
[4]. Budsaereechai *et al*, 2019;
[5]. Çepeliogˇullar, & Pütün 2013;
[6]. Desai & Galage, 2015;
[7]. Manickaraja & Tamilkolundu, 2014;
[8]. Pinto *et al*, 1998;
[9]. Sarker *et al.,* 2011

7.9.2. **Octane Number**: Besides that, the research octane number (RON) and motor octane number (MON) which was important to characterize the anti-knock quality for the gasoline range (C_6–C_{10}) was also determined. The high octane number indicates the better anti-knock quality that the fuel possesses. Knock is usually caused by the rapid combustion of gasoline in an engine that produces an explosive noise and degrades the engine performance over time (Kalghatgi, 2001). Therefore, the anti-knock quality is very important to avoid engine damage. The MON and RON value for HDPE pyrolysis oil was 85.3 and 95.3 respectively. PP pyrolysis oil had higher MON and RON value which were 87.6 and 97.8 accordingly. The RON value for PS also matched the range of standard gasoline value which was in the range of 90–98. This suggests that the octane number of HDPE, PP and PS were comparable with commercial gasoline (MON = 81–85, RON = 91–95).

7.9.3. **Pour point** is known as the temperature at which the fluid stops to flow (Bozbas, 2008). Generally, the increase in viscosity may cause the fluid losses its flow characteristic. Liquid fuel that has lower pour point has lesser paraffin content but greater aromatic content (Schlumberger, 2015). HDPE, PP and PS pyrolysis oil had lower pour point around 5, 9°C and 67°C respectively, than the commercial diesel which having the pour point of 6°C. This indicates that the pyrolysis oil obtained from plastic pyrolysis were rich with aromatic content. This relates to the lower calorific value of HDPE, PP and PS pyrolysis oil in comparison with the commercial gasoline and diesel.

7.9.4. **Flash point** of the liquid is defined as the lowest temperature at which the liquid may vaporize and form a mixture in the air that ignites when an external flame is applied (Horng, 2004). The flash point of HDPE, PVC and LDPE pyrolysis oil were very close to the commercial gasoline. This indicates that the flash point of those three plastics was comparable to the light petroleum distillate fuel. The flash point of PP and PS were lower than both commercial gasoline and diesel. This shows that PP and PS pyrolysis oil easier vaporized and thus need an extra precaution when handling.

7.9.5. **Aniline point** is a temperature at which the aniline compound (C6H5NH2) forms a single phase with the liquid oil (Schlumberger, 2015). Lower aniline point indicates the higher existence of aromatic compound.

Oppositely, the higher aniline point indicates the higher amount of paraffin compound in the oil. Olefin has the aniline point in between those aromatic and paraffin value (Schlumberger, 2015). Referring to Table 13, the aniline point of HDPE and PP pyrolysis oil were 45°C and 40°C respectively which were much lower than the commercial gasoline and diesel. Gasoline and diesel were both having aniline point of 71°C and 77.5°C. This once again proves that the pyrolysis oil obtained from HDPE and PP was rich with aromatic compounds.

