Plastic: Waste to Fuel

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Abstract:

Plastics consumption has increased rapidly throughout the world. Approximately 40% of the plastics have life duration shorter than 1 month, thus there is a huge waste stream creating a serious environmental problem. Thermoplastic polymers make up a high proportion of waste and this amount is continuously increasing, thus posing a more serious environmental challenge because of their huge quantity and disposal problem as thermoplastics do not biodegrade for very long time. Different methods like land filling, incineration, gasification, recycling etc., are used to get rid of them. But by using most of these processes, the resources used to make the plastics are lost and no recovery can be made. In this world of continuously declining natural fuel sources, making of fuel from the waste plastic can be a very beneficial. Various methods like pyrolysis, fluidized catalytic cracking, thermal and catalytic cracking etc., can be used for generation of fuel from waste plastics. Plastics can even be used as fuel themselves in blast furnace with coal. So here is a brief description of the methods used to generate fuel from plastics, Waste Plastics.

Keywords: Plastics, incineration, waste, natural fuel, environmental challenge.

Introduction:

The huge population increase coupled with the improved living conditions of the people led to a dramatic increase of the consumption of plastics worldwide.

The chief usages of polymeric materials are in:

1. Packaging,
2. Household and domestic products,
3. Electrical and electronic goods,
4. Building and construction,
5. Automotive industries, etc…[1]

Plastics consumption has increased rapidly throughout the world. The annual plastic consumption in United States was 30 million tons in 2006 and 48.8 million tons in Western Europe in 2003. In Asia, the consumption rate is less per person but growing faster than that of the US or Europe.[2]

Our modern society is unimaginable without plastics. Nowadays both the consumption and production of polymers are increasing, but the increasing amount of polymer wastes from them generates further environmental problems[3]. Approximately 40% of the waste plastics have life duration shorter than 1 month, thus there is a huge waste stream creating a serious environmental problem[4].

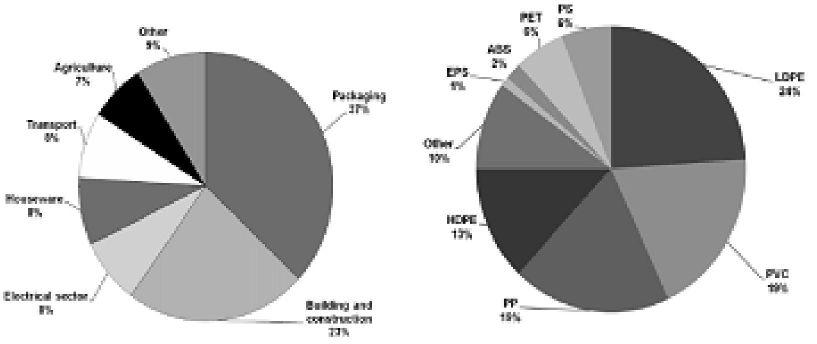


Figure: 1: Plastic Consumption, according to industryand polymer. UK[5]

Thermoplastic polymers make up a high proportion of waste and this amount is continuously increasing, posing a more serious environmental challenge because thermoplastics do not biodegrade for very long time[1]. Plastic products, such as polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PSI, polyurethane and polyphenols, make up 83% of the production of plastics[5]. See figure1.

MAJOR METHODS TO GET RID OF PLASTIC WASTE:

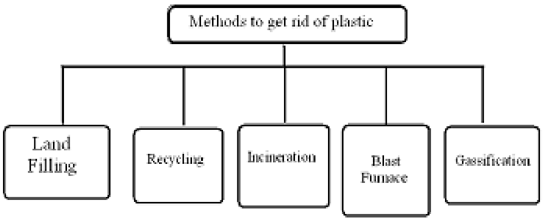


Figure: 2 Methods to get rid of Plastic[6]

1. Land Filling:

The disposal of solid tire wastes from human activity is a growing environmental problem for the modern society, especially in developing countries. This organic solid waste is non-biodegradable. One common way of disposal is land filling. Land filling for disposal of used tires is connected with some problems: it needs a considerable amount of space because the volume of tires cannot be compacted.

Dumped scrap tire in massive stockpiles is one of the possible causes of ideal breeding grounds for disease carrying mosquitoes and other vermin with the aid of rain water, which is deposited in the free space of the tire wall. Also, land filling is a potential danger because of the possibility of accidental fires with high emissions of hazardous gases.[6]

2. Recycling

Currently, however, only somewhere between 5 and 25% of plastic waste is being recycled. Recycling of plastics should be carried in such a manner to minimize the pollution during the process and to enhance the efficiency of the process and conserve the energy. Plastics recycling technologies have been historically divided into four general types -primary, secondary, tertiary and quaternary.

Primary recycling involves processing of a waste/scrap into a product with characteristics similar to those of original product.

Secondary recycling involves processing of waste/scrap plastics into materials that have characteristics different from those of original plastics product.

Tertiary recycling involves the production of basic chemicals and fuels from plastics waste/scrap as part of the municipal waste stream or as a segregated waste.

