

Strategies for conversion of recyclable plastic waste to fuels – A Review

K. S. R. Murthy^{1,*}, Srinivas Tadepalli²

¹ *Department of Chemistry, Applied Science Cluster, School of Engineering, University of Petroleum and Energy Studies, Dehradun 248007 INDIA*

² *Department of Chemical Engineering ; Imam Mohammad Ibin Saud Islamic University, P.O Box 5701, Riyadh -11432 Saudi Arabia*

** Author for correspondence: srmurthy@ddn.upes.ac.in; Mobile : +91 9557382753*

Abstract

Plastic waste generation has increased enormously over the past decades. The recycling techniques of waste plastics presently used include filling, incineration, chemical or mechanical recycling, and conversion to fuel. There are several conversion techniques are currently in use, they include thermal pyrolysis, catalytic pyrolysis, co-pyrolysis and gasification. The techniques used depend on the types of plastic waste. The fuel oils from waste plastics have properties (calorific value, density, and viscosity), which are better or equal to that of commercial diesel fuel. This paper aims to conduct a feasibility study and strategies for producing fuel from plastic waste. It is a suggested approach to deal with the huge production of synthetic plastic around the world, to avoid its accumulation in landfills and the depletion of resources. Several types of research have addressed the conversion of plastic waste into energy, and in this study, the author focused on using various strategies concerning pyrolysis to convert plastic to liquid oil. Accordingly, the volume of the waste was reduced significantly, and the produced liquid oil had a high calorific value in comparison to fossil fuel. The conversion of plastic waste into fuel helps to resolve two important problems: one is avoiding the negative impacts of plastic pollution on the environment and the second is to produce an alternative fuel for diesel engines, thus reducing the demand for fossil fuels.

Introduction:

Plastics have become an indispensable part of today's world, due to their lightweight, durability, and energy efficiency, coupled with a faster rate of production and design flexibility; these plastics are employed in an entire gamut of industrial and domestic areas; hence, plastics have become essential materials and their applications in the industrial field are continually increasing. At the same time, waste plastics have created a very serious environmental challenge because of their huge quantities and their disposal problems. Waste plastic pyrolysis in liquid fuel (gasoline, diesel oil, etc.) or chemical raw materials not only can effectively solve the problem of white pollution but also can alleviate (reduce) the energy shortage to a certain extent. Recycling waste plastics is expected to become the most effective way. Waste plastics' recycling, regeneration, and utilisation have become a hot spot of research at home and abroad and gradually formed a new industry.

The increase in the use of plastic products caused by a sudden growth in living standards had a remarkable impact on the environment. Plastics have now become indispensable materials, and the demand is continually increasing due to their diverse and attractive applications in households and industries. Mostly, thermoplastic polymers make up a high proportion of waste, and this amount is continuously increasing around the globe. Hence, waste plastics pose a very serious environmental challenge because of their huge quantity and disposal problem as thermoplastics do not biodegrade for a very long time. The consumption of plastic materials is vast and has been growing steadily because of the advantages derived from their versatility, relatively low cost, and durability (due to their high chemical stability and low degradability). Some of the most used plastics are polyolefins such as polyethylene and polypropylene, which have a massive production and consumption in many applications such as packaging, building, electricity and electronics, agriculture, and health care [1]. In turn, the property of high durability makes the disposal of waste plastics a very serious environmental problem, landfilling being the most used disposal route. Plastic wastes can be classified as industrial and municipal plastic wastes according to their origins; these groups have different qualities and properties and are subjected to different management strategies [2, 3]. Plastic materials production reached global maximum capacities levelling at 260 million tons in 2007, whereas in 1990 the global production capacity was estimated at 80 million tons [1]. Plastic production is estimated to grow worldwide at a rate of about 5% per year [4]. Polymer waste can be used as a potentially cheap source of chemicals and energy. Due to the release of harmful gases like dioxins, hydrogen chloride, airborne particles, and carbon dioxide, the incineration of polymer possesses serious air pollution problems. Due to high cost and poor biodegradability, it is also undesirable to dispose of by landfill. Recycling is the best possible solution to the environmental challenges facing the plastic industry. These are categorized into primary, secondary, tertiary, and quaternary recycling. Chemical recycling, that is, the conversion of waste plastics into feedstock or fuel has been recognized as an ideal approach and could significantly reduce the net cost of disposal. The production of liquid hydrocarbons from plastic degradation would be beneficial in that liquids are easily stored, handled, and transported. However, these aims are not easy to achieve [4]. An alternative strategy to chemical recycling, which has attracted much interest recently, to convert waste plastics into basic petrochemicals is to be used as hydrocarbon feedstock or fuel oil for a variety of downstream processes [3]. There are different methods of obtaining fuel from waste plastic such as thermal degradation, catalytic cracking, and gasification [3, 5].

Current Scenario of Plastics

Over many years, drastic growth has been observed in the plastic industry such as in the production of synthetic polymers represented by polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl alcohol (PVA), and polyvinyl chloride (PVC). It has been estimated that almost 60% of plastic solid waste (PSW) is discarded in open spaces or landfilled worldwide. According to a nationwide survey conducted in the year 2003, more than 10,000 MT of plastic waste is generated daily in our country, and only 40 wt% of the same is recycled; the balance 60 wt% is not possible to dispose of [4].

India has been a favoured dumping ground for plastic waste mostly from industrialized countries like Canada, Denmark, Germany, the U.K., The Netherlands, Japan, France, and The United States of America. According to the government of India, import data of more than 59,000 tons and 61,000 tons of plastic waste found their way into India in the years 1999 and 2000, respectively [3, 6]. India pledges to combat plastic pollution as part of World Environment Day, 2018. The theme of this paper is to comprehend the current scenario of Plastic Waste Management (PWM) in India, particularly in the context of achieving sustainable development goals in 2030. It is estimated that out of the 8.3 billion metric tons of plastic produced globally as of date, 6.3 billion metric tons end up as trash, whereas only 9% is recycled, 12% is incinerated and the rest 79% is accumulated in landfills. It is anticipated that global plastic waste totals 4.9 billion tonnes and will reach 12 billion tonnes by 2050. India generates around 56 lakh tonnes of plastic waste annually and Delhi being the highest generator of plastic waste in India accounts for 9,600 MT per day among the top ten cities, followed by Chennai, Kolkata, Mumbai, Bangalore and a few others. The paper presents a general overview of plastic waste inventorization, composition and its effects on health and the environment. It discusses the legislation governing Plastic Waste Management and Handling Rules (2011, 2016 and 2018) in India, amendments, the current status of implementation as well as opportunities and challenges in PWM. A small survey is carried out to thoroughly understand PWM in a community. Critical gaps between the legislation framed and its enforcement are identified. This paper also appraises the concept of 4R's in PWM and their role in the circular economy. Global initiatives on the ban of plastics, and collection and recycling mechanisms of plastic waste are addressed and compared with the Indian scenario. Responsible production and consumption of plastics, and emerging trends in PWM about Integrated Waste Management (IWM) are highlighted. To conclude, the authors provide the best possible options and divergent solutions for tackling plastic waste from an Indian perspective towards turning vision into reality.