7.9.6. **Diesel index** evaluates the ignition quality of the diesel fuel in which the higher diesel index of the fuel indicates the higher quality of the fuel (Cookson *et al*., 1984; Kumar *et al*., 2013). The diesel index of the HDPE pyrolysis oil was 31.05 while PP was 34.35. Even though the diesel index was not meeting the ASTM 1979 standard, the mixing of additives to fuel oil can improve the ignition quality of the diesel fuel and has shown growing acceptance nowadays Nino and Nino 1997. Therefore, Ahmad *et al*. (2014) concluded that liquid product produced by HDPE and PP met the commercial fuel grade and suggested to be a blend of gasoline and diesel hydrocarbon range. In PP and HDPE pyrolysis oil, Jung *et al*. (2010) observed that the liquid oil contained primarily aliphatic, monoaromatic and polyaromatic compounds. As for the PP fraction, the increase in the temperature reduced the aliphatic concentration in the oil to 2.9 wt% at 746°C. In contrast, high aliphatic concentration was found in HDPE pyrolysis oil around 20 wt% at 728°C. This indicates the complexity of the HDPE structure to degrade during thermal degradation process. Besides that, the BTX aromatics in PP pyrolysis oil (53 wt%) were found higher than in the HDPE fraction (32 wt %) at the same temperature as mentioned previously. The most abundant compound comprised in the BTX aromatics was the benzene. The concentration of benzene and toluene increased with the temperature except xylene compound which did not have a significant difference with the temperature. In terms of hydrocarbon product distribution, paraffins were the main product observed (66.55%) for PP derived liquid compared than HDPE (59.70%). Hence, PP pyrolytic oil was more value added than the HDPE derived liquid since paraffins released extra energy for combustion than other hydrocarbon groups such as olefins and naphthenes. As for the LDPE derived liquid oil, Williams and Williams (1998^a) reported that the aliphatic compound which consisted of alkanes, alkenes and alkadienes was the main composition found. As the temperature increased, the aliphatic concentration was in decreasing trend.

However, the aromatic compound showed an opposite trend in which the aromatic concentration increased with the temperature. Among the aromatic compound, benzene and toluene concentration showed a dramatic increase as the temperature increased except xylene and this observation matched the trend observed in PP and HDPE pyrolysis as reported by Jung *et al*. 2010. However, it should be noted that the chemical concentration depends strongly on the pyrolysis operating temperature. According to Williams and Williams (1998^a), the oil contained no aromatic and polyaromatic hydrocarbon at temperature of 500–550°C. Nevertheless, a significant increase in the single ring aromatic compound and polycyclic aromatic compound (PAH) happened when the temperature increased to 700°C that comprised around 25% of the liquid oil composition. For PS pyrolysis oil, Onwudili *et al*.

(2009) reported that the benzene, toluene and ethyl benzene were three main components in the PS oil product that increased with the temperature. Miandad *et al* (2016) found that liquid oil contains mainly styrene (48%), toluene (26%) and ethyl-benzene (21%) compounds.

On the other hand, styrene monomer kept decreasing with the temperature and this suggest that the styrene radical formed during the degradation process of PS was very reactive. Liu *et al.* (2009) also reported the same observation. The styrene and monoaromatics were among the major components in the liquid oil product that they covered around 80 wt% in the liquid fraction. These components were categorized in the low boiling point fraction of less or equal to 200°C.

VIII. BY-PRODUCTS OF THE PLASTIC PYROLYSIS

Pyrolysis of plastics also produces char and gas as by-products. The proportion of by-product in pyrolysis strongly depends on several parameters such as temperature, heating rate, pressure and residence time. Some information about the by-products generated is discussed below.

8.1. Tar: A dark, oily, viscous material, sonsisting mainely of high moleular weight hydrocarbons: causes blockage, plugging and corrosion in downsteatm fule lines, filters, engine nozzles etc. Methods to reduce/remove tar are 1. Primary – (a) by high temperature gasification- (b) Add bed materials such as dolomite. 2. Secondary by using –(a) Hot gas filters (b) wet scrubbers (c) catalytic cracking.

8.2. Char

The residue (char) left after the pyrolysis process can be utilized for several environmental applications. Several researchers activated the char via steam and thermal activation (Lopez *et al.*, 2009; Heras *et al.*, 2014). Generally, slow heating rate at very low temperature and long residence time maximizes the char formation in pyrolysis process. Even though the char formation in fast pyrolysis process is commonly low, it is worth noting the properties and usage of the char to fully maximize the potential of plastic pyrolysis. Jamradloedluk and Lertsatitthanakorn (2014) analyzed the char properties obtained from the pyrolysis of HDPE plastic waste. From the proximate analysis, volatile matter and fixed carbon were found to be the main components of the char (>97 wt%) while moisture and ash were the minorities. These components were closely related to the proximate analysis of the raw plastic as tabulated in Table 15, showing that most plastics were composed from almost 99 wt% of volatile matter. The calorific value of the char was about 18.84 MJ/ kg. Furthermore, the low sulfur content made it suitable to be used as fuel, for instance in combustion with coal or other wastes.