Quaternary recycling retrieves the energy content of waste/scrap plastics by burning / incineration. This process is not in use in India.[7]

Mechanical recycling processes are limited to thermoplastics and technical limitations for the treatment of mixed plastic wastes, together with the limited size of the market for recycled products, difficulties in maintaining product quality and fluctuations in the price.[8]

The problems associated with the recycling process are as follows:

- Many types of plastics are used hence it is difficult to segregate them for specific purpose.
- Plastics contain a wide range of fillers & additives.
- Many times plastic is associated with metal, glass etc.
- Sorting of plastic is technically difficult as well as expensive.
- Recycling of plastic degrades the quality of the end product

3. Incineration

Often practiced in developed economies is incineration with energy recovery. In this, waste is burnt, thereby significantly reducing the volume of waste requiring disposal. Incineration with energy recovery is not an action specific to the packaging waste, but is relevant to municipal waste at large. If the overall goal of the waste management system is to minimise the disposal to landfills[9], incineration can complement the recycling systems. Incineration with energy recovery is a feasible option in countries where material recycling is low and waste has a high calorific value.

In the case of India, incineration with energy recovery may not be a feasible option, considering the fact that material recycling of plastics is as high as 60%. This may not leave waste with much calorific value, thus making incineration with energy recovery a non-viable option.[10]

Due to the generation of unacceptable emissions of gases such as nitrous and sulphur oxides, dusts, and dioxins, incineration can no longer be an important mode of waste disposal.[8]

4. Blast furnace

Waste plastic may be used in place of coke and pulverized coal after forming into particles of the required size and subsequently injected into the blast furnace. The injected plastic is broken down to form reducer gas ($CO + H_2$), which rises through the raw material in the furnace and reacts with the iron ore. The injection of chlorine-contained plastics such as PVC in the blast furnace generates hydrogen chloride. The limestone used in the blast furnace to control the composition of the slag neutralizes the hydrogen chloride in the furnace and decrease its concentration.

But substitution of coke with plastic is limited to approximately 40% wt only.[9-11]

5. Gasification

Gasification is essentially thermal decomposition of organic matter under inert atmospheric conditions or in a limited supply of air. If the feed contains chlorinated compound like PVC then it is advisable to do gasification at a lower temperature to remove chlorine then the temperature is raised to convert higher hydrocarbons.

There are problems in controlling the combustion temperature and the quantity of unburned gases.[12]

In Europe, recycling rates for post-use plastic waste were as follows:

1. Incineration with energy recovery (14%),
2. Mechanical recycling (6%)
3. Feedstock or chemical recycling (0.3%).[13]

<u>Different Steps involved before carrying out the above or the below mentioned process:</u>

Figure: 3 Different Steps involved [13]

1. Collection:

When thinking about setting up a small-scale recycling enterprise, it is advisable to first carry out a survey to ascertain the types of plastics available for collection, the type of plastics used by manufacturers (who will be willing to buy the reclaimed material), and the economic viability of collection.

The method of collection can vary. The following gives some ideas;

- House to house collection of plastics and other materials (e.g. paper).
- House to house collection of plastics only (but all types of polymer).
- House to house collection of certain objects only.
- Collection at a central point e.g. market or church.
- Collection from street boys in return for payment.
- Regular collection from shops, hotels, factories, etc.
- Purchase from scavengers on the municipal dump.
- Scavenging or collecting by oneself.

The method will depend upon the scale of the operation, the capital available for set-up, transport availability, etc.

2. Initial upgrading

Once the plastic has been collected, it will have to be cleaned and sorted. The techniques used will depend on the scale of the operation and the type of waste collected, but at the simplest level will involve hand washing and sorting of the plastic into the required groups. More sophisticated mechanical washers and solar drying can be used for larger operations.

Sorting of plastics can be by polymer type (thermoset or thermoplastic for example), by product (bottles, plastic sheeting, etc.), by colour, etc.

3. Size reduction techniques

Size reduction is required for several reasons; to reduce larger plastic waste to a size manageable for small machines, to make the material denser for storage and transportation, or to produce a product which is suitable for further processing.

There are several techniques commonly used for size reduction of plastics:

- *Cutting* is usually carried out for initial size reduction of large objects. It can be carried out with scissors, shears, saw, etc.

- *Shredding* is suitable for smaller pieces. A typical shredder has a series of rotating blades driven by an electric motor, some form of grid for size grading and a collection bin. Materials are fed into the shredder via a hopper which is sited above the blade rotor. The product of shredding is a pile of coarse irregularly shaped plastic flakes which can then be further processed.
- *Agglomeration* is the process of pre-plasticising soft plastic by heating, rapid cooling to solidify the material and finally cutting into small pieces. This is usually carried out in a single machine. The product is coarse, irregular grain, often called crumbs. See figure 4.

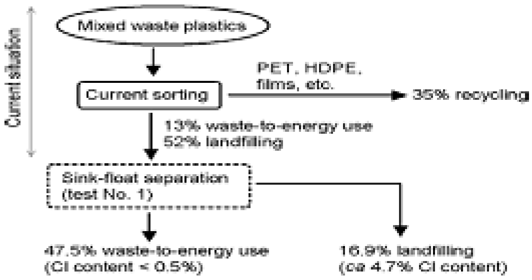


FIGURE: 4 [14]

FUEL FROM PLASTIC:

Management of plastic wastes is a hot issue and currently about 90% of the plastic wastes are disposed in landfills and incineration, but both these applications are not environmental friendly and create other problems[14]. To avoid environmental problems and use plastic waste as a resource, alternative solutions are needed.

It can be converted into useful products for resource recovery. To overcome the current energy crises in the world, new energy resources should be explored among which waste high-density polyethylene could be used as raw material. One of the possible solutions is thermal/catalytic degradation of the plastic materials to obtain a useful and selective degradation product like fuel oil and laboratory chemicals[15].

