



ABSTRACT

Plastics have woven their way into our daily lives and now pose a tremendous threat to the environment. Over a 100million tones of plastics are produced annually worldwide, and the used products have become a common feature at over flowing bins and landfills. Though work has been done to make futuristic biodegradable plastics, there

FUEL FROM PLASTIC WASTE

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INTRODUCTION

Every year humans produce nearly 280 million tons of plastic, and much of that plastic ends up in the environment, harming marine life and other ecosystems. The chemical bonds that makes plastic so durable makes it equally resistant to natural processes of degradation. Since plastics are non-biodegradable in nature, it is very difficult to eliminate the waste plastics from nature. Since 1950s 1 billion tons of plastic have been discarded and may persist for hundreds or even thousands of years. Expenditure incurred on disposal of plastic waste throughout the world is around US\$ 2 billion every year. Even for a small country like Honk Kong spends about US\$ 14 million a year on the exercise [1]. The majority of the plastic waste ends up in landfills, and becomes a carbon sink where it may take up to 1000 years to decompose and potentially leak pollutants into the soil and water.

Also the plastic wastes are dumped in the oceans threatening the health and safety of marine life. The uncontrolled incineration of plastic produces polychlorinated dibenzo-p-dioxins, a carcinogen. So, converting the waste



have not been many conclusive steps towards cleaning up the existing problem. Here, the process of converting waste plastic into value added fuels is explained as a viable solution for recycling of plastics. Thus two universal problems such as problems of waste plastic and problems of fuel shortage are being tackled simultaneously. In this study, plastic wastes (low density polyethylene) were used for the pyrolysis to get fuel oil that has the same physical properties as the fuels like petrol, diesel etc. Pyrolysis runs without oxygen and in high temperature of about 300°C which is why a reactor was fabricated to provide the required temperature for the reaction. The waste plastics are subjected to depolymerisation, pyrolysis, thermal cracking and distillation to obtain different value added fuels such as petrol, kerosene, and diesel, lube oil etc. Converting waste plastics into fuel hold great promise for both the environmental and economic scenarios. Thus, the process of converting plastics to fuel has now turned the problems into an opportunity to make wealth from waste. The hazards of plastic waste are well known to us. The conversion of oil from plastic has dual benefits. First of all the oil produced can be used as a fuel for domestic purposes and also in vehicles and industries when further refined. Secondly the various types of pollution caused due to waste plastics can be minimized. Plastic in the first place is manufactured from natural gas specifically from ethane which is a constituent of natural gas. Therefore the waste plastic can be converted back into it. For the process of conversion a machine can be used which will heat the plastic to a temperature so that it melts and does not burns.

Keywords: *plastic; reactors; pyrolysis; cracking; cataly.*

plastic into crude oil will have two benefits. First of all, the hazards caused due to plastic waste can be reduced and secondly, we will be able to obtain some amount of oil from it, which can be further purified to be used as a fuel in different areas such as domestic fuel, fuel for automobiles and industries etc. Thereby, our dependency on fossil fuels will reduce to a certain extent.



PLASTICS

As a brief introduction to plastics, it can be said that plastics are synthetic organic materials produced by polymerization. They are typically of high molecular mass, and may contain other substances besides polymers to improve performance and/or reduce costs. These polymers can be moulded or extruded into desired shapes.

1) There are two main types of plastics: thermoplastics and thermosetting polymers. Thermoplastics can repeatedly soften and melt if enough heat is applied and hardened on cooling, so that they can be made into new plastics products. Examples are polyethylene, polystyrene and polyvinyl chloride, among others.

2) Thermosets or thermosettings can melt and take shape only once. They are not suitable for repeated heat treatments; therefore after they have solidified, they stay solid.