Besides that, the char formation was found to be increased with the temperature and this trend was observed by Jung *et al.* (2010) in pyrolysis of PE and PP wastes. The char formation was increased from 2 wt% to 4 wt% in PP pyrolysis and from 0.7 wt% to 2 wt% in PE pyrolysis as the temperature was raised from 668°C to 746°C. Unfortunately, the char obtained from both plastics consisted mainly of inorganic matters up to 98.9 wt% which originated from the inorganic substance in the feed fraction. In this case, the inorganic matters caused the application of char as fuel to be different. However, it still has potential of char as fuel to be difficult. However, it still has potential to be used as road surfacing and as a building material Jung *et al.* (2010).

Table XIV. Fuel properties

Properties	**PE**	**PP**	**PS**	**Nylon**	**PP 50% PE 43% Nylon 7%**	**Polyester Styrene Copolymer**
Flash point (°C)	33.6	27.8	26.1	34.8	26	26
Pour point (°C)	2.7	-39	-67	-28	-5.0	
Water content (ppm)	0.18	0.13	0.67	2500	310	
Ash (wt%)	0.013	0.010	0.006	0.018	0.001	0.53
Viscosity est (50°C)	2.19	1.9	1.4	1.8	1.485	3.9
Density (kg/m3)	0.858	0.792	0.96	0.926	0.799	0.83
Cetane rating		56.8	12.6		54.3	
Carbon(w%)						86.1
Hydrogen (w%)						7.2
Sulphur (w%)	0.01	0.01	0.01	0.01	0.013	0.0
Initial B.Pt. (°C)						75
10%B.Pt. (°C)						93
50%B.Pt. (°C)						189
90%B.Pt.(°C)						354
CV (Mj/Kg)	5.23	53.4	50.4	44.4	46.3	33.6

https://www.rsc.org/images/PaulWilliams_tcm18-216275.pdf

Table XV. Main oil composition from the pyrolysis of plastics.