Energy recovery as fuel is a preferred option for utilizing plastic wastes when their potential recycling as raw material for product manufacturing is not possible because their physical properties have been damaged during long exposure to sunlight. [16]

It was found that the degradation process is a suitable technique for converting waste polymers into liquid hydrocarbons. The volatile products could be used as feedstock components, e.g. in refineries. Their further utilization for petrochemical purposes has not yet been solved. One possibility is a fuel-like application or mixing in fuels as a blending component. Before blending the high olefin content is to be saturated with hydrogen, or hydroisomerized. These steps result in a high quality synthetic diesel fuel, with high cetane number, and theoretically free from sulphur, nitrogen and metals. In practice these fractions generally have a very low heteroatom content, even if the raw material was pure and not waste, because most polymers contain, e.g. sulphur containing anti-flame or antioxidant additives, etc. [17]. See Figure5.

Figure: 5 [17]

A research-cum-demonstration plant was set up at Nagpur, Maharashtra for conversion of waste plastics into liquid fuel. The process adopted is based on random de-polymerization of waste plastics into liquid fuel in the presence of a catalyst. The entire process is undertaken in a closed reactor vessel followed by condensation, if required. Waste plastics while heating upto 270^0C to 300^0C convert into liquid-vapour state, which is collected in a condensation chamber in the form of liquid fuel while the tarry liquid waste is topped-down from the heating reactor vessel. The organic gas is generated which is vented due to lack of storage facility. However, the gas can be used in dual fuel diesel-generator set for generation of electricity. Process is as shown in the diagram above. [17]

India has been a favored dumping ground for plastic wastes, mostly from industrialized countries like Canada, Denmark, Germany, UK, the Netherlands, Japan, France and the United States. According to the Government of India import data, 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.[18] See table 1.

Table 1 [19]:

India is the fourth highest Asian importer of plastic waste.

Country	No. of Shipments	Total (kg)
Hong Kong	586	1,71,37,118.00
Philippines	58	24,45,200.00
Indonesia	50	22,48,443.00
India	**11**	**9,98,046.00**
Malaysia	7	2,54,935.00
China	6	95,746.00
Taiwan	6	1,56,453.00
Thailand	6	1,23,974.00
Korea	6	1,09,807.00
Japan	5	51,210.00
Singapore	6	71,437.00
Total	**747**	**23,692,369.00**

DIFFERENT WAYS: WASTE PLASTIC TO FUEL

1. Pyrolysis:

Pyrolysis provides an excellent alternative for the disposal of plastic wastes with the recovery of valuable transportation fuels like gasoline, kerosene and diesel.

1.1 Thermal pyrolysis of plastic yields a very broad compositional range of low-value mixture of liquid hydrocarbons

1.2 Catalytic pyrolysis yields a more narrow range of products, most suitable for transportation fuels.

Pyrolysis of waste plastic affords high rates of conversion into liquid fuels that can be used as feedstock in refinery[20]. The advantage of pyrolysis is that the waste plastics do not have to be separated ahead of time, thereby, eliminating the labor-intensive step as required in the hydrolysis and mechanical recycling methods. The production of transportation fuels from waste plastics is an emerging technological solution to the huge amount of waste plastics that cannot be economically recovered by conventional mechanical recycling processes. The pyrolysis of mixed plastics has been considered as an effective way to convert waste plastics into environmental and industrially useful hydrocarbon products.[21]

The mechanism of thermal degradation of waste plastic is very complex and includes, amongst others, the following reactions: chain fission, radical recombination, carbon–hydrogen bond fission, hydrogen abstraction, mild-chain α-scission, radial addition, etc.[21]

Example 1: Pyrolysis of waste from agricultural and packaging sector**:**

Selectively collected waste high-density polyethylene (HDPE) and polypropylene (PP) from agriculture and packaging sectors were used as raw materials. Both waste plastics were washed and shredded before pyrolysis. It is also clear that both plastic wastes have sulphur content (238 and 49 mg/kg respectively), while nitrogen, phosphorus and calcium additionally have been found only in the case of polypropylene (963 mg/kg, 47 mg/kg and 103 mg/kg). In all probability fertilizers (possibly superphosphate and ammoniumnitrate) can be accumulated in the surface of polyethylene agricultural wastes, which could not be removed by washing procedure. The super-phosphate and ammonium-nitrate are widely used fertilizers, in which generally are also calcium and sulphur containing other chemicals. See figure6.

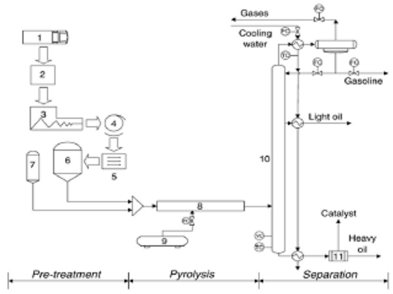
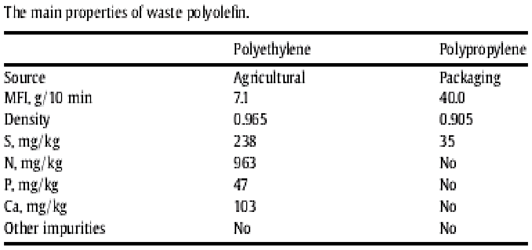


Figure: 6 Applied apparatus for pyrolysis of waste polymers . 1—Transportation, 2—Selective collection, 3—Shredding, 4—Washing, 5—Drying, 6—Waste storage, 7—Catalyst storage, 8—Reactor, 9—Heating gas storage, 10—Separation unit, 11—Catalyst filter [22]

Pyrolysis of waste polymers was carried out in continuous reactor with feed rate of 9.0 kg/h at 520°C. As shown in the figure 6, plastics with suitable grain size had been stored in a raw material storage unit. Raw material was mixed with the catalyst (For supporting the more intensive cracking of C-C bonds of main polymer structure a commercial ZSM-5 catalyst was tested in concentration of 5.0%.) then that mixture was fed in the reactor by an electrically heated extruder, where the polymer was preheated. The outside wall temperature of the feeder was 280°C in each case. The extruder was directly connected to the reactor in the beginning section. See table 2.