TARGET WASTE PLASTICS

Waste plastics are one of the most promising resources for fuel production because of its high heat of combustion and due to the increasing availability in local communities. Unlike paper and wood, plastics do not absorb much moisture and the water content of plastics is far lower than the water content of biomass such as crops and kitchen wastes. The conversion methods of waste plastics into fuel depend on the types of plastics to be targeted and the properties of other wastes that might be used in the process. Additionally the effective conversion requires appropriate technologies to be selected according to local economic environmental, social and technical characteristics.

In general, the conversion of waste plastic into fuel requires feedstock which are non-hazardous and combustible. In particular each type of waste plastic conversion method has its own suitable feedstock. The composition of the plastics used as feedstock may be very different and some plastic articles might contain undesirable substances (e.g. additives such as flame-retardants containing bromine and antimony compounds or plastics containing nitrogen, halogens, sulphur or any other hazardous substances) which pose potential risks



to humans and to the environment. The types of plastics and their composition will condition the conversion process and will determine the pretreatment requirements, the combustion temperature for the conversion and therefore the energy consumption required, the fuel quality output, the flue gas composition (e.g. formation of hazardous flue gases such as NO_x and HC₁), the fly ash and bottom ash composition, and the potential of chemical corrosion of the equipment, Therefore the major quality concerns when converting waste plastics into fuel resources are as follows:

1) Smooth feeding to conversion equipment: Prior to their conversion into fuel resources, waste plastics are subject to various methods of pre-treatment to facilitate the smooth and efficient treatment during the subsequent conversion process. Depending on their structures (e.g. rigid, films, sheets or expanded (foamed) material) the pre-treatment equipment used for each type of plastic (crushing or shredding) is often different.

2) Effective conversion into fuel products: In solid fuel production, thermoplastics act as binders which form pellets or briquettes by melting and adhering to other non-melting substances such as paper, wood and thermosetting plastics. Although wooden materials are formed into pellets using a pelletizer, mixing plastics with wood or paper complicates the pellet preparation process. Suitable heating is required to produce pellets from thermoplastics and other combustible waste.

In liquid fuel production, thermoplastics containing liquid hydrocarbon can be used as feedstock. The type of plastic being used determines the processing rate as well as the product yield. Contamination by undesirable substances and the presence of moisture increases energy consumption and promotes the formation of byproducts in the fuel production process.

3) Well-controlled combustion and clean flue gas in fuel user facilities: It is important to match the fuel type and its quality to the burner in order to improve heat recovery efficiency. Contamination by nitrogen, chlorine, and inorganic species, for instance, can affect the flue gas composition and the amount of ash produced. When



using fuel prepared from waste plastics, it must be assured that the flue gas composition complies with local air pollution regulations. In the same way, ash quality must also be in compliance with local regulations when disposed at the landfill. If there aren't any relevant regulations, both the producers and consumers of the recycled fuel should control the fuel quality and the emissions at combustion in order to minimize their environmental impact.

FUEL DEMAND

The present rate of economic growth is unsustainable without saving of fossil energy like crude oil, natural gas or coal. International Energy Outlook 2010 reports the world consumption of liquid and petroleum products grows from 86.1 million barrels per day in 2007 to 92.1 million barrels per day in 2020 and 110.6 million barrels per day in 2035 and natural gas consumption increases from 108 trillion cubic feet in 2007 to 156 trillion cubic feet in 2035. This way, the oil and gas reserve available can meet only 43 and 167 years further. Thus mankind has to rely on the alternate/renewable energy sources like biomass, hydropower, geothermal energy, wind energy, solar energy, nuclear energy, etc.