PET	**HDPE**		**PVC**	**LDPE**		**PP**		**PS**	
[2]	[3]	[1]	[2]	[5]	[1]	[3]	[1]	[4]	[1]
1-Propanone	1-Methyl cyclopentene	Eicosane ($C_{20}H_{42}$, 3.31%)	Azulene	Benzene	Eicosane ($C_{20}H_{42}$, 3.14%)	2-Methyl-1-Pentene	1-Tricosene ($C_{23}H_{46}$, 14.98%)	Benzene	
Benzoic acid	3-Methylcyclopentene		Naphthalene	1-methyl-Toluene		3-Methyl cyclopentene	1-Pentadecene ($C_{15}H_{30}$, 7.76%)	Toluene	Toluene (C_7H_8, 7.93%)
Bipheny	l 1-Hexene	Heptadecane ($C_{17}H_{36}$, 3.27%)	Biphenyl	Xylene		1-Heptene	2,4-Dimethyl-1-heptene (C_9H_{18}15.08%)	Ethylbenzene	Ethylbenzene (C_8H_{10}, 15.07%)
Diphenyl methane	Cyclohexene		Naphthalene, 1-ethyl	Dimethylbenzene		1-Octene	3-Octadecene, (E)-($C_{18}H_{36}$, 7.78%)	Xylene	
4-Ethyl benzoic acid	1-Heptene		Naphthalene, 1-(2-propenyl)	Trimethyl benzene		C4–C13 hydrocarbon		Styrene	Styrene (C_8H_8, 20.12%)
4-Vinyl benzoic acid	1-Octene		Naphthalene, 2,7-dimethyl	Indane		Over C14 hydrocarbon		Cumene	
Fluorene	1-Nonene		Naphthalene, 1,6-dimethyl-	Indene		Benzene		Propylbenzene	
Benzophenone	1-Decene		Naphthalene, 1,7-dimethyl	Methylindenes		Toluene		2-Ethyl toluene	
4-Acetylbenzoic acid	1-Undecene		Naphthalene1,4-dimethyl-	Naphthalene	Pentadecane ($C_{15}H_{32}$, 2.98%)	, Xylene		Naphthalene	
Anthracene	1-Tridecene	Hexadecane ($C_{16}H_{34}$, 3.32%)	Naphthalene, 1,6,7-trimethyl	Methylnaphthalenes	Hexadecane ($C_{16}H_{34}$, 3.12%)	Ethybenzene		Diphenyl methane	
Biphenyl-4-carboxylic acid	C4–C13 hydrocarbon		9H-Fluorene	Ethyl naphthalene	Heptadecane ($C_{17}H_{36}$, 3.06%)	Indene		Anthracene	
1-Butanone	Over C14 hydrocarbon	Nonadecane ($C_{19}H_{40}$, 3.43%)	Naphthalene 1-(2-propenyl)-	Dimethyl naphthalene	Nonadecane ($C_{19}H_{40}$, 3.11%)	Biphenyl		1,2-Diphenyl ethane	
m-Terphenyl	Benzene		Phenanthrene, 1-methyl	Acenaphthylene				2,2-Diphenyl propane	
	Toluene		Fluoranthene,	2-methyl-Acenaphthene			1-Decene, 2,4-dimethyl-($C_{12}H_{24}$, 4.33%)	3-Eicosene, (E)-($C_{20}H_{40}$, 7.11%)	Benzene, 1,1′-(1,3-propanediyl)bis-($C_{15}H_{16}$, 11.17%)
	Xylene		1H-Indene, 2,3-dihydro-5-methyl-	Trimethyl naphthalenes				Phenyl nphthalene	
			Naphthalene	, 2-phenyl-Fluorene				Diphenyl benzene	
				Tetramethyl naphthalene				Triphenyl benzene	α-Methyl styrene (C_9H_{10}, 10.38%)

References
[1] Budsaereechai, *et al*, 2019
[2] Cepeliogullar & Putun, 2013^b
[3] Jung *et al.*, 2010
[4] Onwudili *et al* , 2009
[5] Williams & Williams, 1998^b

8.2. Syngas is an abbreviation for synthesis gas, which is a mixture comprising of carbon monoxide, carbon dioxide, and hydrogen. The syngas is produced by gasification of a carbon containing fuel to a gaseous product that be used to produce fuel, power and heat. Some of the examples of syngas production include gasification of coal emissions, waste emissions to energy gasification, and steam reforming of coke. The name syngas is derived from the use as an intermediate in generating synthetic natural gas and to create ammonia or methanol. It is a gas that can be used to synthesize other chemicals, hence the name synthesis gas, which was shortened to syngas. Syngas is also an intermediate in creating synthetic petroleum to use as a lubricant or fuel. syngas is composed of 85% carbon monoxide and hydrogen and small amounts of methane and carbon dioxide. However, tar content and fine particulates, pollutants such as Sox etc. are challenges for the subsequent process after the gasification of waste.