Table 2



The main properties of waste polyolefin.

	Polyethylene	Polypropylene
Source	Agricultural	Packaging
MFI, g/10 min	7.1	40.0
Density	0.965	0.905
S, mg/kg	238	35
N, mg/kg	963	No
P, mg/kg	47	No
Ca, mg/kg	103	No
Other impurities	No	No

Inside the gas heated reactor the waste polymer had melted and their carbon chain cracked into fragments with lower molecular weights. To reach better heat transfer the hydrocarbon flow had been driven by using special mixing equipment inside the reactor tube. For adjusting the temperature constant thermocouples and electronic PID controllers were used both in the extruder and pyrolysis reactor.

Table 4:

In the distillation column hydrocarbons were separated into different products: gases, gasoline, light and heavy oil. The column bottom temperature was 380°C.

Catalyst was separated from the bottom product by filtration in thermo-catalytic pyrolysis.

Gases from polypropylene pyrolysis consisted mainly of C_3 hydrocarbons both catalytic and non-catalytic cases (55.9% and 54.6%), in contrast to agricultural waste, where the C_2 (52.0% and 45.6%) and C_4 (31.7% and 25.5%) compounds were the most significant fractions. For these results basically the chemical structure of raw materials is blamed too. See table 3.

Table 3:

The composition of gases obtained by plastic waste pyrolysis.

	HDPE	HDPE + catalyst	PP	PP + catalyst
Methane	3.1	2.5	4.2	4.8
Ethene	30.6	26.1	11.4	6.6
Ethane	21.4	19.5	7.3	6.4
Propene	8.9	8.9	30.0	30.1
Propane	4.3	6.8	25.9	24.5
Butene	17.1	14.6	11.8	9.5
Butane	14.6	10.9	9.4	6.2
i-Butane	0.0	10.7	0.0	11.9

The carbon chain of PP cracked in highest likelihood at the ramification of the chain, which resulted to high amount of propylene (30.0% and 30.1%) and propane (25.9% and 24.5%). Data also well demonstrates that the formation of alkenes was a bit higher than alkanes of the same carbon number.

The calculated heating values of gases were 45.9–46.6 MJ/kg, which is enough for high energy generation to heat consumption of pyrolysis.

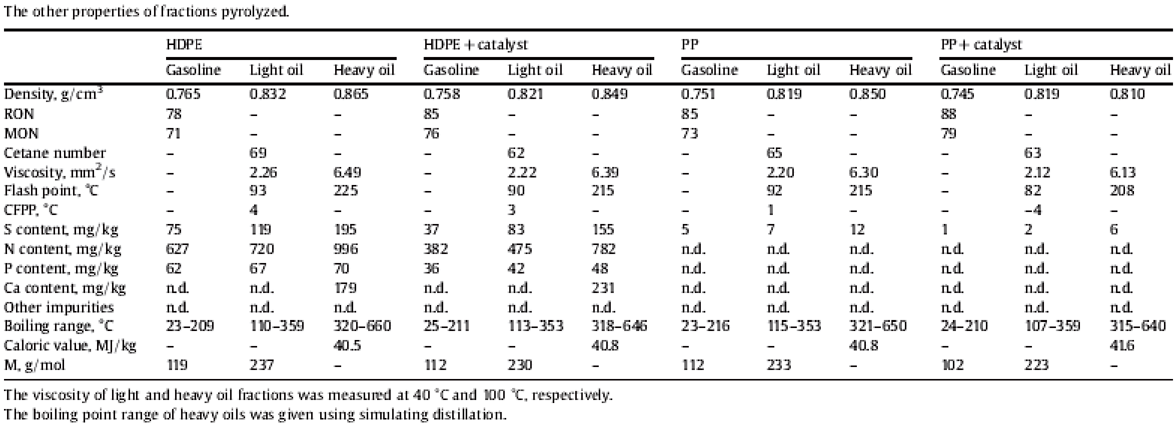
It is well discernible that carbon-chain isomerization takes place in the presence of catalysts, but the yields of branched hydrocarbons were lower in the case of polyethylene than polypropylene. For the high level of α-olefins basically the α -scissions are blamed, which are the ruling reaction in thermal case. See table 4.

The structure of gasoline and light oil fractions.

