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Review

Plastics waste management: A review of pyrolysis technology

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Abstract: The world is today faced with the problem of plastic waste pollution more than ever before. Global plastic production continues to accelerate, despite the fact that recycling rates are comparatively low, with only about 15% of the 400 million tonnes of plastic currently produced annually being recycled. Although recycling rates have been steadily growing over the last 30 years, the rate of global plastic production far outweighs this, meaning that more and more plastic is ending up in dump sites, landfills and finally into the environment, where it damages the ecosystem. Better end-of-life options for plastic waste are needed to help support current recycling efforts and turn the tide on plastic waste. A promising emerging technology is plastic pyrolysis; a chemical process that breaks plastics down into their raw materials. Key products are liquid resembling crude oil, which can be burned as fuel and other feedstock which can be used for so many new chemical processes, enabling a closed-loop process. The experimental results on the pyrolysis of thermoplastic polymers are discussed in this review with emphasis on single and mixed waste plastics pyrolysis liquid fuel.

Keywords: conventional waste plastics recycling; pyrolysis; liquid fuel; microwave-assisted pyrolysis; properties of liquid fuel

1. Introduction

The discovery of synthetic plastics in 1907 and it(s) rapid commercialization in the early 1950's [1] has brought about advances in technology cutting across all facets of human endeavours. For instance, plastics have contributed extensively to the development of computers, cell phones, light weight automobile parts, roofing and ceiling materials as well as most of the lifesaving advances of modern medicine among many other areas of application. Even the current fight against COVID 19 pandemic will be impossible without personal protective gears made largely from plastics [2,3]. Furthermore, plastics have shown excellent insulating and dielectric properties and as such are widely employed in the fields of electrical and electronics [4,5].

Owing to the increasing these applications and more, we have become increasingly addicted to this modern material most of which are single-use articles.

In recent decades, the production and consumption of plastics have increased. Between 1950 and 2015, about 8,300 million tonnes (Mt) of virgin plastics were produced across the globe, generating approximately 6,300 Mt of plastic wastes, of which about 9% have been recycled, 12% incinerated, and 79% accumulated in landfills [6]. Consequently, the volumes of post-consumer plastic waste (PCPW) are steadily on the increase in the environment [7,8]. Global plastic production was estimated at around 300 million tons per year and is continuously increasing every year [9,10]. Waste generated from indiscriminate disposal of used plastics represents a considerable proportion of the total waste stream in many countries today [11,12]. Even more worrisome is the marine plastic litters which have been found to disintegrate into microplastics and nanoplastics, and are consumed by aquatic animals [13–16]. Research has shown that this poses serious negative impact on population and mortality of zooplankton which is an important source of energy for marine environment [15].

Presently, plastic wastes pose danger to global economy, human, animal and environment, especially for under developed and developing countries, which lack modern recycling facilities and weak policies on plastics production, usage and regulation [17].

Depending on type, application and service condition, plastic may contain some if not all of the following additives; plasticizers, fire retardants, antioxidants, light stabilisers, lubricants, pigments, antistatic agents and thermal stabilisers. Research has shown that many of these additives find their ways into human and animal systems and has the ability to mimic, block, or interfere with hormones in the body's endocrine system as such, are classified as endocrine disrupting chemicals (EDCs) [18]. Many have also been listed as Persistent organic pollutants (POPs), sometimes known as "forever chemicals". They are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes. Most flame retardants; polychlorinated biphenyls (PCBs), hexachlorobenzene, polybrominated diphenyl ethers (PBDs), hexabromobiphenyls (HBB), hexabromocyclododecane (HBCD), short-chain chlorinated paraffins (SCCPs) and the fluorinated tensides like perfluorooctanoic acid (PFOA) are all in this class [19].

While plastics have demonstrated excellent properties and uses towards advances in modern technology, inappropriate use, disposal of its waste and weak regulation on addition of additives in plastics meant for food packaging may result in the release of toxic substances, which is fueled by open burning of domestic and industrial plastics [20]. In this regard authorities around the world have resorted to non-scientific approach, such as waste plastic buyback, partial to outright ban of some categories of plastic articles in a bid to circumvent pollution from used discarded plastics [21,22]. However, these

policies have not yielded substantial positive impact because of both; negative economic, legislative, political, technical and operational limitations [23,24].

To keep-up with the technological advances brought about by the use of plastics and its sustainable economic growth, it will require more than the mechanical recycling techniques; where used plastics are down cycled or up-cycled to a more holistic close loop approach. Mechanical recycling only delays the time taken for used plastics to get to the dumpsites and marine environment. The only way to permanently eliminate plastic waste is by destructive thermal treatment, such as controlled combustion or pyrolysis. Pyrolysis of plastic wastes is a holistic close-loop approach; a technique used to convert plastic waste into energy, in the form of solid, liquid and gaseous fuels [25–27].