A global material balance study on plastics points out that **79 per cent** of the total plastics produced in the world enters our environment as waste. Only **9 per cent** of the total plastic waste in the world is recycled. A Central Pollution Control Board (CPCB) report (2018-19) puts the total annual plastic waste generation in India at a humongous **3.3 million metric tonnes per year**. Even this data, frightening as it is, might be an underestimation [7-9]. While India's plastic waste problem is not as huge as that of the rich world, it is growing. Richer states like Goa and Delhi produce as much as **60 grams and 37 grams per capita per day** respectively – against a national average of **8 grams per capita per day**.

An estimated 318 million tonnes of plastic resin is produced every year, much of it directly contributing to the 218 million tonnes of total annual solid plastic waste generation as a part of Municipal Solid Waste (year of reference: 2016). Global average plastic recycling rates are only 15%, while around 40% (90 million tonnes per year) is mismanaged and ultimately leaked to the environment by littering, and stormwater washouts like that. It is estimated that around 50 million tonnes per year of plastic waste are openly burned, whilst 10 million tonnes per year enter the ocean's aquatic environment. Land-based sources contribute approximately 90% of plastics entering the oceans.

These facts show that plastic waste is one of the major challenges faced by waste managers today, everywhere on our planet[10]. This is not only due to the high volume of plastic waste generated but also because of designed-in material properties, such as durability, low density and non-degradability. Whilst these properties are beneficial for plastic products, they are undesirable in a solid waste stream, resulting in stress on existing waste management systems or challenges when introducing new waste management practices and easy leaking into the environment as well as long residence times in the environment followed by negative impacts on fauna by entanglement and finally entering the food chain (as microplastic) by mistake.

The major objective here is to establish effective waste collection schemes to minimize open burning and other leakages to the environment. Depending on the local context the use of collected plastic-(rich) waste as an alternative fuel might be a favourable option for managing the quantity of plastic waste whilst making use of the energy content of plastic at the same time. Significant investment is needed to achieve comprehensive processing and subsequent recycling of plastic wastes, so a modern recycling system is not considered feasible for the time being for Case (A) countries. Recycling options, such as using plastics as a substitute for sand or using it to pave walkways and roads should be evaluated from a sustainability point of view more in-depth as to prevent leakage to the environment in an even less desired form, such as microplastics.

Additionally, import restrictions for low-quality plastic waste are the right measure for developing countries to prevent additional stress on local waste management systems that are not yet fit to deal with the quality and quantity of plastic waste that cannot yet be recycled in those localities. Despite the challenging variety of plastics in commerce and thus in the waste stream, there are technologies available, such as Near Infra-Red (NIR) sorting and other mechanical treatment options to process conditioned plastic wastes such that recovered plastics are of sufficiently high quality to serve as secondary material that can replace primary resources. Also, other alternatives, such as feedstock recycling are gaining importance and will expand the available options for high-quality recovery[11-15]. As a matter of fact, so far all these technological processes do result in a certain share of rejects that cannot yet be recycled. This can only be addressed by putting a focus on the design for recycling, packaging and products made (partly) out of plastics. In some cases, considerations of banning the production of certain products made with difficult-to-recycle materials might even be a justifiable option.

Chemical routes

With increased production of plastics comes from increased plastic material wastage, and thus new technologies are needed for waste refining. The development of chemical recycling technologies is motivated by two main needs, which are (i) the need to safely and efficiently process materials difficult to treat with mechanical recycling and (ii) the need to produce recycled materials of high quality. Chemical recycling encompasses a variety of technologies, examples of which are presented in this chapter, including, for example, thermochemical treatments and depolymerization. Basic operation principles, recent developments, and future application areas of the technologies are presented.

Secondary plastic products

Presently, mechanical plastic recycling is already established as a sizable business, and several types of plastic are being recycled for different applications. However, manufacturers of recycled plastics operate in the same market as virgin plastics producers, and due to the rather low oil price and downcycled quality of the plastics, often it is not easy to make recycled plastic production economically competitive. Currently, in the European Union, half of the plastic waste collected for recycling is exported to be treated in countries outside the European Union. It is likely soon, when more recycling routes, including also chemical ones, are brought into use, new value chains for plastics recycling emerge [16]. In this review, examples of current application areas of recycled plastics are presented, including a discussion on future market trends. There are clear signals about the increasing demand for recycled content in plastics.

Health issues and ecological problems of plastic waste

Plastic waste poses a spectrum of risks to wildlife and human populations. In this chapter, we provide an overview of the principal hazards created by discarded plastics. Discussed are entrapment of animals and habitat destruction, hazards related to the ingestion of plastics, and impacts of plastic components on mammalian and human health, with notable outcomes including endocrine disruption, psychological and neurological effects, and impairment of liver and kidney function. Important sources of exposure to plastic components include ingestion of contaminated food products, leaching of plastic components from plastic packaging, and inhalation of microplastics in the form of airborne fibers and dust. Potential strategies for reducing exposure to plastics include the use of nonsynthetic food packaging materials, avoidance of high-risk plastic polymers, avoidance of foods known to be enriched in microplastics, and a reduction of plastic used to decrease production volume and limit the chances of polymers to escape from recycling and solid waste management process streams [17-19]

Efforts to recycle plastic waste have grown in a meteoric fashion over the past two decades, yet the challenges associated with harnessing postconsumer plastics as feedstock for new products are sufficiently severe that the relative amount of plastics recycled remains embarrassingly low [11]. In 2015, approximately 262 MT of municipal solid waste (MSW) was generated in the United States [12]. Of the 262 MT of MSW, a full 13% (34.5 Mt) was constituted of putatively recyclable plastic waste. Of these 34.5 MT of plastic waste, however, only 9% was recycled. This compares with 16% that was incinerated and 75% that was landfilled.

Contrast these low recycling numbers with the striking fact that an energy saving to society of approximately seven barrels of oil is accrued for every ton of mixed plastic waste that is recycled [13] and it becomes self-evident that oil and energy conservation could be astronomical if we could implement an effective recycling strategy. It is possible when we reach the apex of accomplishment by recycling all of the plastic waste, consumption of nearly a quarter billion barrels of oil could be saved each year from the recycling of U.S. plastic alone. Certainly, not all plastics can be as easily recycled as others.

In 2015, about 18% of PET was recycled, while only 10% of high-density polyethylene (HDPE), 6% of low-density polyethylene (LDPE)/linear low-density polyethylene (LLDPE), and < 1% of PP were recycled [12]. A plethora of complexities affects recycling rates, from practical considerations of collection, sorting, and pretreatment (e.g., what contaminants, adhesives, colourants, or residues might be present), to more technical considerations such as chemical reactivity.¹⁰ To better understand the state-of-the-art in addressing these complexities, it is instructive to introduce the four classifications of recycling: primary recycling, secondary recycling, tertiary recycling, and energy recovery. Primary recycling, also known as closed-loop recycling, is the process of taking uncontaminated discarded plastics and directly turning that material into the same “new” product, ideally without loss of properties [14]. A familiar example of this would be to use clean aluminium pipes and use the metal to make new aluminium pipes. Secondary recycling refers to mechanical recycling, wherein the chemical identity of the polymer is unchanged, but the polymer is in some way physically reprocessed, and thus generally used for a different purpose than its original use [15]. An example of this is taking waste tyres and using the rubber crumb as an additive in rubber flooring or park benches. In the context of polymers, the most prevalent problems with primary and secondary recycling are related to stability[20]. As the polymers are continually reprocessed, the polymer may degrade to varying extents, which will have drastic effects on the mechanical properties of the post-recycled product. Additionally, the need for pure/clean plastic waste is a significant barrier when post-consumer, mixed-source plastic is targeted for recycling.

