

Review Article

Alternate Strategies for Conversion of Waste Plastic to Fuels

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The present rate of economic growth is unsustainable without saving of fossil energy like crude oil, natural gas, or coal. There are many alternatives to fossil energy such as biomass, hydropower, and wind energy. Also, suitable waste management strategy is another important aspect. Development and modernization have brought about a huge increase in the production of all kinds of commodities, which indirectly generate waste. Plastics have been one of the materials because of their wide range of applications due to versatility and relatively low cost. The paper presents the current scenario of the plastic consumption. The aim is to provide the reader with an in depth analysis regarding the recycling techniques of plastic solid waste (PSW). Recycling can be divided into four categories: primary, secondary, tertiary, and quaternary. As calorific value of the plastics is comparable to that of fuel, so production of fuel would be a better alternative. So the methods of converting plastic into fuel, specially pyrolysis and catalytic degradation, are discussed in detail and a brief idea about the gasification is also included. Thus, we attempt to address the problem of plastic waste disposal and shortage of conventional fuel and thereby help in promotion of sustainable environment.

1. Introduction

The increase in use of plastic products caused by 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 household and industries. Mostly, thermoplastics 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 in view 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, land

filling 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 has reached global maximum capacities leveling at 260 million tons in 2007, where 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 release of harmful gases like dioxins, hydrogen chloride, airborne particles, and carbon dioxide, incineration of polymer possesses serious air pollution problems. Due to high cost and poor biodegradability, it is also undesirable to dispose 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, 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

TABLE 1: Plastics consumption, by major world areas, in kg and GNI dollars per capita.

Main world areas	Plastics consumption, 000s tons	Population millions	Kg/capita	GNI/capita
Europe W, C, and E	40 000	450	90	18 000
Eurasia, Russia, and others	4 000	285	14	1 600
North America	45 000	310	145	32 000
Latin America	11 000	500	22	3 500
Middle East, including TR	4 000	200	20	2 500
Africa, North and South	2 500	190	13	2 000
Other Africa	500	610	<1	300
China	19 000	1285	14	800
India	4 000	1025	4	450
Japan	11 000	125	90	35 000
Other Asia Pacific, rest	13 000	1120	11	600
Total world	154 000	6 100	25	5 200

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, with the aim of converting 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].

2. Current Scenario of Plastics

Over many years, a drastic growth has been observed in 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 space or land filled 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; balance 60 wt% is not possible to dispose off [4]. India has been a favored dumping ground for plastic waste mostly from industrialized countries like Canada, Denmark, Germany, 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 have found its way into India in the years 1999 and 2000, respectively [3, 6].

2.1. Present Scenario in India. With the formal and informal sector failing to collect plastic waste the packaging and polyvinyl chloride (PVC) pipe industry are growing at 16–18% per year. The demand of plastic goods is increasing from household use to industrial applications. It is growing at a rate of 22% annually. The polymers production has reached the 8.5 million tons in 2007. Table 1 provides the total plastics waste consumption in the world and Table 2 provides the total plastic waste consumption in India during the last decade. National plastic waste management task

TABLE 2: Plastics consumption in India.

S. no.	Year	Consumption (tons)
1	1996	61,000
2	2000	3,00,000
3	2001	4,00,000
4	2007	85,00,000

force in 1997 projected the polymers demand in the country. Table 3 documents the demand of different polymers in India during years 1995-96, 2001-02, and 2006-07. The comparison of demand and consumption from Tables 2 and 3 indicates that projections are correct. More than one fourth of the consumption in India is that of PVC, which is being phased out in many countries. Poly bags and other plastic items except PET in particular have been a focus, because it has contributed to host problems in India such as choked sewers, animal deaths, and clogged soils.