Unlike mechanical recycling, Pyrolysis seems to be a suitable way to recover materials and energy from wastes plastic without selectivity of plastic type (thermoplastic or thermosetting) [28], component separation or sorting into various plastic type [27], provided an efficient method for reducing toxic compounds is applied.

In this reviews, we present conventional approach for plastics waste management with emphasis on their drawbacks and critical review on pyrolysis techniques as an effective depolymerisation approach for energy and resource recovery from waste plastics.

2. Conventional approach for plastic wastes management

The conventional and new technologies for plastic waste management are shown in Figure 1. The conventional methods include:

2.1. Landfilling

Landfilling is the most common conventional approach for waste management in many countries, however, due to increasing human population and consequential urbanization has lead to scarcity of space for landfills. Plastic waste landfilling is the least favoured waste management option today because of growing environmental and public health concern. The types and quantities of toxic chemicals and their potential for leaching at landfill sites into groundwater is a huge public health issue [29].

2.2. Incineration or open burning

Open burning of plastics fraction in municipal solid waste (MSW) is an old practice that is still prevalent in most communities around the world especially in underdeveloped and developing countries. Incineration of plastic waste in open fields is a major source of air pollution. About 12 percent of most municipal solid waste is made up of plastics of different kind, and 40 percent of the world's garbage is burned [30].

The burning of plastics releases toxic gases like dioxins, furans, mercury and polychlorinated biphenyls (better known as BCPs) into the atmosphere, and poses a threat to vegetation, and human and animal health [20]. Disposal of waste into landfills implies an irreversible loss of valuable raw materials and energy. The incomplete combustion of Polyethylene (PE), Polypropylene (PP) and Polystyrene (PS)

during open burning can cause high concentrations of carbon monoxide (CO) and noxious emissions, while PVC generates dioxins, carbon black and aromatics like pyrene and chrysene.

Furthermore, the by-products of plastic combustion are airborne particulate emission (soot) and solid residue ash (black carbonaceous colour). Many studies have reported that soot and solid residue ash possess a high potential of causing health and environmental concerns, especially Volatile organic compounds (VOCs), semi-VOCs, smoke (particulate matter), particulate bound heavy metals, polycyclic aromatic hydrocarbons (PAH's), polychlorinated dibenzofurans (PCDF's) and dioxins [20,31].

Currently, landfills and dumpsites pose threat in most cities around the world as plastic fraction in MSW is burnt along with other wastes, a concerted and deliberate effort is needed to communicate information about danger of this practice, its health and environmental consequences in the long and short time.

2.3. Mechanical recycling

Mechanical recycling of plastics refers to the processing of plastics waste into secondary raw material or products without significantly changing the chemical structure of the material. In principle, all types of thermoplastics can be mechanically recycled with little quality impairment which depends on the number of time the article is recycled. Additions of additive and blending with virgin plastic could help improve the quality of the new article. It is currently the almost, if not, the sole form of recycling in most countries, representing more than 99% of the recycled quantities.

The burden from collection, sorting, transport and recycling operations tends to render the process cost ineffective; as such most plastic processing companies tends to prefer the use of virgin material to the detriment of the environment.

Mechanical recycling of plastic wastes can be classified into: downcycling and upcycling.

2.3.1. Downcycling of plastic waste

Downcycling, is the recycling of plastic waste where the recycled material is of lower quality and functionality than the original material. However, unlike other materials like glass and metal, recycled plastics are not able to continually serve the same purpose after recycling. This is usually so because plastics tend to lose certain qualities like, mechanical integrity, optical clarity and other inherent properties, as such renders it unfit for its initial application. For example, a plastic water bottle may be downcycled to become artificial turf or plastic furniture. Generally, mechanical recycling of plastics by heating and rmoulding operations leads to downcycling in the long run; this is because the material overtime is no longer suitable for articles with stringent engineering requirements.

2.3.2. Upcycling of plastic waste

Upcycling, also known as creative reuse, is the process of transforming waste plastic materials into new materials or products perceived to be of greater quality, such as artistic value or environmental value. For example, Plastic bottles can be upcycled into flower pots, bird feeders, garden sprinklers, green parking canopy, chandeliers, Christmas trees, kid's toys, and more. However, as stated earlier in 2.3.1 above, if heating and remoulding is involved in the repurposing process of waste plastics articles is not able to serve in most stringent engineering application over time, hence are downcycled. Upcycling of waste single and mixed plastics have been achieved through thermo-chemical processes. pyrolysis is one of such thermo-chemical processes techniques that is gaining much attention today.