Tertiary recycling, sometimes referred to as chemical recycling, uses chemical processes to break down the polymer into value-added commodities. Typical processes include hydrolysis [21,22] and pyrolysis of waste plastics. The product obtained is then used as a feedstock for the production of fuels and polymers. The last form of recycling is the incineration of the polymer for energy recovery. In this process, the polymer is incinerated, and some amount of energy is recovered in the form of heat. This is generally a “last resort” process when no more value-added application is achievable. Incineration of many plastics also releases hazardous gases and leaves behind toxic residues, presenting undesirable hazardous waste remediation and collection costs and downstream ecological consequences [23].

The overall efficiency of recycling plastic waste begins with the sorting and pretreatment process of plastic waste. Different plastics have different properties and thus have different recycling methods. From the typical mixed waste model, each type of plastic must first be sorted. Contaminated plastics in the waste stream can lead to unwanted decomposition reactions that will decrease the efficiency of plastic recycling as well as alter the end product. While many different types of sorting processes have been utilized and are currently being studied for optimization [24,25]. This review will focus on chemical recycling methods of plastic waste that occur once sorting is complete.

Recycling of poly (ethylene terephthalate)

Poly (ethylene terephthalate), often abbreviated PET or PETE, is a semicrystalline, thermoplastic polymer that is known for its high strength. Industrially, PET is synthesized through a polycondensation reaction between ethylene glycol (EG) and terephthalic acid (TA) or a transesterification reaction between dimethyl terephthalate (DMT) and EG [26].

Efficient recycling of PET has reached the most advanced stage of maturity among the common plastics, and a variety of methods have proven utility on a large scale.^[21-23] There have been instances where PET undergoes primary and secondary recycling, that is, the recycling of plastic bottles. However, a significant remaining problem with recycling PET is that the mechanical properties of the nonvirgin material are greatly reduced with each reuse. The strain-at-break (the percent of the length that a sample can be stretched before the sample breaks) for virgin PET, for example, is 42%, whereas, after only the fifth cycle of extrusion, the strain-at-break was only 0.7%.^[24] This downcycling process limits the ability to thermo-mechanically recycle PET. For this reason, tertiary recycling via chemical processes has been the main focus of research in the past few years [27].

PET can undergo pyrolysis to yield its precursor monomers, TA, and EG which shows that the pyrolysis of PET at 450°C yields TA and oligomers thereof, which can be further hydrolyzed to obtain the TA monomer. Despite such promising advances, the pyrolysis of PET is seldom used as a method to depolymerize PET into its monomeric units on an industrial scale because pyrolysis generally leads to other liquid and gaseous side products, reducing process efficiency, and necessitating the costly separation steps.

Du et al. [27] used PET from carpet waste as a source and studied the thermal and catalytic decomposition of this waste into oils. The catalytic degradation focused on using an aluminosilicate zeolite, ZSM-5, or CaO as the catalyst. They also looked at how steam would affect the final decomposition products. They found that using a catalyst, namely CaO and steam during the pyrolysis process would yield large percentages of benzene in high purity. These studies foreshadow the promise held by many decades of plastic waste to serve as the next source of what are typically viewed as petrochemicals. Another chemical process that has shown great promise for the depolymerization of PET into its monomeric units is hydrolysis (reaction with water at elevated temperatures and/or with a catalyst). The products yielded from this method are TA (or a terephthalate salt) and EG. Three different types of hydrolysis have been studied in the greatest detail: acidic, alkaline, or neutral hydrolysis. While acidic hydrolysis can take place using concentrated acids, such as phosphoric or nitric, the most common acid used is sulfuric acid. Although the yields obtained from this method are generally high, the separation of the EG from the highly acidic solution is a major drawback of this method. Additionally, the amount of acid needed to industrialize this process pose economic, process, and environmental problems.

Alkaline hydrolysis generally employs aqueous solutions of 4–20 wt% NaOH. This process yields the sodium terephthalate and EG in relatively good yields, up to 100% PET conversion. However, longer reaction times (3–5 hr) and high temperatures (>200°C) than needed for acidic hydrolysis techniques are notable drawbacks of this method. It has been observed that recently improved the alkaline hydrolysis process, demonstrating that the addition of a phase transfer catalyst (trioctyl methyl ammonium bromide) facilitated the reaction at lower temperatures (70–95°C) while yielding high purity (99.6%) TA in up to 93% yield.

Neutral hydrolysis employs water or steam in the presence of catalysts.^[30] This process uses high temperatures (200–300°C) and elevated pressures (1–4 MPa). Neutral hydrolysis, without the need for stoichiometric acid or base, would be ideal, but these processes generally produce low-purity monomers and have a relatively slow rate of reaction.

This process does not take into account any mechanical impurities, such as sand and particulates, which can reduce the purity of the monomer for further use. It is found that the use of large ratios of water: PET (5:1) is needed for the complete depolymerization of PET.

Another method to depolymerize PET into its monomers is through methanolysis. In this process, methanol reacts with PET at high temperatures (180–280°C) and pressures (20–40 atm) in the presence of a catalyst, most commonly zinc acetate.[28,29]. This reaction leads to the formation of DMT and EG, which can then be used to resynthesize PET through a transesterification reaction. A major drawback of this method, outside of the high temperatures and pressures, is again the purification process. The crude product contains not only DMT and EG but also other alcohols and phthalate derivatives. An interesting method was developed and has demonstrated that DMT recovered from the methanolysis of PET could be exploited as a starting material for the synthesis of gasoline and jet fuel.

Aminolysis of PET is an area that has not been widely exploited, likely because this process requires an amine (which is often toxic or expensive) to depolymerize PET, yielding diamides of TA. The reaction temperatures generally range from 20 to 100°C. In a study, it was observed that four different amines—methylamine, ethylenediamine, ethanolamine, and butylamine—were reacted with PET. Unprecedented conversion of PET into lower molecular weight oligomers was achieved at ambient temperatures and pressures, but this required reaction times ranging from 10 to 85 days. Also studied ammonolysis of PET with a variety of amines and achieved complete degradation of the PET to the diamide after 45 days of reaction. However, it has been shown that ethylenediamine was even more effective and was able to depolymerize PET to yield a range of oligomers after only 17 hr at 100°C. Significantly, longer reaction times were needed to achieve degradation to small molecules; however, several catalysts, such as dibutyl tin oxide, sodium acetate, and cetyltrimethylammonium bromide, are under development that show promise for shorter reaction times and improved selectivity, but these have not yet demonstrated large-scale applicability.