Products	Gasoline				Light oil			
	HDPE	HDPE + catalyst	PP	PP + catalyst	HDPE	HDPE + catalyst	PP	PP + catalyst
n-Paraffin	49.6	33.9	18.8	8.3	49.2	35.5	14.4	7.9
i-Paraffin	3.0	20.4	41.1	51.4	3.3	15.4	47.1	52.1
Vinyl olefin	43.9	9.3	4.2	2.7	41.5	8.8	3.7	3.1
Vinilydene olefin	2.5	2.1	34.0	22.7	2.1	3.6	31.0	20.5
Vinilene olefin	1.0	32.6	1.4	12.9	3.9	35.2	3.4	14.5
Aromatic	0.0	1.7	0.5	2.0	0.0	1.5	0.4	1.9

In catalytic case ions should be isomerized and result to branched hydrocarbons and internal olefins. The carbon frame isomerization effect was more notable in gasoline than that of light oil. When catalyst had been used, the concentration of branched compounds was 6.8

(polyethylene) and 1.3 (polypropylene) times more in gasoline related to the catalyst free pyrolysis, while the increase was only 4.6 (polypropylene) and 1.1 (polypropylene) times in light oil. Therefore the catalytic effect was more significant of smaller molecules. See table 5.



The other properties of fractions pyrolyzed.

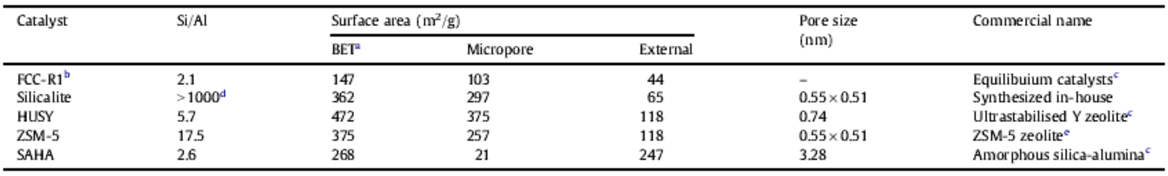
	HDPE			HDPE + catalyst			PP			PP + catalyst		
	Gasoline	Light oil	Heavy oil	Gasoline	Light oil	Heavy oil	Gasoline	Light oil	Heavy oil	Gasoline	Light oil	Heavy oil
Density, g/cm^3	0.765	0.832	0.865	0.758	0.821	0.849	0.751	0.819	0.850	0.745	0.819	0.810
RON	78	–	–	85	–	–	85	–	–	88	–	–
MON	71	–	–	76	–	–	73	–	–	79	–	–
Cetane number	–	69	–	–	62	–	–	65	–	–	63	–
Viscosity, mm^2/s	–	2.26	6.49	–	2.22	6.39	–	2.20	6.30	–	2.12	6.13
Flash point, °C	–	93	225	–	90	215	–	92	215	–	82	208
CFPP, °C	–	4	–	–	3	–	–	1	–	–	−4	–
S content, mg/kg	75	119	195	37	83	155	5	7	12	1	2	6
N content, mg/kg	627	720	996	382	475	782	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
P content, mg/kg	62	67	70	36	42	48	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ca content, mg/kg	n.d.	n.d.	179	n.d.	n.d.	231	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other impurities	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Boiling range, °C	23–209	110–359	320–660	25–211	113–353	318–646	23–216	115–353	321–650	24–210	107–359	315–640
Caloric value, MJ/kg	–	–	40.5	–	–	40.8	–	–	40.8	–	–	41.6
M, g/mol	119	237	–	112	230	–	112	233	–	102	223	–

The viscosity of light and heavy oil fractions was measured at 40 °C and 100 °C, respectively.
The boiling point range of heavy oils was given using simulating distillation.

Table 5:

Their caloric values were about 41.0 MJ/kg, which is quite high to application of these fractions for energy producing.[22]

Table 6:



Catalyst	Si/Al	Surface area (m^2/g)			Pore size (nm)	Commercial name
		BET[a]	Micropore	External		
FCC-R1[b]	2.1	147	103	44	–	Equilibuium catalysts[c]
Silicalite	>1000[d]	362	297	65	0.55 × 0.51	Synthesized in-house
HUSY	5.7	472	375	118	0.74	Ultrastabilised Y zeolite[c]
ZSM-5	17.5	375	257	118	0.55 × 0.51	ZSM-5 zeolite[e]
SAHA	2.6	268	21	247	3.28	Amorphous silica-alumina[c]

Example 2: Pyrolysis of hospital plastic waste:

The mixture of hospital waste plastics used in this study was obtained from post-consumer polymer waste stream in North-Taiwan with the component of polyethylene (~62 wt.% PE=~38 wt. % HDPE+~24 wt.% LDPE), polypropylene (~34 wt.% PP), polyvinyl chloride (~3 wt.% PVC) and with about 1 wt.% polystyrene (PS) mixtures.

Typically, the content of waste plastic sample tested by element analysis was about:

84.84% C, 12.31% H, 2.72% Cl, 0.06% O, 0.07% N, and 0.13% S.

A three-zone heating furnace with digital controllers was used and the temperatures of the furnace in its upper, middle and bottom zones were measured using three thermocouples. By these means the temperature of the pre-heated nitrogen below the distributor and catalyst particles

(See table 6) in the reaction volume could effectively controlled to within ±1 °C. The polymer feed system was designed to avoid plugging the inlet tube with melted polymer and to eliminate air in the feeder. The feed system was connected to a nitrogen supply to evacuate polymer into the fluidized catalyst bed. See figure 7.

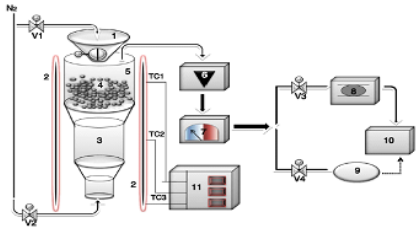


Figure: 7: Schematic diagram of a catalytic fluidized-bed reactor system. [23]

1. feeder, 2. furnace, 3. sintered distributor, 4. fluidised catalyst, 5. reactor, 6. condenser, 7. de-ionized water trap, 8. 16-loop automated sample system, 9. gas bag, 10. GC, and 11. digital controller for three-zone furnace.