Figure 1. Conventional and new technology for plastics waste management.

3. Pyrolysis

Pyrolysis is the thermal degradation of plastic waste at different temperatures (300–900°C), in the absence of oxygen, to produced liquid and gaseous fuel [9]. In pyrolysis, feedstock such as waste plastic is heated in the absence of oxygen or low-oxygen environment and, instead of burning, breaks down into mixture of simpler hydrocarbons. This process is simply thermal depolymerisation, plastics are made from small building blocks (monomers) through a process known as polymerization. Pyrolysis is a process that revert used, discarded plastics into valuable resource in the form of monomers, fuel and other useful resources.

Pyrolysis presents a several advantages over other conventional waste plastic management approaches. For instance most waste plastics during recycling are down cycled; plastics are used in producing articles of lower quality and application. This is because the plastic tends to lose properties such as clarity, strength and flexibility as they are recycled again and again.

Secondly, the cost associated with sorting, washing and blending before waste plastics are recycled mechanically is completely non-existing in pyrolysis technique.

Furthermore, mechanical recycling involves melting and remolding of used or discarded plastics into new articles. This implies that only wastes from thermoplastic articles are suitable for this technique, therefore thermoset fraction will persist in the dumpsites since they cannot be remolded. On the other

hand, in pyrolysis techniques, both thermoset and thermoplastic can be used as feedstock [26]. Pyrolysis technique can also be used to treat waste of many novel materials, such as composites [32], especially in the emerging technology were polymer composites are replacing traditional materials in most engineered application.

Finally, depending on the feedstock composition, process condition (temperature, heating rate, reaction gas) and presence of catalyst (catalytic pyrolysis) or absence of catalyst (thermal pyrolysis), the product and yield composition can be varied.

3.1. Classification of pyrolysis base on heating rates

3.1.1. Slow pyrolysis (non-isothermal)

Slow pyrolysis is the slow heating of the feedstock in absence of oxygen. Instead of combusting, the volatiles from the organic material evaporate partly, and a product (char) remains, consisting for a large part (normally 80%) of carbon. Slow pyrolysis is also called carbonisation, and emphasises the solid char as main product, instead of fast pyrolysis which emphasises the liquid product. Heating rates is kept at 10°C/s.

3.1.2. Fast pyrolysis (Isothermal)

Fast pyrolysis involves rapidly heating the feedstock to moderate temperatures (400–600°C) at short residence time (few seconds) to yield high amount of pyrolysis liquid fuel. Fast pyrolysis provides a condition to maximize the production of the liquid, the reactor is considered to operate isothermally. It is the most common of the methods, both in research and in practical use in pyrolysis of plastics. Heating rates is kept at 100° C/s.

3.1.3. Ultra-fast/flash pyrolysis.

Ultra-fast, or flash pyrolysis is an extremely rapid thermal decomposition pyrolysis, with a high heating rate, the main products are gases and bio-oil. Heating rates can vary from 100–10,000°C/s and residence times are short in duration.

3.2. Other classification of pyrolysis

3.2.1. Thermal pyrolysis technique

Thermal cracking or pyrolysis involves the depolymerisation or cracking of the plastics materials by heating them to a very high temperature in the absence or low oxygen environment. The temperature ranges between 350 and 900°C. The products formed include; gaseous, liquid and carbonized char (solid residues). The liquid fuel is usually recovered from the condensable fraction of the volatile product, while the remaining is a noncondensable high calorific value gas.

Thermal pyrolysis is a thermochemical treatment (TCT) its liquid product is a mixture of paraffins, isoparaffins, olefins, naphthenes, and aromatics. Because of chain scission, breaking of bonds, the

intermolecular and intramolecular forces, elevated temperatures of up to 900°C are required [33]. Scott et al. [34] reported in their work that at temperatures lower than 700°C the major part of the product yielded was solid, whereas at higher temperatures the main product was a gas. Thermal pyrolysis of most single plastics has been widely reported in literature. The physical properties of the liquid fuel obtained by this process largely vary with the plastic type [35]. Table 1, Gave a summary of some of the properties of liquid fuel from the pyrolysis of different single plastics as reported in literatures.