Glycolysis of PET is an area that has been widely studied. This is a very versatile process due to the various potential applications of the products obtained. In this process, PET is depolymerized by glycols to form monomers, oligomers, and/or polyols, which can then be used for different applications. Some of the glycols that have drawn particular recent interest for this application include ethylene glycol, diethylene glycol (DEG), propylene glycol, butylene glycol, and dipropyleneglycol (DPG). If EG is used to depolymerize PET, the major product formed is bis(2-hydroxyethyl) terephthalate (BHET), which can be used to synthesize PET. A challenge in these promising reactions is the immiscibility of PET with the polyols. It has been observed that this problem by conducting a careful study on the role of different solvents in the conversion of PET to BHET. DMSO proved most effective among solvents screened for effective cosolvation of EG and PET and thus showed an increase in BHET yield to 82% (when compared to 20% without the addition of DMSO) with remarkably short reaction times of 1 min at 190°C and atmospheric pressure.

Catalyst development has also been an area of active research. For many years, zinc acetate was the primary catalyst used in the glycolysis of PET. It has been developed a titanium (IV) phosphate catalyst for the glycolysis of PET using EG, DEG, or 1,2-propylene glycol. This catalyst achieved shorter reaction times than previous catalysts, with increased yield and selectivity for BHET formation.

Titanium is advantageous because it is non-toxic, though the catalyst could not be efficiently recycled. In another study, it was observed that to exploit sustainably produced organ catalysts such as urea in place of transition metal catalysts. Urea was quite an effective catalyst, facilitating 100% conversion of PET with 74% selectivity of BHET. Additionally, urea could be recycled five times without loss of activity or selectivity for BHET.

Ionic liquids can also be used as a catalyst for the glycolysis of PET. Despite their high initial cost, ionic liquids have become increasingly attractive tools for green chemistry because of their low volatility and recyclability. Consequently, it has been explored the utility of 1-butyl-3-methylimidazolium hydroxide, ([Bmim]OH) to serve as a catalyst. A 100% conversion of the PET with a selectivity of 72% of BHET was achieved, compared to only a 11% conversion of PET without the addition of the ionic liquid as a catalyst. In a follow-up study, it has been found that Lewis acidic ([Bmim] ZnCl₃) ionic liquid likewise facilitated a 100% PET conversion but with improved selectivity of 84% for BHET and minimal catalyst loading (0.16 wt%). Also reported that deep eutectic solvents could also be used to catalyze the glycolysis of PET with EG. They found that the combination of 1,3-dimethylurea (1-3-DMU) with 5 wt% Zn(OAc)₂ was able to convert 100% of the PET with 82% selectivity for BHET at 190°C in just 10 min. They associated the high selectivity with relatively mild reaction conditions due to the acid–base synergistic effects between 1-3-DMU and Zn (OAc)₂. The catalyst was also recycled up to five times without any loss in conversion efficiency. However, the zinc content was shown to decrease by 25% after the five cycles, which limits further the recycling ability of the catalyst.

Whereas the foregoing discussion highlights efforts to leverage the glycolysis of PET with EG to synthesize BHET as a monomer feedstock, an emerging area of interest is the use of chemically recycled PET products as feedstocks for other polymer formulations. Also, it has been used different glycols to convert PET into lower-weight oligomers having hydroxyl end groups that were then reacted with toluene diisocyanate to produce urethane oils. The recycled urethane oils showed similar Koenig hardness values and touch/hard-to-dry times to commercially available oils. It has been found that synthesized polyol blends by reacting PET waste with plant-derived starch. The oligomers so formed were then esterified with fatty acids themselves primary constituents of low-value, high-volume waste products from other industries. The esterified materials were then used to synthesize polyurethanes. It has also been demonstrated the facile tunability of adhesion, flexibility, and chemical resistance properties of the polyurethanes as a function of PET products present in the formulation.

It has been used DEG and PET to synthesize oligomers that proved effective as secondary plasticizers in PVC formulations resulting in improved thermal stability and flexibility of the final PVC product. Furthermore, migration of PET-derived plasticizer migration was greatly decreased compared to traditional PVC plasticizers such as di(2-ethylhexyl) phthalate (DHEP) which leach out over time. Initial PET oligomerization was achieved in this instance by the action of a Ca/Zn stearate catalyst at 250°C for only 20 min. Recently, Sirohi et al. [30-31] have described the alcoholysis of PET to synthesize oligomers that can be used as a plasticizer in nitrile-PVC rubber blends. They used a ZnCl₂ catalyst and 1-decanol as the alcohol with reaction temperatures of 190°C for 4 hr. Once resultant depolymerized products were blended with nitrile-PVC rubber blends, the tensile properties and the ageing resistance of the materials was significantly buttressed.

The structural variability and relative chemical inertness of PE have relegated most studies on PE recycling to variations in pyrolysis. A primary difficulty associated with efforts to recycle PE by pyrolysis is that the thermal degradation of PE usually proceeds via random scissions at C = C bonds. This homolytic scission generates two radical chains that can go on to form a complex mixture of olefinic products and highly crosslinked polymeric products [31]. Moreover, the melt flow index (a key figure of merit for processability) changes by two orders of magnitude, from 2.25 (reasonable flow) for virgin LDPE to a nearly unprocessable melt flow index of 0.02 g/10 min after 100 extrusion cycles [32]. This changing behavior is accompanied by drastic, deleterious drift of mechanical properties of the recycled LDPE, so these approaches do not provide a long term, sustainable path forward for PE recycling. When mechanical processing of PE is no longer feasible, depolymerization of PE through pyrolysis to yield hydrocarbons for fuel/energy applications is often the final stage of use for such materials.

There are two major processes for the pyrolysis of PE: thermal or catalytic pyrolysis. Thermal pyrolysis is simply heating PE at high pressure to break down the polymer backbone to form smaller organic molecules. Catalytic pyrolysis utilizes a catalyst to reduce the temperature and reaction time and thus improve economic viability and, in some cases, selectivity. In another study, it has been observed that the thermal pyrolysis of commercially available HDPE pellets at 350°C yielded a liquid oil product with 81% yield. The oil consisted mainly of paraffinic hydrocarbons, most of which, contained between 6 and 16 carbon atoms. Specificity for a single chemical commodity from PE pyrolysis, however, remains elusive. An interesting strategy has been devised [33] that eschewed the selectivity problem and instead sought to take waste HDPE and chemically transform it into a complex mixture akin to “crude” oil. As long as the complex mixture is comprised of molecules similar to those found in petroleum, such a complex mixture could hypothetically be processed by established petroleum refining and cracking techniques. This nascent approach used waste HDPE that had already been sorted, washed, and shredded. The HDPE samples so prepared were then heated in a batch autoclave reactor at 430°C with short reaction times, up to 38 min, to yield what they refer to as “plastic oil,” with impressive yields of up to 85–90 wt% oil recovered. While the oil obtained is not clean enough to be used directly in place of fuel, this plastic oil can be refined by established methodologies to yield target products. The main drawback of this creative approach is the potentially high energy required to produce plastic oil on large scales [34-35]

While many researchers focus on pristine or near-ideal PE sources in their proof-of-principle studies, it has been examined that the important difference between utilizing virgin and waste plastic products. Additionally, a mixed waste feedstock mixture of different polymers was used. The mixture consisted of HDPE, LDPE, and PP. The virgin polymers were obtained commercially, and the waste plastics were obtained in the form primarily of packaging plastics, plastic containers, and bottles. The thermal pyrolysis of this mixed waste was undertaken at 350 or 400°C and the reaction time was 8 hr. Lower temperature reactions yielded lighter hydrocarbons (< C₂₀) while an increase in temperature yielded heavier hydrocarbons (> C₂₀). This offers the potential to tune the oil obtained by varying reaction temperatures and holds promise for exploiting mixed waste streams and thereby circumventing some of the challenges associated with waste separation.