Thus, commingled polymer particles were purged under nitrogen into the top of the reactor and allowed to drop freely into the fluidized bed. Volatile products leaving the reactor were passed through a glass-fiber filter to capture catalyst fines, followed by an ice-acetone condenser to collect any condensable liquid product.

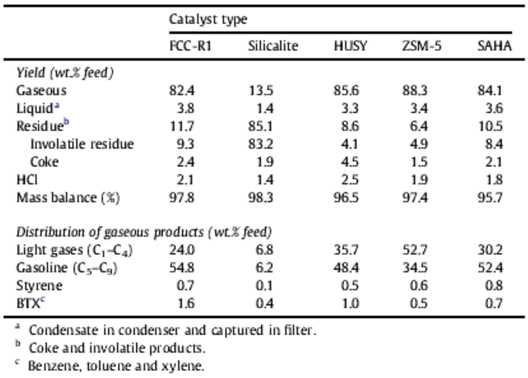
A de-ionized water trap was placed in series after the condenser to catch any HCl produced by the degradation of PVC component. A three-way valve was used after the condenser to route product either into a sample gas bag or to an automated sample valve system with 16 loops. The Tedlar bags, 15 L capacity, were used to collect time-averaged gaseous samples. The bags were replaced at intervals of 10 min. throughout the course of reaction.

Summary of the main products of post-consumer waste plastics degradation at reaction temperature of 390°C over various catalysts (fluidizing N_2 rate=570 ml min-1, catalyst to plastic ratio=30 wt.% and catalyst particle size=125–180 µm).

It is also concluded that the use of this reaction system coped with a spent FCC equilibrium catalyst can be a better option

since it may lead to a cheaper process with valuable products and can be further used as an adequate approach for the catalytic recycling of plastic waste.[23] See table 7.

Table 7:



	Catalyst type				
	FCC-R1	Silicalite	HUSY	ZSM-5	SAHA
Yield (wt.% feed)					
Gaseous	82.4	13.5	85.6	88.3	84.1
Liquid[a]	3.8	1.4	3.3	3.4	3.6
Residue[b]	11.7	85.1	8.6	6.4	10.5
Involatile residue	9.3	83.2	4.1	4.9	8.4
Coke	2.4	1.9	4.5	1.5	2.1
HCl	2.1	1.4	2.5	1.9	1.8
Mass balance (%)	97.8	98.3	96.5	97.4	95.7
Distribution of gaseous products (wt.% feed)					
Light gases (C_1–C_4)	24.0	6.8	35.7	52.7	30.2
Gasoline (C_5–C_9)	54.8	6.2	48.4	34.5	52.4
Styrene	0.7	0.1	0.5	0.6	0.8
BTX[c]	1.6	0.4	1.0	0.5	0.7

[a] Condensate in condenser and captured in filter.
[b] Coke and involatile products.
[c] Benzene, toluene and xylene.

Example 3: Pyrolysis of motorcycle tyre waste:

A variety of scrap tires are available in the modern society. These are bicycle and rickshaw tires, motorcycle and auto-rickshaw tires, car and taxi tires, microbus and jeep tires, tractor tires, bus and truck tires. Tires contain vulcanized rubber in addition to the rubberized fabric with reinforcing textile cords, steel or fabric belts, and steel-wire reinforcing beads Other components in the tire are: carbon black, extender oil, which is a mixture of aromatic hydrocarbons, sulphur, accelerator, typically an organo-sulphur compound, zinc oxide, and stearic acid.

There are many different manufacturers and countless different formulations available all over the world; the composition of the tire varies depending on the tire grade and manufacturers. Consequently, the tire pyrolysis products may also vary in terms of yield and chemical composition depending on the source and grade of the tires.

Very different experimental procedures have been used to obtain liquid products from automotive tire wastes by pyrolysis technology including fixed-bed reactors, fluidized-bed pyrolysis units, vacuum pyrolysis units, spouted-bed reactors, etc., ranging from laboratory to commercial scale plants.

The Indian made ‘‘MRF” brands of motorcycle tires, which are mostly consumed in Bangladesh, has been taken into consideration as feedstock The main components of tires such as rubber, fillers like carbon black, steel, sulfur, zinc oxide, processing oil, vulcanization accelerators, etc. are heterogeneously distributed over the cross-section.

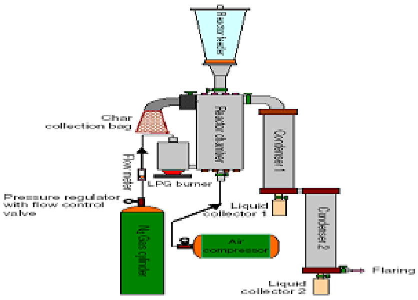


Figure: 8 Schematic diagram of the fixed-bed .re-tube heating pyrolysis system[24]

The experimental unit consists of eight major components: (1) a fixed-bed re-tube heating reactor chamber with a power system; (2) a gravity feed type reactor feeder; (3) two ice cooled condensers, each of them having a liquid collecting glass bottle; (4) an N_2 gas cylinder with a pressure regulator, a flow control valve and a gas flow meter; (5) an N_2 gas pre-heater with LPG burner; (6) an air compressor; (7) char collecting bag; and (8) Ktype (chromel–alumel) thermocouples, whose measurement accuracy is ±2.5°C with a temperature controller. At a distance of 30 mm from the closed bottom of the reactor, a distributor plate was fitted to support the feedstock. See figure 8.The distributor plate was made of stainless-steel plate having 150 holes of 3 mm diameter. The N_2 gas inlet was 20 mm below the distributor plate. Eight equally spaced stainless steel, 10 mm diameter .re-tubes containing insulated electric coil of a total capacity 1.60 kW were fixed inside the reactor. The .re-tubes and pre-heated N_2 gas provided uniform heating across the cross-section of the reactor chamber. The reactor was thermally insulated with asbestos cylinder. The reactor height from the distributor to the gas exit was 270 mm and its diameter was 100 mm, which provided an apparent vapor residence time of 5 s.