Plastic fuel	Density 40°C (g/cm ³)	Viscosity at 40°C (cSt)	Flash point (°C)	Calorific value (MJ/kg)	Appearance	References
HDPE	0.800-0.920	2.420-2.52	40–48	45.4	Light oil,	Kunwar, et al.
					Brown	[36]
LDPE	0.768-0.8020	1.650-1.801	50	39.1	Light oil,	Shah, et al.
					Brown	[37]
РР	0.767-0.80	2.72	31–36	40	Light oil,	Yohandri, et
					Yellow	al. [38]
PET	0.087-0.90	NA	NA	28.2	Light oil,	Honus, et al.
					Brown	[39]
PS	0.85-0.86	1.4 at 50°C	28	43.0	Light oil,	Miandad, et al.
					deep brown	[40]

Table 1. Some properties of liquid fuel from the pyrolysis of single plastic feed.

Note: NA: not available in literature.

Furthermore, analysis of chemical properties on the produced liquid fuel by thermal pyrolysis technique has shown that it is a mixture of various hydrocarbons Table 2. The chemical properties of the liquid product vary from the other depending on plastic type. The comparative study of chemical structures HDPE, LDPE, PP, PS and PET shows that in HDPE and LDPE similar $-CH_2$ - and $-CH_3$ - group appear in their polymer chain. However, PS and PET in mixed feed contain aromatic benzene compound [41] which are completely not found in HDPE, LDPE products.

Plastic	Temperature (°C)	Liquid yield (%)	Elemental composition (%)			Carbon number distribution	References	
			С	Н	Ν	0		
HDPE	460	86	85.3	14.2	0.5	0.00	C ₃ -C ₂₈	Kunwar et al. [36], Olufemi, et al. [41]
LDPE	430	75.6	85.3	14.2	0.5	0.00	C ₅ -C ₂₈	Olufemi, et al. [41],
РР	350 250	70 45	85.61	14.38	0.00		C ₃ -C ₂₅	Yohandri et al. [38], Olufemi et al. [41]
PS			92.32	7.73	0.00	0.00	NA	Honus, et al. [39]
PET	450 600	59.50 67.70	62.10	4.21	-	33.69	NA	Honus, et al. [39]

Table 2. Yield, carbon distributions and elemental composition of some plastic pyrolysis liquid fuel at various temperatures.

Note: NA: not available.

3.2.2. Microwave-assisted pyrolysis technique

Microwave pyrolysis (also known as microwave-assisted pyrolysis) is pyrolysis that involves microwave dielectric heating. Microwaves interact in three ways with different materials; it is reflected by conductors, transmitted by perfect insulators, or absorbed and decayed on the way inside materials depending on their dielectric properties. The heat is generated in dielectric materials due to agitation of molecules by the alternating electromagnetic fields. The mechanism of plastic microwave pyrolysis is based on absorbing the microwave energy via absorbent and subsequently transferring thermal heat to the plastic via conduction. The physical properties and the volume ratio of the absorbent affect the uniformity of heating distribution. Furthermore, different microwave power gives completely different product distribution.

It has been established that microwave induced pyrolysis can be used to get value added chemicals and fuels through its numerous noted advantages in contrast to thermal and catalytic pyrolysis [42]. The process has the potential for fast, volumetric and selective heating of plastics for the recovery of energy. However, plastics cannot absorb microwave energy, as it has a very low dielectric loss factor. Therefore, an absorbent must be mixed with the plastic to aid in heating the plastic in pyrolysis. Materials with high dielectric loss factor are good candidates as absorbents for plastic pyrolysis e.g. tyre shredded and silicon carbide [43], carbon [44], iron mesh [45]. Microwave pyrolysis of most single plastic types has been reported in literature. Some of these plastics are; polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET) and polyvinylchloride (PVC). None of these plastics is able to absorb microwave without the use of microwave absorbent. Table 3 below summarizes the yield (solid, liquid and gaseous), absorbent to polymer ratio, run time and microwave power of the above mentioned five plastic types using Tires instead of coal as microwave absorber.

Plastic	Microwave	Time (min)	Absorbent-	Solid	Liquid	Gas (wt%)
	power range		plastic ratio	(wt%)	(wt%)	
	(KW)					
HDPE	3	75	1:2	0.40	83.92	15.68
PP	3	68	1:2	15.89	70.82	13.29
PVC	3	21	1:2	14.69	3.44	81.87
PET	1.8–3	40	2.51	38.20	35.32	26.48
PS	3–6	59	1:2	6.83	89.25	8.92

Table 3. Microwave pyrolysis: correlation between microwave power and yield using Tires as microwave absorber.

Note: Source: Undri et al. [46].