Being recognized as the importance of developing strategies to deal with mixed waste. In this study, the plastic waste was collected in the form of disposable plates, grocery bags, and cups and comprised not only linear alkyl polymers (PP and PE) but also aromatic-bearing polystyrene (PS) and PET. The plastic samples were crushed into fine powders and used on their own as well as mixed in varying ratios (as little as 20 wt% PE) with reaction conditions of 450°C for 75 min. Depending on the ratios of the plastic waste liquid oil yields ranged from 24 to 54%. The initial feedstock used was 1 kg, which shows the potential to scale the system to an industrial level. The oil obtained consisted of large amounts of aromatic compounds and showed higher heating values between 41 and 42 MJ/kg, which is comparable to that of commercially available diesel (43 MJ/kg).

The area of catalytic pyrolysis of PE has also achieved notable advances in the last few years concerning increasing yields and lowering reaction time/temperature. It looked at three different zeolites, HZSM-5, USY, and NH₄ZSM-5. These catalysts differ based on pore size, acidic sites, and surface area. This study garnered important insight that catalysts with larger pore sizes led to a greater yield of liquid products and that the less acidic catalysts would yield lighter fractions of gas and liquid products, thus affording flexibility in the process based on end-use.

It has been examined the effects of catalysts on the pyrolysis of an exceedingly complex and disparate waste stream of HDPE, PP, PET and paper biomass (consisting primarily of cellulose). Cobalt complexes were used as catalysts with various chelating agents along with Al₂O₃ and/or CeO₂. The catalytic pyrolysis of the paper waste by itself yielded mainly gaseous and solid products, whereas pyrolysis of the paper/PP/HDPE/PET mixture yielded more liquid products that were rich in aromatics and olefins.

In the pyrolysis process, waste plastics are converted into alternative energy as fuel for diesel engines. Waste plastic fuel has a wide range of chemical characteristics that vary depending on the grade of plastics utilized and the pyrolysis technique employed. The low calorific value and high viscosity of the waste plastic fuel are the two most significant drawbacks of utilizing plastic fuel as a diesel engine. HDPE is known for its structure as a linear long-chain polymer with a considerable degree of crystallinity and little branching that ends up with high endurance characteristics. According to forecasts, global demand for HDPE will reach roughly 95 billion tonnes by 2025, making it one of the most significant contributors to plastic pollution. HDPE offers good resistance to alkalis, dilute acids, and greases. Because of its exceptional strength, it is widely used to produce milk containers, lubricating oil containers, shampoo bottles, detergent bottles, recycling bins, and grocery bags, among other things. HDPE wastes have a high potential for use as a feedstock for pyrolysis and can be recycled many times. Recovered energy from the waste polymers and used it to solar energy applications[34-38]. It is not only environmentally friendly, but it also offers a green way of creating porous carbons for a wide range of applications by converting low-cost waste polymers into high-value-added energy utilization.

The catalytic process is characterized by the use of a catalyst to effect conversion. The pyrolysis of plastic waste involves several process factors, such as temperature, heating rate, catalyst usage, particle size, retention time, moisture content, and feedstock composition, amongst other things(39, 40).

Compared to thermal pyrolysis, the method showed a high likelihood of the transformation of synthetic waste into oil and improved quality at lower reaction durations and temperatures than was previously thought. These variables can reduce energy consumption while simultaneously increasing the output of the whole pyrolysis process. In the pyrolysis process, thermal degradation occurs while the material is held under a vacuum. According to the manufacturer, the catalytic pyrolysis transformation of the HDPE polymers was carried out in a pyrolysis reactor. The shredded plastic trash is put into a muffle furnace that can be operate continuously at 600 °C. A digital controller which monitors and adjusts the temperature via the thermocouple. The catalytic pyrolysis reactor included with a vacuum pump to aid the conversion(41-44). The catalyst that is employed in this procedure will avoid the formation of any dioxins. Depending on the type of plastic materials, the reaction occurs at a specified temperature and time. Sixty minutes of response time was required for HDPE testing, and at 450 °C, HDPE was converted to pyrolysis oil. According to the results, the oil output for HDPE is 50% weight of pyrolysis oil with 25% wax formation and 25% gas, and coke formation is observed.

Many researchers are investigating the different additives that may improve the performance of alternative fuel produced from recycled plastics. Table 1 tabulated the waste plastic fuel investigations and their performance outcome with oxygenated additives. With its renewable bio-resources and oxygenated properties, ethanol is an attractive alternative fuel for diesel engines. These oxygenates are often used in engines due to their higher volatility and latent heating properties. Many studies[45-49] have focused on optimizing diesel fuel, biodiesel, and alcohol mixes as alternate fuels in CI engines. However, there are significant drawbacks, including decreased heating value, phase separation, pour point, and hazardous storage and transit circumstances for ternary blends. Ethanol can be blended with diesel as a engine fuel, which has many favourable properties, including higher oxygen content, low viscosity, less sulfur content, high hydrogen-to-carbon ratio, and a high rate of evaporative cooling. Ethanol has a lower viscosity than pure diesel, ensuing in better atomization of fuel injected into cylinders and improved mixing with air when combined with diesel[45-50]. Additionally, since ethanol has a high latent heat of evaporation, blending it with diesel fuel may increase volume efficiency via the evaporative cooling effect of the ethanol during the intake and compression strokes[51-52].

Conclusion

Plastics are “one of the greatest innovations” and have certainly proved their reputation to be true. Plastic is lightweight, does not rust or rot, is of low cost, is reusable, and conserves natural resources for these reasons, plastic has gained this much popularity. The literature reveals that research efforts on the pyrolysis of plastics in different conditions using different catalysts and the process have been initiated. However, there are many subsequent problems to be solved in the near future. The present issues are the necessary scale-up, minimization of waste handling costs and production costs, and optimization of gasoline range products for a wide range of plastic mixtures or waste.

A huge amount of plastic waste produced may be treated with suitably designed methods to produce fossil fuel substitutes. The method is superior in all respects (ecological and economical) if proper infrastructure and financial support are provided. So, a suitable process which can convert waste plastic to hydrocarbon fuel is designed and if implemented then that would be a cheaper partial substitute for petroleum without emitting any pollutants. It would also take care of hazardous plastic waste and reduce the import of crude oil.

The challenge is to develop the standards for the process and products of post-consumer recycled plastics and to adopt the more advanced pyrolysis technologies for waste plastics, referring to the observations of research and development in this field. The pyrolysis reactor must be designed to suit the mixed waste plastics and small-scaled and middle-scaled production. Also, the analysis would help reduce the capital investment and also the operating cost and thus would enhance the economic viability of the process.