8.2. Gas

According to Prabir (2010), high temperature and long residence time were the best condition to maximize gas production in pyrolysis process. However, these conditions are opposite with the parameters to maximize oil production. Generally, gas production in pyrolysis process of polyolefins and PS plastics were quite low in the range of 5–20 wt% and it is strongly depends on the temperature and type of plastics used in pyrolysis. The effect of temperature and plastic types were further studied by Onwudili *et al*. (2009) in a pyrolysis of LDPE, PS and their mixture. At 350°C, it was discovered that the gas product from the mixture was more than the pyrolysis of individual plastic. The gas continued to increase to 8.6 wt% at 425° where at this point, the gas product was higher than pyrolysis of PS alone but lower than LDPE. At the same temperature, pyrolysis of PS produced some amount of char but not any significant gas product. However, the pyrolysis of LDPE did produce more gas but no char at this temperature. Hence, the authors noted that the amount of gas produced from the mixture was significantly contributed by the LDPE component, whereas char formation related closely to PS. At 450°C, the gas production increased continuously to 12.8 wt% for the plastic mixture. The gas composition depends on the composition of feedstock material. Williams and Williams 1998[b] studied the pyrolysis of HDPE $(C_2H_4)n$, LDPE $(C_2H_4)n$, PP $(C_3H_6)n$, PS $(C_8H_8)n$, PET $(C_{108}O_4)n$ and PVC $(C_2H_3Cl)_n$ individually and they found that the main gas components produced during pyrolysis of each plastic were hydrogen, methane, ethane, ethene, propane, propene butane and butene. The gas produced in pyrolysis process also has significant calorific value. Jung *et al*. (2010) reported that the gas produced from the pyrolysis of PE and PP alone had high calorific value between 42 and 50 MJ/kg. Thus, the pyrolysis gas had high potential to be used as heating source in pyrolysis industrial plant. Additionally, the ethene and propene can be used as chemical feedstock for the production of polyolefins if separated from other gas components. The pyrolysis gas can also be used in gas turbines to generate electricity and direct firing in boilers without the need for flue gas treatment (Fernandez, *et al*., 2011).

IX. SUMMARY

This review showed that many researchers have been done to study the potential of plastic pyrolysis process in order to produce valuable products such as liquid oil and the results were convincing. This technique offers several advantages such as enhancing the waste management system, reducing the reliability to fossil fuels, increasing energy sources and also prevents the contamination to the environment. The technique can be executed at different parameters that resulted in different liquid oil yield and quality. Besides that, this technique offers great versatility and better economic feasibility in terms of the process handling and the variability of the product obtained. As mentioned in the paragraph above, various parameters could influence the liquid oil yield and the most critical factor was the temperature. Different plastics may have different degradation temperature depends on their chemical structures. Therefore, the effective temperatures for the liquid optimization in pyrolysis also varied for each plastic and it also strongly dependent on other process parameters. Such parameters include the type of catalyst used, the ratio of catalyst/polymer and also type of reactors operated.

Table 16 summarized the optimum temperature required to optimize liquid oil yield in thermal and catalytic pyrolysis at different conditions. Other affected parameters include the type of reactors, pressure, heating rate and pyrolysis duration for each type of plastics. All experiments carried out were using nitrogen gas as the fluidizing medium. Based on Table 8, PET and PVC are two plastics that produced very low yield of liquid oil in comparison with other plastic types, which made these plastics infrequently explored by researchers. It also should be noted that not all plastic types are recommended for pyrolysis.

PVC was not preferred in pyrolysis since it produced the major product of harmful hydrochloric acid and very low yield of liquid oil. Additionally, the pyrolysis oil also contained chlorinated compound that would degrade the oil quality and also toxic to the environment.

As summarized in Table 16, it can be concluded that the most effective temperature to optimize the liquid oil yield in plastic pyrolysis would be in the range of 500–550°C for thermal pyrolysis. However, with the usage of catalyst in the pyrolysis, the optimum temperature could be lowered down to 450°C and higher liquid yield was obtained. In most plastics, the usage of catalyst in the process might improve the liquid oil yield, but PS was exceptional. This is because PS degraded very easily without the needs of any catalysts to speed up the reaction and yet 97 wt% of oil was produced (Onwudili *et al*., 2009). Therefore, PS was the best plastic for pyrolysis since it produced the highest amount of liquid oil production among all the plastics. As for the polyolefin plastic type, LDPE produced the highest liquid oil yield (93.1 wt%), followed by HDPE (84.7 wt%) and PP (82.12 wt%) in thermal pyrolysis. However, with addition of catalyst such as FCC and at the right operating temperature, the liquid yield could be further maximized to above 90 wt%.

TABLE XVI. SUMMARY OF STUDIES ON PLASTIC PYROLYSIS.