3.2.3. Catalytic pyrolysis technique

Catalytic pyrolysis involves the degradation of the polymeric materials by heating them in the absence of oxygen and in the presence of a catalyst. Catalysts are employed in plastic pyrolysis primarily to lower the energy requirement, influence the composition of the product through cracking and reduce the process time. The most commonly used catalysts reported in the literature for plastic waste pyrolysis includes silica alumina [47], zeolites [48], fluid catalytic cracking (FCC) [49] and mobil classification of materials (MCM-41) [10]. Higher conversion is usually achieved with zeolite-based catalysts due to their high acid strength compared to nonzeolitic catalysts, as such tends to give more gaseous product.

The conversion of polyethylene into gasoline-range fuels by two-stage catalytic degradation using silica-alumina and HZSM-5 zeolite was studied by Uemichi et al. [50]. They reported that two-stage method provides some advantages compared with the one-stage degradation over each catalyst. There was an improved gasoline yield and a high octane number despite low aromatics content. Significant results were obtained when silica-alumina and HZSM-5 were used in a weight ratio of 9:1 as upper and lower catalysts, respectively, in a flow reactor. The reverse sequence of catalysts showed no advantage. It was suggested that large pores and moderate acidity of the silica-alumina loaded in the upper layer operated favorably to catalyze the degradation of polyethylene into liquid hydrocarbons. The resulting oils showed low quality, and they were transformed into high-quality gasoline on the strongly acidic sites of the HZSM-5 loaded in the lower layer at the expense of oil yield.

Ratnasari et al. [10] reported a study on catalytic pyrolysis of waste plastics using staged catalysis for production of gasoline range hydrocarbon oils. The catalytic process involved staged catalysis, where a mesoporous catalyst was layered on top of a microporous catalyst with the aim of maximising

the conversion of the waste plastic to gasoline range hydrocarbons. The catalysts used were mesoporous MCM-41 followed by microporous ZSM-5, and different MCM-41: zeolite ZSM-5 catalyst ratios were investigated. The MCM-41 and zeolite ZSM-5 were also used alone for comparison. The results showed that using the staged catalysis a high yield of oil product (83.15 wt%) was obtained from high density polyethylene at a MCM-41: ZSM-5 ratio of 1:1 in the staged pyrolysis-catalysis process. The main gases produced were C_2 (mainly ethene), C_3 (mainly propene), and C4 (mainly butene and butadiene) gases. In addition, the oil product was highly aromatic (95.85 wt% of oil) consisting of 97.72 wt% of gasoline range hydrocarbons.

Furthermore, Uddim et al. [51] studied the degradation of four different types of polyethylene (PE) namely high density PE (HDPE), low density PE (LDPE), linear low density PE (LLDPE), and crosslinked PE (XLPE) was carried out at 430°C by batch operation using silica-alumina as a solid acid catalyst and thermally without any catalyst. For thermal degradation, both HDPE and XLPE produced a significant amount of wax-like compounds and the yields of liquid products (58-63 wt%) were lower than that of LDPE and LLDPE (76-77 wt%). LDPE and LLDPE produced a very small amount of waxlike compounds. Thus the structure of the degrading polymers influenced the product yields. The liquid products from thermal degradation were broadly distributed in the carbon fraction of n-C₅ to n-C₂₅ (boiling point range, 36-405°C). With silica-alumina, all of the polyethylenes were converted to liquid products with high yields (77-83 wt%) and without any wax production. The liquid products were distributed in the range of n-C₅ to n-C₂₀ (mostly C₅-C₁₂). A solid acid catalyst indiscriminately degraded the various types of polyethylene into light fuel oil with an improved rate [52,53] in separate studies on the effect of nonacidic catalysts for the pyrolysis of plastics using BaCO₃ and MgCO₃, observed that the % oil yield for MgCO₃ and BaCO₃ is 33.60% and 29.60% respectively when used as catalyst at 450°C pyrolysis of High-density polyethylene. In addition, when CaCO₃ was used as a catalyst under the same reaction conditions, the obtained % oil yield was 32.20%.

Recently, many researchers have focused on the use of clay as catalyst for plastic pyrolysis [26,27,42]. Hakeem et al. [54] carried out research on catalytic pyrolysis of waste polypropylene using Ahoko kaolin from Nigeria. They reported that in the absence of Ahoko kaolin, the process gave yields of liquid, gaseous, and solid products of 67.48, 8.85, and 23.67 wt%, respectively, but with the kaolin clay in catalytic pyrolysis of the same feedstock for catalyst-to-plastic ratio of 1:1, 1:2, 1:3, and 1:4 at the same operating parameters as in thermal cracking. Optimum yield was obtained at a catalyst-to-plastic ratio of 1:3 with a yield of 79.85, 1.48, and 18.67 wt% for liquid, gaseous, and solid products, respectively.