3. Different Recycling Categories [1]

3.1. Primary Recycling. It is also known as mechanical reprocessing. During the process, the plastic waste is fed into the original production process of basic material. So, we can obtain the product with same specification as that of the original one. This process is feasible only with semiclean scrap, so it is an unpopular choice with the recyclers. Degraded plastic waste partly substitutes the virgin material. So, on increasing the recycled plastic fraction in feed mixture, the quality of the product decreases. This type of recycling requires clean and not contaminated waste which is of the same type as virgin resin.

For this reason, steps in the primary recycling process are:

- (1) separate the waste by specific type of resin and by different colors and then wash it,
- (2) the waste has better melting properties so it should be reextruded into pellets which can be added to the original resin.

TABLE 3: Polymers demands in India (million tons).

S. no	Type of polymer	1995-96	2001-02	2006-07
1	Polyethylene	0.83	1.83	3.27
2	Polypropylene	0.34	0.88	1.79
3	Polyvinyl chloride	0.49	0.87	1.29
4	Polyethylene terephthalate	0.03	0.14	0.29

Source: National Plastic Waste Management Task Force Projection (1997).

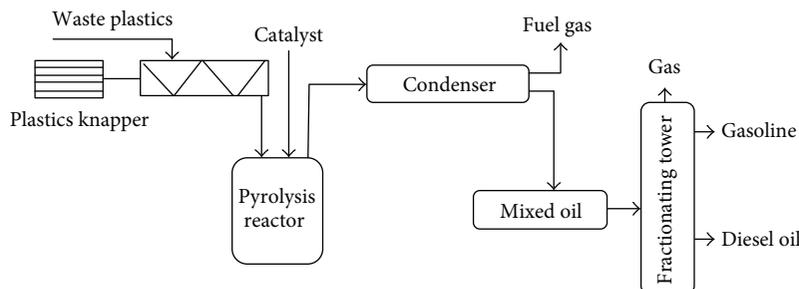


FIGURE 1: Pyrolysis Process of generating fuel oil from the waste plastics [12].

This type of recycling is very expensive compared to other types of recycling due to the requirements of plastic properties mentioned above.

If the waste can be easily sorted by resin but cannot be pelletized due to mixed coloring contamination, then waste can be fed into moulding application, and regarding reactants properties, it is less demanding.

3.2. Secondary Recycling. Secondary recycling uses PSW in the manufacturing of plastic products by mechanical means, which uses recyclates, fillers, and/or virgin polymers. The objective of the process is to retain some energy which is used for plastic production to attain financial advantages. Unlike primary recycling, the secondary recycling process can use contaminated or less separated waste. However, this waste has to be cleaned. The recycling process involves different products and is different compared to original production process.

3.3. Tertiary Recycling. This process is also known as cracking process. The process includes breaking down the plastics at high temperatures (thermal degradation) or at lower temperatures in the presence of catalyst (catalytic degradation), which contain smaller carbon chains. For any chemical production, this feedstock can be used as basic material of lower quality (e.g., polymerization or fuel fabrication). The original value of the raw material is lost. The tertiary recycling process is more important due to high levels of waste contamination. We are able to recover the monomers of condensation polymers. Mechanisms like hydrolysis, methanolysis, or glycolysis can be used, for example, PET (polyethylene terephthalate), polyesters, and polyamide while addition of polymers like polyolefin, polystyrene, and PVC requires stronger thermal treatment, gasification, or catalytic degradation to be cracked.

3.4. Quaternary Recycling. This process includes the recovery of energy content only. As most plastic waste has high heat content so it is incinerated. Generation of the heat energy is the only advantage of this process. The residual of this incineration has 20wt%, respectively, 10 vol% of the original waste and are placed in landfills. Solid waste problem is not solved by this process; in fact it leads to the problem of air pollution.

4. Methods of Converting Plastic to Fuel

4.1. Pyrolysis/Thermal Degradation. Pyrolysis is a process of thermal degradation of a material in the absence of oxygen. Plastic is fed into a cylindrical chamber. The pyrolytic gases are condensed in a specially designed condenser system, to yield a hydrocarbon distillate comprising straight and branched chain aliphatic, cyclic aliphatic, and aromatic hydrocarbons, and liquid is separated using fractional distillation to produce the liquid fuel products. The plastic is pyrolysed at 370°C–420°C.