CLASSIFICATION OF PLASTICS

Plastics are classified into two types, they are

- 1) High-density polyethylene
- 2) Low-density polyethylene

In some studies, high temperature as 700-900°C is essential in achieving decent product yields. The extent and the nature of these reactions depend both on the reaction temperature and also on the residence of the products in the reaction zone, an aspect that is primarily affected by the reactor design. In addition, reactor design also plays a fundamental role, as it has to overcome problems related to the low thermal conductivity and high viscosity of the molten polymers. Several types of reactors have been reported in the literature, the most frequent being fluidized bed reactors, batch reactors and screw kiln



reactors. Characteristics of thermal degradation of heavy hydrocarbons can be described with the following points;

- High production of C1s and C2s in the gas product.
- Olefins are less branched.
- Some olefins made at high temperature.
- Gasoline selectivity is poor; i.e. oil products are a wide distribution of molecular weight.
- Gas and coke products are high.
- Reactions are slow compared with catalytic reactions.

Thermal Pyrolysis of both virgin and waste plastics as well as other hydro-carbonaceous sources has been studied extensively in the past. A good number of these thermal cracking studies are on polyethylene, polypropylene and polystyrene. On the other hand, only a few have worked on the thermal decomposition of other common plastics such as polyvinylchloride, poly methyl methacrylate, polyurethane and polyethylene terephthalate. Generally, thermal cracking results in liquids with low octane value and higher residue contents at moderate temperatures, thus an inefficient process for producing gasoline range fuels. The gaseous products obtained by thermal Pyrolysis are not suitable for use as fuel products, requiring further refining to be upgraded to useable fuel products. A few researchers have sought to improve thermal Pyrolysis of waste polyolefin without employing the use of catalysts; however these changes either yielded insignificant improvements or added another level of complexity and costs to the system.

CATALYTIC CRACKING OF POLYOLEFINS

Addition of catalyst enhances the conversion and fuel quality. As compared to the purely thermal Pyrolysis, the addition of catalyst in polyolefin Pyrolysis

1) Significantly lowers Pyrolysis temperatures and time. A significant reduction in the degradation temperature and reaction time under catalytic conditions results in an increase in the conversion rates for a



wide range of polymers at much lower temperatures than with thermal Pyrolysis_

2) Narrows and provides better control over the hydrocarbon products distribution.

3) Increases the gaseous product yields. Under similar temperatures and reaction times, a much higher gaseous product yield is observed in the presence of a catalyst for polyethylene.

MAIN DEVICES USED IN THE PROCESS

Condenser

It cools the entire heated vapour coming out of the reactor. It has an inlet and an outlet for cold water to run through its outer area. This is used for cooling of the vapour. The gaseous hydrocarbons at a temperature of about 350°C are condensed to about 30 - 35°C.

Reactor

It is a stainless steel tube of length 300mm, internal diameter 225mm, outer diameter 230mm sealed at one end and an outlet tube at the other end. The reactor is placed under the LPG burner for external heating with the raw material inside. The reactor is made with the following: stainless steel, mild steel and clay for lagging. The reactor is heated to a temperature of about 450°C and more.

Process Description

Thermal cracking process without catalyst was used in converting waste plastic into liquid fuel. Two types of waste plastic are selected for this particular experiment. By weight 50% of each Low density polyethylene and polypropylene was selected for the experiment. Both waste plastic are solid hard form. Collected waste plastic was cleaned using liquid soap and water. During waste plastics are cleaned it creates waste water. This waste water is purified for reuse using waste water treatment process. Washed waste plastics are cut into 35 cm size to fit into the reactor conservatively. For experimental purpose we used 600gm sample 300gm of PP and 300gm of LDPE. A vertical steel reactor used for thermal cracking and temperature used ranges from 100°C to 400°C