Catalytic Cracking of Polyethylene over Clay Catalysts and Comparison with an Ultrastable Y Zeolite was conducted by Manos et al. [48], they reported that the clays were found to be less active than US-Y zeolite around 600K, at slightly higher process temperatures, they were able to completely decompose polyethylene. Their yields to liquid products were around 70%, compared to less than 50% over US-Y zeolite. They also observed that the liquid products obtained over the clay catalysts were heavier. These they attribute to the milder acidity of clays.

(1) Effect of Catalyst Contact Mode

There are two basic modes by which catalyst can be used in the pyrolysis of plastics in a reactor: liquid phase contact (in-situ) and vapor phase contact (ex-situ). In the former, the catalyst and polymer are mixed together, and then they are placed in the reactor and heated to appropriate reaction temperature (Figure 2a). However, in the later, the polymer is first subjected to thermolysis to produce

the volatile fraction. The catalyst is introduced in the path of the moving vapour, and as the vapour passes through the catalyst, the hydrocarbon vapour is cracked to get the required product distribution (Figure 2b). Xue et al. [55] studied the effects of feedstock-catalyst contact mode for polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET). It was found that in-situ catalytic pyrolysis produces higher yields of aromatics than ex-situ catalytic pyrolysis for PET, PE and PP. For PS, ex-situ catalytic pyrolysis produced more aromatics than in-situ catalytic pyrolysis because of a high yield of styrene in the products. They concluded that the variations in the product composition from the two modes suggest that the depolymerization of the plastics occur at different reaction mechanisms.



Figure 2. A typical set-up for (a) in-situ and (b) ex-situ plastic pyrolysis (Source: Xue et al. [55]).

(2) Effect of polymer to catalyst ratio

Several studies have reported that polymer to catalyst ratio has significant effect on both the yield and composition of plastic pyrolysis products. However, it can be concluded that with the increase in the amount of catalyst, a direct proportionality in terms of increase in conversion or general effectiveness is not obtained. The increase in catalyst amount increases the conversion up to particular limit, but a further increase in the catalyst percentage does not give any appreciable increase in the conversion rate. Nnamso et al. [56] studied the effect of polymer to catalyst ratio in the degradation of polyethylene over ultrastable Y zeolite catalysts. An initial sharp increase was observed at lower catalyst to polymer ratio,

afterwards a negative correlation was observed with further increase in catalyst composition, showing a maximum at a value around 7% of pure US-Y.

(3) Effect of temperature

Temperature has a strong effect on the pyrolysis process, if the catalytic pyrolysis is taking place at higher operating temperature or at high heating rates, it enhances bond breaking as such tends to favour the production of smaller molecules [57,58]. As the extent of conversion increases with increase in temperature, formation of gaseous product is improved with resulting decrease in liquid products. The effect of different catalysts on the liquid yield and the product distribution becomes less significant with increasing temperature this is because the reaction taking place becomes similar to thermal degradation. Basically, catalytic pyrolysis of plastics proceeds at much lower temperature compared with thermal pyrolysis under the same process condition [59,60]. Increase in the cracking rate at lower temperatures was observed under catalytic conditions [61].

(4) Effect of flow rate of nitrogen Gas

Nitrogen is an inert gas, as such does not interfere with the pyrolysis reaction going on inside the reactor. However, it enhances the movement of volatiles into the condenser thereby leading to availability of gases for condensing into liquid fuel. Usually the nitrogen flow rate is kept at about 10 mL/s for most plastic pyrolysis reported in literature [62].

Nowadays, pyrolysis technology is more and more widely used in the waste plastic management instead of landfill or recovery through secondary recycling, since it can convert various kinds of waste plastics to liquid fuel, which can not only effectively manage waste plastic but also bring very good economic benefit.

4. Advantages of using pyrolysis technology in plastic waste management

4.1. High heating value

The liquid fuel from plastic waste is usually heavier compared to conventional commercial grade fuel, consequently has higher heating value slightly lower or greater than 10,000 kcal/L [63,64]. This property is an advantage for fuel used in boilers, cement factory, steel mill and glass factories.

4.2. Feed selectivity

Pyrolysis technology is suitable for almost all kinds of waste plastic, clean or unwashed and unsorted. For a batch waste plastic pyrolysis plant, no need to do the shredding works. All the processes from plastic to fuel are carried out inside the waste pyrolysis reactor together with its accessory system, very convenient and man-power saving. Co-pyrolysis of plastics with waste paper [65], biomass [66] and even plastics from medical wastes [67] has also been reported.