Three types of products are usually obtained from pyrolysis of tire rubber: solid char, liquid, and gas. The product distributions obtained from pyrolysis of prepared representative sample for temperature range of 375–575°C at every 50°C, feedstock size of 4 cm^3 and vapor residence time of 5 s. See figure 9.

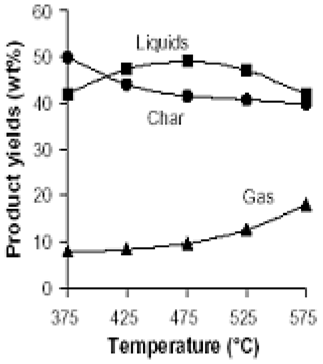
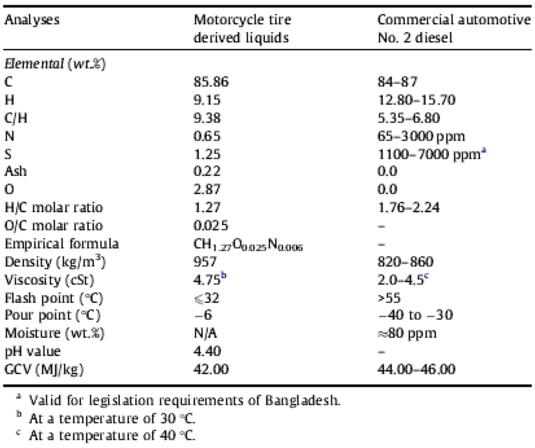


Figure: 9 Effect of temperature on product yields[25]

The pyrolytic liquids obtained from pyrolysis of motorcycle tire wastes, which are oily organic compounds, appears dark brown with a strong acrid smell. Careful handling of the liquids is required since it reacts easily with human skins, leaving permanent yellowish brown marks and an acrid smell for a few days, which is difficult to remove by detergent.

The fuel properties of the pyrolytic liquids in comparison to commercial automotive No. 2 diesel, which is mostly consumed in Bangladesh, are: See table 8.



Analyses	Motorcycle tire derived liquids	Commercial automotive No. 2 diesel
Elemental (wt.%)		
C	85.86	84–87
H	9.15	12.80–15.70
C/H	9.38	5.35–6.80
N	0.65	65–3000 ppm
S	1.25	1100–7000 ppm[a]
Ash	0.22	0.0
O	2.87	0.0
H/C molar ratio	1.27	1.76–2.24
O/C molar ratio	0.025	–
Empirical formula	$CH_{1.27}O_{0.025}N_{0.006}$	–
Density (kg/m^3)	957	820–860
Viscosity (cSt)	4.75[b]	2.0–4.5[c]
Flash point (°C)	⩽32	>55
Pour point (°C)	−6	−40 to −30
Moisture (wt.%)	N/A	≈80 ppm
pH value	4.40	–
GCV (MJ/kg)	42.00	44.00–46.00

[a] Valid for legislation requirements of Bangladesh.
[b] At a temperature of 30 °C.
[c] At a temperature of 40 °C.

Table 8:

The main inferences from pyrolysis of motorcycle tire waste are as follows:

1. The main rubber components in the present motorcycle tire waste are NR and SBR. The motorcycle tire rubber formulation comparatively use larger amount of inorganic materials as additives consequently energy content of the solid tire waste is lower than that of car and truck tire wastes.
2. The optimum liquid yield conditions for the fixed-bed re-tube heating reactor system are: operating temperature 475°C, feed size 4 cm^3 and apparent vapor residence time 5 s. The main effects of operating conditions on the product distributions are that:

   (i) The lower temperature and larger feed size favor incomplete decomposition, which increase in char yields and decrease in the liquid and gas yields,

   (ii) The higher temperature and longer residence time contributes to secondary reactions results in more gaseous products with the expense of liquids while char yields remain almost constant.
3. The fuel properties of the pyrolysis liquids such as density, viscosity, GCV, carbon and hydrogen contents are found almost comparable to those of the commercial automotive diesel fuels but higher sulphur content and lower ash point are problematic. The pyrolytic liquids may be used as diesel fuel or heating oils after the upgrading such as desulphurization and dehydrogenation or blending them with petroleum refinery streams.
4. The pyrolytic liquids abundantly contain olenes, specially limonene and light aromatics, which have higher market values as chemical feedstock than their use as fuels.

5. However, further studies are necessary to utilize pyrolytic liquids as liquid fuels or chemical feedstock.[6]

2. Furnace:

The possibility of using waste plastics as a source of secondary fuel in a blast furnace has been of recent interest. The success of this process, however, will be critically dependent upon the optimization of operating systems. For instance, the supply of waste plastics must be reliable as well as economically attractive compared with conventional secondary fuels such as heavy oil, natural gas and pulverized coal.