The essential steps in the pyrolysis of plastics involve (Figure 1):

- (1) evenly heating the plastic to a narrow temperature range without excessive temperature variations,
- (2) purging oxygen from pyrolysis chamber,
- (3) managing the carbonaceous char by-product before it acts as a thermal insulator and lowers the heat transfer to the plastic,
- (4) careful condensation and fractionation of the pyrolysis vapors to produce distillate of good quality and consistency.

TABLE 4: Main operating parameters for pyrolysis process [7].

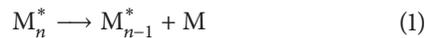
Parameters	Conventional	Fast	Flash
Pyrolysis temprature (K)	550–900	850–1250	1050–1300
Heating rate (K/s)	0.1–1	10–200	>1000
Particle size (mm)	5–50	<1	<0.2
Solid residence (s)	300–3600	0.5–10	<0.5

Advantages of pyrolysis process [5] are

- volume of the waste is significantly reduced (<50–90%),
- solid, liquid, and gaseous fuel can be produced from the waste,
- storable/transportable fuel or chemical feed stock is obtained,
- environmental problem is reduced,
- desirable process as energy is obtained from renewable sources like municipal solid waste or sewage sludge,
- the capital cost is low.

There are different types of pyrolysis process. Conventional pyrolysis (slow pyrolysis) proceeds under a low heating rate with solid, liquid, and gaseous products in significant portions [5, 13]. It is an ancient process used mainly for charcoal production. Vapors can be continuously removed as they are formed [5, 14]. The fast pyrolysis is associated with tar, at low temperature (850–1250 K) and/or gas at high temperature (1050–1300 K). At present, the preferred technology is fast or flash pyrolysis at high temperatures with very short residence time [5, 15]. Fast pyrolysis (more accurately defined as thermolysis) is a process in which a material, such as biomass, is rapidly heated to high temperatures in the absence of oxygen [5, 15]. Table 4 [7] shows the range of the main operating parameters for pyrolysis processes.

4.1.1. Mechanism of Thermal Degradation. Cullis and Hirscher had proposed detailed study on the mechanism of thermal degradation of polymers [3, 16]. The four different mechanisms proposed are: (1) end-chain scission or unzipping, (2) random-chain scission/fragmentation, (3) chain stripping/elimination of side chain, (4) cross-linking. The decomposition mode mainly depends on the type of polymer (the molecular structure):



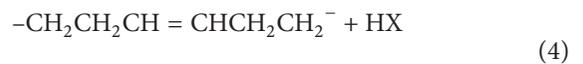
Equations (1) and (2) represent the thermal degradation, and (3) represents the random degradation route of the polymers pyrolysis. The fourth type of mechanism, that is, cross-linking often occurs in thermosetting plastics upon heating at high temperature in which two adjacent “stripped” polymer chains can form a bond resulting in a chain network (a higher MW species). An example is char formation.

4.2. Catalytic Degradation. In this method, a suitable catalyst is used to carry out the cracking reaction. The presence of catalyst lowers the reaction temperature and time. The process results in much narrower product distribution of carbon atom number and peak at lighter hydrocarbons which occurs at lower temperatures. The cost should be further reduced to make the process more attractive from an economic perspective. Reuse of catalysts and the use of effective catalysts in lesser quantities can optimize this option. This process can be developed into a cost-effective commercial polymer recycling process for solving the acute environmental problem of disposal of plastic waste. It also offers the higher cracking ability of plastics, and the lower concentration of solid residue in the product [3].

4.2.1. Mechanism of Catalytic Degradation. Singh et al. [3, 17] have investigated catalytic degradation of polyolefin using TGA as a potential method for screening catalysts and have found that the presence of catalyst led to the decrease in the apparent activation energy. Different mechanisms (ionic and free radical) for plastic pyrolysis proposed by different scientists are as given below.