Table.1 Polymers demands in India (million tons)

S. No.	Type of polymer	2011-12	2016-17	2020-21
1	Polyethylene	3.81	4.57	6.03
2	Polypropylene	1.69	2.09	3.1
3	Polyvinyl chloride	1.34	2.89	3.4
4	Polyethylene terephthalate	0.37	0.67	0.79

Table 2. Main operating parameters for the pyrolysis process

Parameters	Conventional	Fast	Flash
Pyrolysis temperature (K)	550–900	850–1200	1050–1200
Heating rate (K/s)	0.1–1	10–250	>1100
Particle size (mm)	5–50	<1	<0.5
Solid residence (s)	300–3600	0.5– 15	<1.0

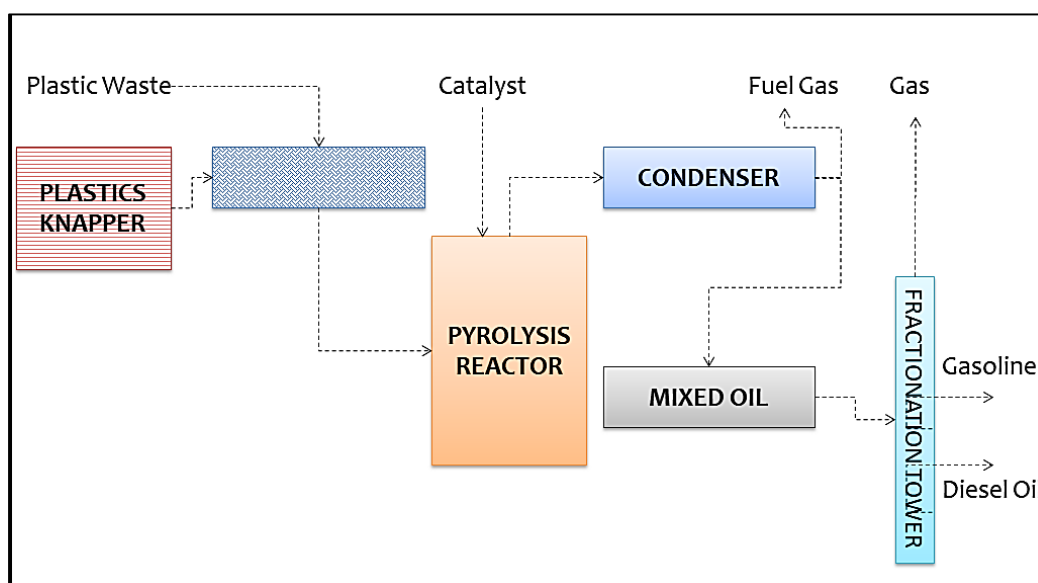


Fig. 1 Pyrolysis Process of generating fuel oil from the waste plastics

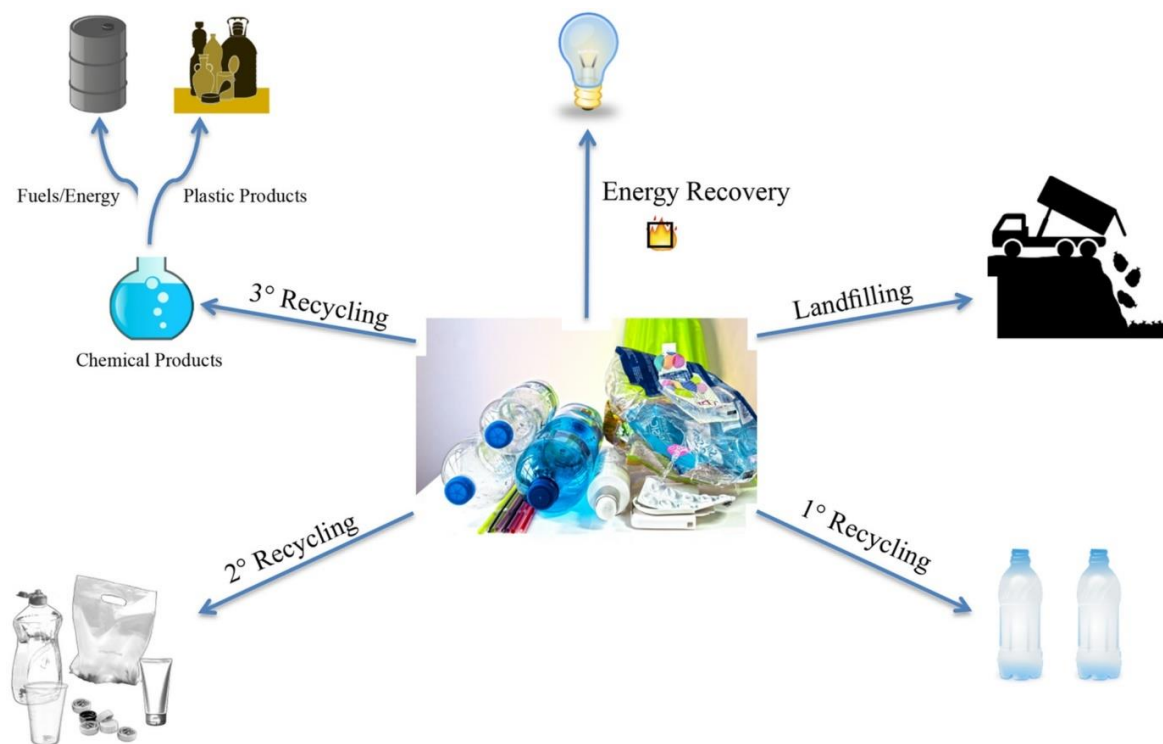


Fig. 2. Common fates for current plastic waste [Color figure can be viewed at wileyonlinelibrary.com]