Type of Plastic	**Reactor**	**Process parameters**				**Yield**			**Others**	**Reference***
		Temp (º C)	***Pressure***	***Heating rate (ºC /min)***	***Duration (min)***	***Oil (wt%)***	***Gas (wt%)***	***Solid (wt%)***		
PET	Fixed bed	500	–	10	–	23.1	76.9	0		Cepeliogullar & Putun. 2013^{b}
PET	–	500	1 atm	6	–	38.89	52.13	8.98		Fakhrhoseini and Dastanian, 2013
HDPE	Horizontal steel	350	–	20	30	80.88	17.24	1.88		Ahmad *et al*., 2014
HDPE	Semi-batch	400	1 atm	7	–	82	16	2	Stirring rate 200 RPM, FCC catalyst 10 wt%	Kyong *et al.,* 2002
HDPE	Batch	450	– –	– –	60	74.5	5.8	19.7		Miskolczi *et al.,* 2004
HDPE	Semi-batch	450	1 atm	25	–	91.2	4.1	4.7	Stirring rate 50 RPM, FCC catalyst 20 wt%	Abbas-Abadi, et al., 2013
HDPE	Fluidized bed	500	– –	– –	60	85	10	5	Silica alumina catalyst	Luo *et al*., 2000
HDPE	Batch	550	–	5	–	84.7	16.3	0		Marcilla etlal, 2009
HDPE	Fluidized bed	650	–	–	20–25	68.5	31.5	0		Mastral *et al*., 2001
PVC	Fixed bed	500	–	10	–	12.3	87.7	0		Cepeliogullar & Putun , 2013^{b}
PVC	Vacuum batch	520	2 kPa	10	–	12.79	0.34	28.13	Also yield HCl = 58.2 wt%	Miranda *et al.*, 1998
LDPE	Pressurized batch	425	0.8–4.3 MPa	10	60	89.5	10	0.5		Onwudili, *et al.*, 2009
LDPE	Batch	430	–	3	–	75.6	8.2	7.5	Also yield wax = 8.7 wt%	Uddin *et al.*, 1996
LDPE	–	500	1 atm	6	–	80.41	19.43	0.16		Fakhrhoseini& Dastanian 2013
LDPE	Fixed bed	500	–	10	20	95	5	0		Bagri &, Williams,2001
LDPE	Batch	550	–	5	–	93.1	14.6	0		Marcilla *et al.*, 2009
LDPE	Fluidized bed	600	1 atm	–	–	51.0	24.2	0	Also yield wax = 24.8 wt%	Williams & Williams1998^{a}
PP	Horizontal steel	300	–	20	30	69.82	28.84	1.34		Ahmed, *et al.*, 2004
PP	Batch	380	1 atm	3	–	80.1	6.6	13.3		Sakata, *et al.*, 1999
PP	Semi-batch	400	1 atm	7	–	85	13	2	Stirring rate 200 RPM, used FCC catalyst 10 wt%	Kyong, *et al.*, , 2002
PP	Semi-batch	450	1 atm	25	–	92.3	4.1	3.6	Stirring rate 50 RPM, used FCC catalyst 10 wt%	Abbas-Abadi, *et al.*, 2014
PP	–	500	1 atm	6	–	82.12	17.76	0.12		Fakhrhoseini& Dastanian 2013
PP	Batch	740	–	–	–	48.8	49.6	1.6		Demirbas 2004
PS	Semi-batch	400	1 atm	7	–	90	6	4	Stirring rate 200 RPM, used FCC catalyst, cat/poly = 10 w/w	Kyong *et al.*, 2002
PS	Pressurized batch	425	0.31–1.6 MPa	10	60	97	2.50	0.5		Onwudili, *et al.*, 2009
PS	Batch	500	–	–	150	96.73	3.27	0	Used Zn catalyst, cat/poly = 5 w/w	Adnan & Shah, 2014
PS	Batch	581	–	–	–	89.5	9.9	0.6	64.9 wt% of liquid comprised of styrene	Demirbas, 2004

* All experiments used nitrogen gas as fluidizing medium.

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