Example: 1 PE as fuel for furnace:

Considering that in volume-wise PE makes up the largest portion in waste plastics, recycled PE was used as a representative. The bulky samples, obtained from local recycling center, were cleaned and dewatered before use, and exposed to liquid nitrogen for easier fracture in a ball mill. Thus, prepared pallets were classified into three types based on the final particle size (1.0–1.5, 3.0–5.0, and 8.0–10.0 mm) and were stored in a desiccator for further use.

Figure 10 shows a schematic of a simulated blast furnace, named as *hot model*. Three LPG type gas heaters were used to blow hot air through the blow-pipe, and by this set up the temperature could be efficiently controlled in the range of 900–1100°C. Oxygen could be also injected simultaneously with hot air. In the upper part of the blast, a coke injection chamber was installed, and blast could be operated continuously for 30 min with one fill-up. Upon reaching the preset temperature, waste plastics and/or pulverized coal (size is about 75mm) were injected at a rate of 45 kg/h through the side of the blow-pipe.

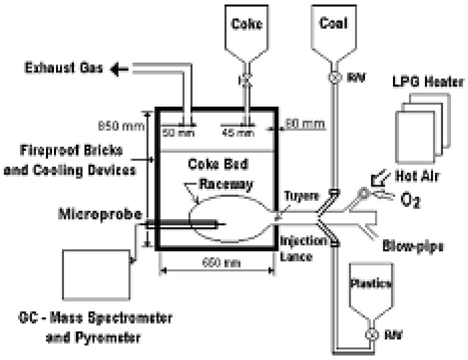


Figure: 10 Schematic Diagram of Blast Furnace[26]

PE thermally decomposes into oily liquid and gas phase successively. In Figure 11, thermogravimetric results for commercial low-density polyethylene (LDPE) and waste PE are shown. Detectable weight decrease starts from 300°C followed by fast thermal decomposition that ends around 400°C. The overall decomposition behavior for both samples were similar; however the inflection points of 50% of weight loss are, respectively, about 392 and 385°C for commercial LDPE and recycled PE, and this may be ascribed to more porous structure of recycled PE.

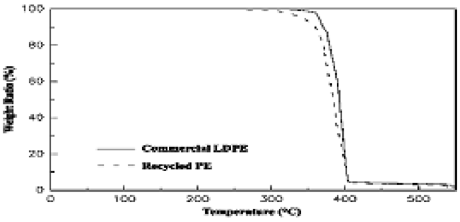


Figure: 11 TG curves for commercial LDPE and recycled PE [26]

It was found that with the increase of both blast temperature and the level of oxygen enrichment, and with the decrease of particle size, the combustion of waste PE occurred at shorter distance from the tuyere (figure 12). This strongly suggests that the combustibility of waste plastics can be improved by controlling these variables. Lastly the combustion behavior of the mixture of pulverized coal and waste PE was investigated. Although the efficiency of coal combustion was found to decrease with the addition of plastics, the combustion efficiency of the mixture could be comparable at longer distance from the tuyere. [26]

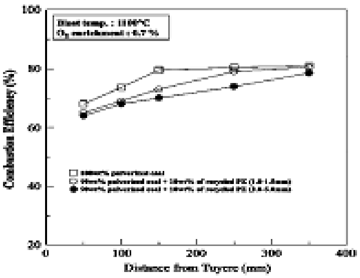


Figure: 12 Combustion behaviors of pure pulverized coal and mixtures of recycled plastics and pulverized coal [26]

Other methods that can be used are:

3. Thermal and Catalytic Process:

Thermal or catalytic cracking of waste plastics is one of the possible methods of their utilization[1-8]. As a result of the cracking at 400°C or higher process temperature some quantities of hydrocarbon mixtures in the form of gas, liquid products (gasoline and diesel fuel boiling range) as well as higher boiling liquid residue or solid can be obtained[1,6,8]. All these products can be used as fuels or fuel components. Especially liquid products of gasoline and diesel fuel boiling range can be applied as components of engine fuels. It is however necessary to remember that products of cracking or pyrolysis of polyolefines are highly unsaturated and therefore they have to be further submitted to hydrogenation and skeletal isomerization if they are to be applied as engine fuels. Application of cracking or hydrocracking catalyst and higher process temperature can enlarge conversion of waste plastics. The main goal of application of hydrocracking catalyst and hydrogen is hydrocracking of plastics and hydrogenation of olefins in process products.

4. Fluidized Catalytic Cracking:

A more interesting approach, however, is that of adding waste polymers into the usual feed-stocks of the process of fluid catalytic cracking of hydrocarbons (FCC) because, under standard process conditions, a large number of plastics, including polyolefins, can be dissolved into vacuum gas oils (VGO) and in this way, they can be converted into a mixture of hydrocarbon compounds. The idea has been tested with different plastics and laboratory conditions.

Conclusion:

Thus hereby we can conclude that, plastics can be well converted to fuel by either of the above said processes. The low molecular weight hydrocarbon obtained can be a good source of fuel. Plastics like PP, PE, PS, rubber, etc can be used for the purpose. It is, but important that the parameters of the process be well known and the process be carried out properly. Or else the yield of the process will change. Hydrocarbon polymers can be as said, easily used as fuel source, but when chlorinated polymers like PVC, PVDC, etc., are to be used, it is important that the process is able to handle the liberated HCl gas in an environmental friendly and non-hazardous manner.

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