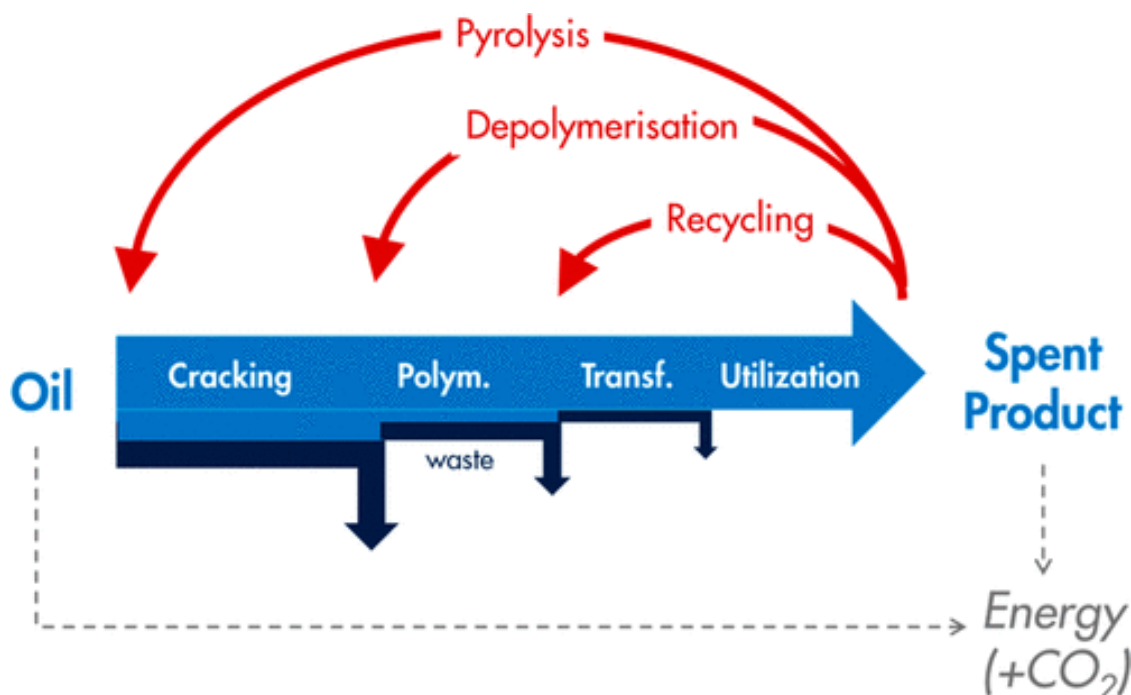


Fig. 3. Options for recycling plastic waste for retransformation (mechanical recycling), repolymerization (chemical recycling to monomer), or re cracking (chemical recycling to feedstock). Adapted with permission from ref [33]. Copyright 2002 Royal Society of Chemistry.

References

1. T. S. Kpere-Daibo, *Plastic catalytic degradation study of the role of the external catalytic surface, catalytic reusability and temperature effects [Doctoral thesis]*, University of London Department of Chemical Engineering University College London, WC1E 7JE.
2. A. G. Buekens and H. Huang, "Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes," *Resources Conservation and Recycling*, vol. 23, no. 3, pp. 163–181, 1998.
3. A. K. Panda, R. K. Singh, and D. K. Mishra, "Thermolysis of waste plastics to liquid fuel. A suitable method for plastic waste management and manufacture of value-added products—a world perspective," *Renewable and Sustainable Energy Reviews*, vol. 14, no. 1, pp. 233–248, 2010.
4. S. M. Al-Salem, P. Lettieri, and J. Baeyens, "The valorization of plastic solid waste (PSW) by primary to quaternary routes: from re-use to energy and chemicals," *Progress in Energy and Combustion Science*, vol. 36, no. 1, pp. 103–129, 2010.
5. R. P. Singha, V. V. Tyagi, T. Allen et al., "An overview for exploring the possibilities of energy generation from municipal solid waste (MSW) in Indian scenario," *Renewable and Sustainable Energy Reviews*, vol. 15, no. 9, pp. 4797–4808, 2011.
6. J. Scheirs and W. Kaminsky, *Feedstock Recycling of Waste Plastics*, John Wiley & Sons, 2006.
7. A. Demirbas, "Biorefineries: current activities and future developments," *Energy Conversion & Management*, vol. 50, pp. 2782–2801, 2009.
8. W.-C. Huang, M.-S. Huang, C.-F. Huang, C.-C. Chen, and K.-L. Ou, "Thermochemical conversion of polymer wastes into hydrocarbon fuels over various fluidizing cracking catalysts," *Fuel*, vol. 89, no. 9, pp. 2305–2316, 2010.
9. T.-T. Wei, K.-J. Wu, S.-L. Lee, and Y.-H. Lin, "Chemical recycling of post-consumer polymer waste over fluidizing cracking catalysts for producing chemicals and hydrocarbon fuels," *Resources, Conservation and Recycling*, vol. 54, no. 11, pp. 952–961, 2010.
10. H.-T. Lin, M.-S. Huang, J.-W. Luo, L.-H. Lin, C.-M. Lee, and K.-L. Ou, "Hydrocarbon fuels produced by catalytic pyrolysis of hospital plastic wastes in a fluidizing cracking process," *Fuel Processing Technology*, vol. 91, no. 11, pp. 1355–1363, 2010.
11. J. Aguado, D. P. Serrano, and J. M. Escola, "Fuels from waste plastics by thermal and catalytic process: a review," *Industrial & Engineering Chemistry Research*, vol. 47, no. 21, pp. 7982–7992, 2008.
12. G. H. Zhang, J. F. Zhu, and A. Okuwaki, "Prospect and current status of recycling waste plastics and technology for converting them into oil in China," *Resources, Conservation and Recycling*, vol. 50, no. 3, pp. 231–239, 2007.
13. S. Katyal, "Effect of carbonization temperature on combustion reactivity of bagasse char," *Energy Sources A*, vol. 29, no. 16, pp. 1477–1485, 2007.
14. D. Mohan, C. U. Pittman Jr., and P. H. Steele, "Pyrolysis of wood/biomass for bio-oil: a critical review," *Energy Fuels*, vol. 20, no. 3, pp. 848–889, 2006.

15. A. Demirbas, "Producing bio-oil from olive cake by fast pyrolysis," *Energy Sources A*, vol. 30, pp. 38–44, 2008.
16. C. F. Cullis and M. M. Hirschler, *The Combustion of Organic Polymers*, Oxford Clarendon Press, 1981.
17. B. Singh and N. Sharma, "Mechanistic implications of plastic degradation," *Polymer Degradation and Stability*, vol. 93, no. 3, pp. 561–584, 2008.
18. E. Butler, G. Devlin, K. McDonnell, Waste polyolefins to liquid fuels via pyrolysis: a review of commercial state-of-the-art and recent laboratory research, *Waste Biomass Valorization* 2 (2011) 227–255.
19. S.M. Al Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): a review, *Waste Manage.* 36 (2009) 103–129.
20. J. Aguado, D.P. Serrano, J.M. Escola, Fuels from waste plastics by thermal and catalytic process: a review, *Ind. Eng. Chem. Res.* 47 (2008) 7982–7992.
21. A.K. Panda, R.K. Singh, D.K. Mishra, Thermolysis of waste plastics to liquid fuel. A suitable method for plastic waste management and manufacture of value-added products – a world perspective, *Renew. Sustain. Energy Rev.* 14 (2010)233–248
22. S. Kumar, A.K. Panda, R.K. Singh, A review on tertiary recycling of high-density polyethylene to fuel, *Resour. Conserv. Recycl.* 55 (2011) 893–910.
23. J. Ceamanos, J.F. Mastral, F. Liesa, Modeling of the pyrolysis of large samples of polyethylene including the melting process, *Energy Fuels* 16 (2002) 436–442.
24. M. Della Zassa, M. Favero, P. Canu, Two-step selective thermal depolymerization of polyethylene. 1: Feasibility and effect of devolatilization heating policy, *J. Anal. Appl. Pyrol.* 87 (2010) 248–255.
25. J.A. Conesa, R. font, A. Marcilla, A.N. García, Pyrolysis of polyethylene in a fluidized bed reactor, *Energy Fuels* 8 (1994) 1238–1246.
26. W. Kaminsky, M. Predel, A. Sadiki, Feedstock recycling of polymers by pyrolysis in a fluidised bed, *Polym. Degrad. Stabil.* 85 (2004) 1045–1050
27. J.F. Mastral, C. Berruero, J. Ceamanos, Modelling of the pyrolysis of high-density polyethylene. Product distribution in a fluidized bed reactor, *J. Anal. Appl. Pyrol.* 79 (2007) 313–322
28. S.H. Jung, M.H. Cho, B.S. Kang, J.S. Kim, Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor, *Fuel Process. Technol.* 91 (2010) 277–284.
29. G. Elordi, M. Olazar, G. Lopez, M. Artetxe, J. Bilbao, Product yields and compositions in the continuous pyrolysis of high-density polyethylene in a conical spouted bed reactor, *Ind. Eng. Chem. Res.* 50 (2011) 6650–6659.
30. M.L. Mastellone, U. Arena, Bed defluidisation during the fluidised bed pyrolysis of plastic waste mixtures, *Polym. Degrad. Stabil.* 85 (2004) 1051–1058.