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4.3. Pyrolysis of mixed waste plastics

A major advantage of pyrolysis technology for plastic waste management is its ability to use various types and class of plastics as a single feedstock without the need for disassembling and sorting. Unlike recycling, pyrolysis does not require a careful sorting of different plastics. Most plastics are not compatible with each other consequently, cannot be processed together during recycling. For example, a little fraction of PVC in PET recycle stream will degrade the whole PET resin by becoming yellowish and brittle [68].

Demirbas [69] on polyolefin and PS mixture collected from landfill which was approximately 46.6 wt% of total plastic waste yielded 35 wt% of solid and of 2.2 wt% of gas. Baiden [67] carried out pyrolysis of mixed waste plastics comprising HDPE, LDPE, PP and Thermoplastic Polyurathane, TPU. They reported that the highest liquid product yield was obtained using 80 V for 55 min and was 89.5 wt% of the initial weight of the plastic waste sample pyrolyzed. The recorded maximum reaction temperature recorded for this yield was 497–500°C.

Donaj et al. [70] conducted a study on pyrolysis of polyolefin mixed plastics. The mixed plastics consist of 75 wt% LDPE, 30 wt% HDPE and 24 wt% PP. They conducted two sets of experiments at 650 and 730°C by thermal pyrolysis and at 500 and 650°C using Z–N catalyst in fluidized quartz-bed reactor. The ratios of gas/liquid/solid mass fractions via thermal pyrolysis were: 36.9/48.4/15.7 wt%. and 42.4/44.7/13.9 wt% at 650 and 730°C while via catalytic pyrolysis were: 6.5/89.0/4.5 wt% and 54.3/41.9/3.8 wt% at 500 and 650°C, respectively.

Pratama and Saptoadi [71] studied the pyrolysis of mixed waste plastics in two stages batch reactors: pyrolysis and catalytic reforming reactor, at maximum temperature 500°C and 450°C respectively. They used Waste Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Polyethylene Terepthalate (PET) were used as raw material. They reported that the highest weight percentage of liquid fuel derived from mixture of PE waste (50 wt%), PP waste (40 wt%) and PS waste (10 wt%) is 45.13 wt%.

Eze et al. [26] conducted a study on thermal and catalytic pyrolysis using five different types of plastics that dominates in municipal solid wastes stream, mimicking the proportion in which they are found. Figure 3 shows the composition of the feedstock and yield.

The catalyzed liquid sample with the optimum yield of 46.7wt% was obtained using 10.49 wt%, 32.42 wt%, 27.09 wt% and 30 wt%, of Zeolite-Y, metakaolin, aluminun hydroxide and sodium silicate respectively as catalyst, while the thermal pyrolysis gave a liquid yield of 66.9 wt% (Figure 3).

The use of the zeolite-Y base catalyst led to reduction of pyrolysis temperature from 490°C to 350°C, this is a huge energy reduction for the overall process. Some of the physical properties reported in this study include; density at 23°C (0.8945 g/cm³), dynamic viscosity at 32°C (2.03 mPa.s), fire point (90°C) and calorific value (14,751 J/g) for thermal pyrolysis. The corresponding values for catalytic pyrolysis were density at 23°C (0.8336 g/cm³), dynamic viscosity at 32°C (1.03 mPa.s), fire point (84°C) and calorific value (24,919 J/g) respectively.



Figure 3. Feed composition and yield of mixed plastics pyrolysis (Source: Exe et al. [26]).

4.3.1. Chemical properties of liquid fuel from mixed plastic waste pyrolysis

Gas Chromatography and Mass Spectrometer (GC/MS) analysis of most studies on mixed waste plastics (MWPs) liquid fuel reveals that catalysed liquid fuel contain light liquid product with carbon range C_6-C_{13} and absence of long chain alkanes and alkenes such as Eicosane, nonadecane, heptadecane, octadecene, pentadecane, tetradecane and undecene compared to the thermal pyrolysis liquid product with carbon range of C_7-C_{20} [26,54,67,72].

Wathakit et al. [72] studied the chemical compositions and physicochemical properties of distilled waste plastic oil (WPO) and crude waste plastic oil (CWPO). The experimental results show that CWPO contains the highest percentage of carbon atoms in the C_4 – C_{11} group, while WPO contains the highest percentage of carbon atoms in the C_{12} – C_{20} group, similar to the main compositions of diesel fuel.