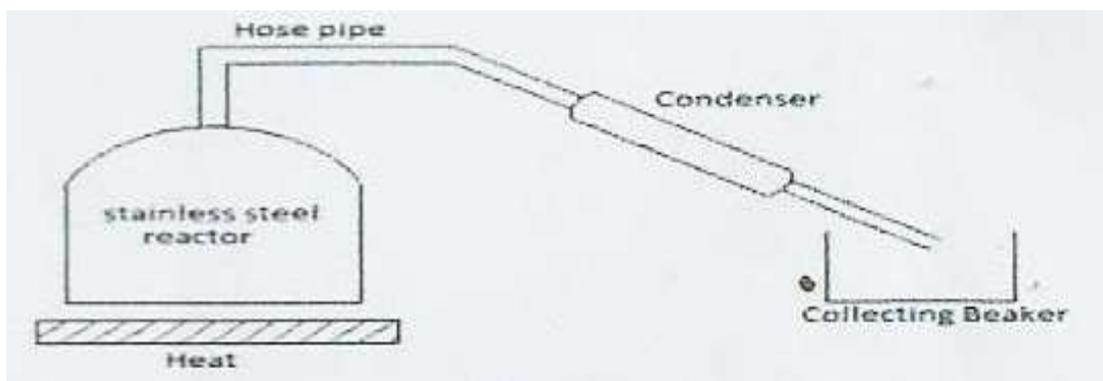


Fig. 1. Photograph of Experimental. setup.

When temperature is increased to 270°C liquid slurry turns into vapour and the vapour then passes through a condenser unit. At the end we collect liquid fuel. Between 100°C and 250°C around 20 -30% of the fuel is collected and then when raised to 325°C the next 40% is collected and finally when held at 400°C the yield is fully completed.

During the thermal cracking process plastic portions are not broken down immediately because plastics have short chain hydrocarbon to long chain hydrocarbon. 1st stage of heat applied breaks down only the short chain hydrocarbon. When temperature profile is increased the plastic carbon-carbon bond breakdown slowly. As the temperature is increased the long chains are breakdown step by step. During in this thermal cracking process some light gas such as methane, ethane, propane and butane are produced.

Catalytic Pyrolysis of plastic

Compared with gasification pyrolysis produces less amount of heat i.e. between 840 and 1,020 degrees F so it is more energy efficient .Through catalytic pyrolysis, a system was devised to convert waste plastics into liquid hydrocarbons, coke and gas, which can then be used as boiler fuel for power generation. The technology uses lower temperatures than gasification-significantly lower, so it's more energy efficient to produce. Through "random de-polymerization," or selective breaking of carbon-to-carbon bonds, in addition to feeding in proprietary catalytic additives, the reactor melts and vaporizes waste plastic in one step at temperatures between 840 and 1,020 degrees F. On average, 79-80



percent of every pound of plastic fed into the system is converted to liquid hydrocarbons, coke and gas. The resultant coke can be further processed to produce additional fuel oil. This catalytic pyrolysis system additional fuel oil. This catalytic pyrolysis system processes polyolefin like polyethylene and polypropylene with up to 5 percent other plastic.

Process of Pyrolysis of Waste Plastics Technology

Pyrolytic Conversion Common features of these systems include: Some level of pre-treatment: this could be as minor as size reduction or as involved as cleaning and moisture removal. Conversion: pyrolytic processes are used to convert the plastic to a gas.

Distillation

The gas is converted to liquid form Acid removal process: removal of acids that form in the breakdown of some scrap plastics. These acids require removal because they can be corrosive to the **PTF** systems as well as the engines that will consume the fuel. Separation/refining/final blending: the final steps required to make this product consumer ready can either be done on site or in some other plant. The total yield of fuel oil is 50-65% [3]. The problem for this process is the pyrolysis equipment's corrosion incurred by PVC in mixed plastic wastes. [4]. However, the temperature caused by pyrolysis is higher and all the reactive time is longer than the other methods. The octane number of gasoline gained is relatively low and the pour point of diesel oil is high. More paraffin is produced in the process of pyrolysis. Although this process is simple and convenient, the converting rate and yield is still lower.