There are different steps in carbonium ion reaction mechanism such as H-transfer, chain/beta-scission, isomerisation, oligomerization/alkylation, and aromatization which is influenced by acid site strength, density, and distribution [3, 18]. Solid acid catalysts, such as zeolites, favor hydrogen transfer reactions due to the presence of many acid sites [3, 5]. Both Bronsted and Lewis acid sites characterize acid strength of solid acids. The presence of Bronsted acid sites supports the cracking of olefinic compounds [3, 19]. The majority of the acid sites in crystalline solid acids are located within the pores of the material, such as with zeolites [3, 20]. Thus, main feature in assessing the level of polyolefin cracking over such catalysts is the microporosity of porous solid acids. The carbonium ion mechanism of catalytic pyrolysis of polyethylene can be described as follows [3, 21] (see Table 5).

(1) *Initiation.* Initiation may occur on some defected sites of the polymer chains. For instance, an olefinic linkage could be converted into an on-chain carbonium ion by proton addition:



The polymer chain may be broken up through β -emission:

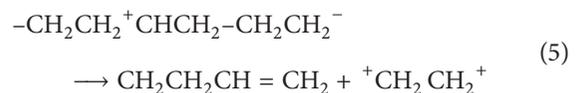
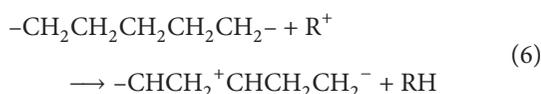


TABLE 5: List of catalysts in use.

Sr. no.	Catalyst	Pore size (nm)	Commercial name	References
1	USY	0.74	H-Ultrastabilised, Y-zeolite	[8–10]
2	ZSM-5	0.55 × 0.51	H-ZSM-5 zeolite	[8–10]
3	MOR	0.65 × 0.70	H-Mordenite	[8, 9]
4	ASA	3.15	Synclyst 25 (silica-alumina)	[8, 9]
5	MCM-41	4.2–5.2	—	[8, 9, 11]
6	SAHA	3.28	Amorphous silica-alumina	[10]
7	FCC-R1	—	Equilibrium catalyst	[10]
8	Silicalite	0.55 × 0.51	Synthesized in house	[10]

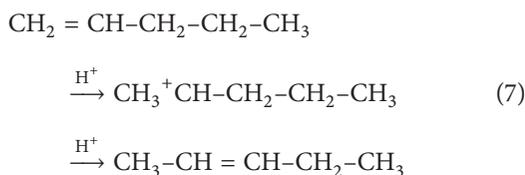
Initiation may also take place through random hydride-ion abstraction by low-molecular-weight carbonium ions (R^+):



The newly formed on-chain carbonium ion then undergoes β -scission.

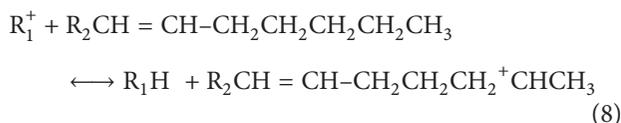
(2) *Depropagation*. The molecular weight of the main polymer chains may be reduced through successive attacks by acidic sites or other carbonium ions and chain cleavage, yielding oligomer fraction (approximately C_{30} – C_{80}). Further, cleavage of the oligomer fraction probably by direct β -emission of chain-end carbonium ions leads to gas formation on one hand and a liquid fraction (approximately C_{10} – C_{25}) on the other.

(3) *Isomerization*. The carbonium ion intermediates can undergo rearrangement by hydrogen- or carbon-atom shifts, leading to a double-bond isomerization of an olefin:



Other important isomerization reactions are methyl-group shift and isomerization of saturated hydrocarbons.