31. M.J. San José, M. Olazar, F.J. Peñas, J.M. Arandes, J. Bilbao, Correlation for calculation of the gas dispersion coefficient in conical spouted beds, *Chem.Eng. Sci.* **50** (1995) 2161–2172.
 32. G. Jiménez-García, R. Aguilar-López, R. Maya-Yescas, The fluidized-bed catalytic cracking unit building its future environment, *Fuel* **12** (2011) 3531–3541.
 33. Lange, J.-P. Sustainable development: efficiency and recycling in chemicals manufacturing. *Green Chem.* **2002**, *4*, 546– 550, DOI: 10.1039/b207546f.
 34. Lopez, G.; Artetxe, M.; Amutio, M.; Elordi, G.; Aguado, R.; Olazar, M.; Bilbao, J. Bilbao, Recycling poly-(methyl methacrylate) by pyrolysis in a conical spouted bed reactor. *Chem. Eng. Process.* **2010**, *49*, 1089– 1094, DOI: 10.1016/j.cep.2010.08.002
 35. Yu, J.; Sun, L.; Ma, C.; Qiao, Y.; Yao, H. Thermal degradation of PVC: A review. *Waste Manage.* **2016**, *48*, 300– 314, DOI: 10.1016/j.wasman.2015.11.041
 36. Miranda, R.; Yang, J.; Roy, C.; Vasile, C. Vacuum pyrolysis of PVC I. Kinetic study. *Polym. Degrad. Stab.* **1999**, *64*, 127– 144, DOI: 10.1016/S0141-3910(98)00186-4
 37. Cit, I.; Sinag, A.; Yumak, T.; Ucar, S.; Mısırlıoğlu, Z.; Canel, M. Comparative pyrolysis of polyolefins (PP and LDPE) and PET. *Polym. Bull.* **2010**, *64*, 817– 834, DOI: 10.1007/s00289-009-0225-x
 38. Dimitrov, N.; Kratofil Krehula, L.; Pticek Sirocic, A.; Hrnjak-Murgic, Z. Analysis of recycled PET bottles products by pyrolysis-gas chromatography. *Polym. Degrad. Stab.* **2013**, *98*, 972– 979, DOI: 10.1016/j.polymdegradstab.2013.02.013
 39. Yoshioka, T.; Grause, G.; Eger, C.; Kaminsky, W.; Okuwaki, A. Pyrolysis of poly(ethylene terephthalate) in a fluidised bed plant. *Polym. Degrad. Stab.* **2004**, *86*, 499– 504, DOI: 10.1016/j.polymdegradstab.2004.06.001
 40. Yu, J.; Liu, S.; Cardoso, A.; Han, Y.; Bikane, K.; Sun, L. Catalytic pyrolysis of rubbers and vulcanized rubbers using modified zeolites and mesoporous catalysts with Zn and Cu. *Energy* **2019**, *188*, 116– 117, DOI: 10.1016/j.energy.2019.116117
 41. Zhang, F.; Zeng, M.; Yappert, R. D.; Sun, J.; Lee, Y.-H.; LaPointe, A. M.; Peters, B.; Abu-Omar, M. M.; Scott, S. L. Polyethylene upcycling to long-chain alkylaromatics by tandem hydrogenolysis/aromatization. *Science* **2020**, *370*, 437– 441, DOI: 10.1126/science.abc5441
 42. Celik, G.; Kennedy, R. M.; Hackler, R. A.; Ferrandon, M.; Tennakoon, A.; Patnaik, S.; LaPointe, A. M.; Ammal, S. C.; Heyden, A.; Perras, F. A.; Pruski, M.; Scott, S. L.; Poepelmeier, K. R.; Sadow, A. D.; Delferro, M. Upcycling Single-Use Polyethylene into High-Quality Liquid Products. *ACS Cent. Sci.* **2019**, *5*, 1795– 1803, DOI: 10.1021/acscentsci.9b00722
 43. Rorrer, J. E.; Beckham, G. T.; Román-Leshkov, Y. Conversion of Polyolefin Waste to Liquid Alkanes with Ru-Based Catalysts under Mild Conditions. *JACS Au* **2021**, *1*, 8– 12, DOI: 10.1021/jacsau.0c00041
 44. Gazi, S.; Đokić, M.; Chin, K. F.; Ng, P. R.; Soo, H. S. Visible Light-Driven Cascade Carbon-Carbon Bond Scission for Organic Transformations and Plastics Recycling. *Adv. Sci.* **2019**, *6*, 1902020, DOI: 10.1002/advs.201902020
 45. Chen, L.; Malollari, K. G.; Uliana, A.; Sanchez, D.; Messersmith, P. B.; Hartwig, J. F. Selective, Catalytic Oxidations of C-H Bonds in Polyethylenes Produce Functional Materials with Enhanced Adhesion. *Chem.* **2021**, *7*, 137– 145, DOI: 10.1016/j.chempr.2020.11.020
-

46. Williamson, J. B.; Na, C. G.; Johnson, R. R., III; Daniel, W. F. M.; Alexanian, E. J.; Leibfarth, F. A. Chemo- and Regioselective Functionalization of Isotactic Polypropylene: A Mechanistic and Structure-Property Study. *J. Am. Chem. Soc.* **2019**, *141*, 12815– 12823, DOI: 10.1021/jacs.9b05799
 47. Lange, J.-P. *Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges and Opportunities*; Derouane, E. G., , eds; Kluwer, 2005; pp 51– 83.
 48. Narancic, T.; Cerrone, F.; Beagan, N.; O'Connor, K. E. Recent Advances in Bioplastics: Application and Biodegradation. *Polymers* **2020**, *12*, 920, DOI: 10.3390/polym12040920
 49. Xu, S.-Y.; Zhang, H.; He, P.-J.; Shao, L.-M. Leaching behaviour of bisphenol A from municipal solid waste under landfill environment. *Environ. Technol.* **2011**, *32*, 1269– 1277, DOI: 10.1080/09593330.2010.535175
 50. Wowkonowicz, P.; Kijewska, M. Phthalate release in leachate from municipal landfills of central Poland. *PLoS One* **2017**, *12*, e0174986 DOI: 10.1371/journal.pone.0174986
 51. Osako, M.; Kim, Y.-J.; Sakai, S.-I. Leaching of brominated flame retardants in leachate from landfills in Japan. *Chemosphere* **2004**, *57*, 1571– 1579, DOI: 10.1016/j.chemosphere.2004.08.076
 52. Intrakamhaeng, V.; Clavier, K. A.; Liu, Y.; Townsend, T. G. Antimony mobility from E-waste plastic in simulated municipal solid waste landfills. *Chemosphere* **2020**, *241*, 125042, DOI: 10.1016/j.chemosphere.2019.125042
-