Similarly, Eze et al. [26] studied the effect of zeolite-y based catalyst on pyrolysis fuel from mixed waste plastics comprising HDPE, LDPE, PP and PS in the ratio shown in Figure 3. The result of the study revealed that catalysed liquid sample consist of predominantly gasoline (93%) and 7% diesel range of fuel compared to the thermal pyrolysis liquid sample with 59%, 36% and 5% of gasoline, diesel and fuel oil respectively Table 4. The organic elemental analysis (CHNS) result of the MWPs for both thermal and catalysed sample with optimum yield is shown in Table 5. Sulphur content of the catalysed pyrolysis fuel was slightly lower than that of the thermal pyrolysis product; this can be attributed to the activities of the catalyst. Lower sulphur content is necessary to reduce possibility of formation of sulfur oxides (SOx) when fuel is burn in internal combustion engines [73]. The sulphur content of MWPs for both thermal and catalysed samples are significantly higher than gasoline (0.014%), diesel (0.15%), and other types of fuel oil because waste plastic contains some contamination [63]. However, plastic pyrolysis fuel can be subjected to desulphurization to bring its sulphur content to acceptable limit.

	Gasoline (wt%) (C ₆ –C ₁₂)	Diesel (wt%) (C ₁₃ –C ₁₈)	Fuel oil (wt%) (C ₁₉ –C ₂₃)	Residual fuel (wt%) (C ₂₄)
Thermal pyrolysis	59	36	5	-
Catalysed pyrolysis	93	7	-	-

Table 4. Range of hydrocarbon and fuel type distribution in the thermal pyrolysis and catalysed liquid fuel samples.

Note: Source: Eze et al. [27].

Table 5. Elemental analysis of mixed waste plastic pyrolysis liquid samples.

Wt%	Thermal pyrolysis	Catalysed pyrolysis
С	94.24	97.11
Н	11.73	10.12
Ν	0.61	0.28
S	4.8	4.36

Note: Source: Eze et al. [27].

5. Disadvantages of using pyrolysis technology in Plastic waste management

5.1. High sulphur content

Liquid fuel from plastic waste has higher sulfur content than conventional fuel, even though many industries are equipped with environment protection devices to scrubber the smoke produced in the heating process, this becomes a huge concern for automobile and transportation fuel. The presence of sulphur in vehicle fuels causes emissions of oxides of sulphur into the atmosphere which is a major contributor of acid rain.



Figure 4. Sulphur content of different types of fuel oil (Source: Khan et al. [63]).

Liquid fuel from pyrolysis of different plastic types has been reported to have sulphur content significantly higher than conventional gasoline, kerosene and commercial grade diesel. Khan et al. [63] carried out pyrolysis of High density polyethylene, HDPE, to obtain waste plastic pyrolysis oil (WPPO). They reported sulphur content of 0.246% for the WPPO which is significantly higher than 0.15% for diesel and 0.014% for gasoline Figure 4. Furthermore, Eze et al. [27] reported that the sulphur content of both thermal (4.8%) and catalytic (4.36%) pyrolysis liquid fuel obtained from mixed waste plastics Table 3, are higher than the desired acceptable standard for low sulphur and ultra low sulfur fuel [74].

5.2. Lower flash point

The flash point of liquid fuel from plastic waste is <40 degrees, though it may vary depending on the plastic type used as feed. For single feed plasticlike polyethylene it could be as low as 10 degrees. The flash point of conventional diesel is about 50 degrees. A low flash point indicates the presence of highly volatile materials in the fuel that is a serious safety concern in handling and transporting [63].

6. Conclusions

Authorities around the world are intensifying their call for ban of certain catigories of plastics; this is because the conventional approaches have not impacted the environment positively. Furthermore, mechanical recycling of plastics is being considered as one of the most widely accepted remedies to the threat of growing volume of plastic waste by both the public and scientists. In practice, the approach is associated with many difficulties, such as problems related to separation, sorting and cleaning operations, high transport and electricity costs, coupled with feed stock selectivity.

Instead of combustion and incineration, pyrolysis can be another alternative method which is known to produce less toxic substances provided the process conditions are appropriate; fuel and several other useful raw materials are recovered in the process. Furthermore, the increasing amounts of plastic waste and the increasing fraction of thermosetting plastics highlight the importance of pyrolysis as a holistic approach. However, there are understandable issues surrounding the toxic byproducts generated by the pyrolysis of certain plastics like polyvinyl chloride, this can be negated through proper feedstock selection. Finally, liquid fuel from plastic pyrolysis may not be suitable for most engineered application due to high sulphur content. However, by further treatment and blending with commercial grade fuel, this can be circumvented.

Conflict of interest

The authors declare no conflict of interest.

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