(4) *Aromatization*. Some carbonium ion intermediates can undergo cyclization reactions. An example is when hydride ion abstraction first takes place on an olefin at a position several carbons removed from the double bond, the result being the formation of an olefinic carbonium ion:



The carbonium ion could undergo intramolecular attack on the double bond.

Panda et al. [3] and Sekine, and Fujimoto [22] have proposed a free radical mechanism for the catalytic degradation

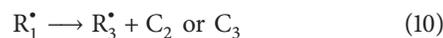
of PP using Fe/activated carbon catalyst. Methyl, primary and secondary alkyl radicals are formed during degradation and methane, olefins and monomers are produced by hydrogen abstractions and recombination of radical units [3, 23].

The various steps in catalytic degradation are shown below [3].

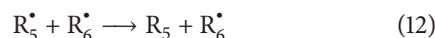
(1) *Initiation*. Random breakage of the C–C bond of the main chain occurs with heat to produce hydrocarbon radicals:



(2) *Propagation*. The hydrocarbon radical decomposes to produce lower hydrocarbons such as propylene, followed by β -scission and abstraction of H-radicals from other hydrocarbons to produce a new hydrocarbon radical:



(3) *Termination*. Disproportionation or recombination of two radicals:



During catalytic degradation with Fe activated charcoal in H_2 atmosphere, hydrogenation of hydrocarbon radical (olefin) and the abstraction of the H-radical from hydrocarbon or hydrocarbon radical generate radicals, and thus, enhancing degradation rate. At reaction temperature lower than $400^\circ C$ or a reaction time shorter than 1.0 h, many macromolecular hydrocarbon radicals exist in the reactor, and recombination occurs readily because these radicals cannot move fast. However, with Fe activated carbon in a H_2 atmosphere, these radicals are hydrogenated, and therefore, combination may be suppressed. Consequently, it seems as if the decomposition of the solid product is promoted, including low polymers whose molecular diameter is larger than the pore size of the catalysts.

4.3. *Gasification*. In this process, partial combustion of biomass is carried out to produce gas and char at the first stage

and subsequent reduction of the product gases, chiefly CO₂ and H₂O, by the charcoal into CO and H₂. Depending on the design and operating conditions of the reactor, the process also generates some methane and other higher hydrocarbons (HCs) [5, 24]. Broadly, gasification can be defined as the thermochemical conversion of a solid or liquid carbon-based material (feedstock) into a combustible gaseous product (combustible gas) by the supply of a gasification agent (another gaseous compound). The gasification agent allows the feedstock to be quickly converted into gas by means of different heterogeneous reactions [5, 25–27]. If the process does not occur with help of an oxidising agent, it is called indirect gasification and needs an external energy source gasification agent, because it is easily produced and increases the hydrogen content of the combustible gas [5, 28].

A gasification system is made up of three fundamental elements: (1) the gasifier, helpful in producing the combustible gas; (2) the gas clean up system, required to remove harmful compounds from the combustible gas; (3) the energy recovery system. The system is completed with suitable subsystems, helpful to control environmental impacts (air pollution, solid wastes production, and wastewater).

Gasification process represents a future alternative to the waste incinerator for the thermal treatment of homogeneous carbon based waste and for pretreated heterogeneous waste.

5. Summary

Plastics are “one of the greatest innovations of the millennium” and have certainly proved their reputation to be true. Plastic is lightweight, does not rust or rot, is of low cost, reusable, and conserves natural resources and 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 cost, and optimization of gasoline range products for a wide range of plastic mixtures or waste.

Huge amount of plastic wastes produced may be treated with suitably designed method to produce fossil fuel substitutes. The method is superior in all respects (ecological and economical) if proper infrastructure and financial support is 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 of the petroleum without emitting any pollutants. It would also take care of hazardous plastic waste and reduce the import of crude oil.

Challenge is to develop the standards for process and products of postconsumer 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, analysis would help reducing the capital investment and also the operating cost and thus would enhance the economic viability of the process.

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