The other problem for this process is the pyrolysis equipment's corrosion incurred by PVC in mixed plastic wastes. Therefore it is strongly recommended to establish a reasonable sorting system and apply an efficient technique to eliminate the toxic emissions and highly corrosive hydrochloric acid that is formed. Since the total yield of the fuel oil with pyrolysis is still lower and the quality of oil is not satisfied as gasoline and diesel oil, the upgrade by catalytic cracking for the crude products gained with pyrolysis can be used. Stages of Conversion



Indirect heating of waste plastics the feedstock would be placed in a specially designed cartridge. Now the air should be heated with a light industrial burner and re-circulated around the cartridge, transforming the plastic feedstock from a solid to a liquid to a gas. Gasification and movement Using a combination of temperature and vacuum (or negative pressure), the gases are to be pulled from the cartridge into a central condensing system. Condensing gases into oil in the condensing system, the gases are to be cooled and condensed into synthetic crude oil. Waste impurities are then removed from the stream. Final transfer and storage of oil the crude oil product which leaves the condensing system should enter into a coalescing and settling process and eventually transferred to an exterior storage tank.

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. (1) Evenly heating the plastic to a narrow temperature range without excessive temperature variations,

1. Purging oxygen from pyrolysis chamber,
2. Managing the carbonaceous char by-product before it acts as a thermal insulator and lowers the heat transfer to the plastic,
3. Careful condensation and fractionation of the pyrolysis vapours' to produce distillate of good quality and consistency.

Advantages of pyrolysis process are

- (a) Volume of the waste is significantly reduced (<5090%),
- (b) Solid, liquid, and gaseous fuel can be produced from the waste,
- (c) storable/transportable fuel or chemical feed stock is obtained,
- (d) Environmental problem is reduced,



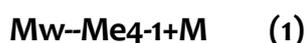
(e) Desirable process as energy is obtained from renewable sources like municipal solid waste or sewage sludge,

(l) 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. Vapours' can be continuously removed as they are formed [5, 14]. The fast pyrolysis is associated with tar, at low temperature (850-1250K) 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].

Mechanism of Thermal Degradation

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):

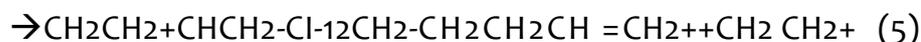


Equations (1) and (2) represent the thermal degradation, and (3) represents the random degradation route of the polymers pyrolysis.

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

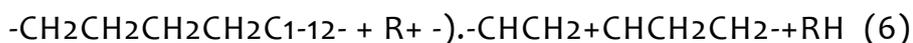


The polymer chain may be broken up through 1 - emission:





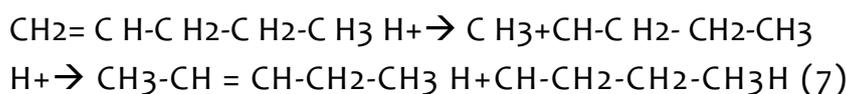
Initiation may also take place through random hydride-ion abstraction by low-molecular-weight carbonium ions (R⁺):



The newly formed on-chain carbonium ion then undergoes **1-scission**.

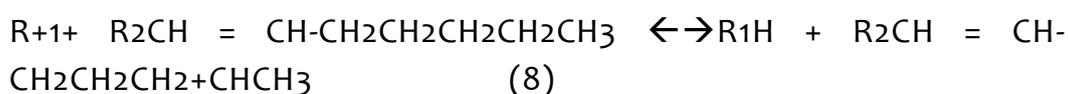
Depropagation: The molecular weight of the main polymer chains may be reduced through successive attacks by acidic sites or other carbonium ions and chain cleavage, yielding in gas oligomer fraction (approximately C₃₀-C₈₀). Further, cleavage of the oligomer fraction probably by direct 1-emission of chain-end carbonium ions leads to gas formation on one hand and a liquid fraction (approximately C₁₀-C₂₅) on the other.

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



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

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 olefin carbonium ion:



(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 1-scission and abstraction of H-radicals from other hydrocarbonsto produce a new hydrocarbon radical:





(3) Termination Dis-proportionation or recombination of two radicals:



EFFECT OF TEMPERATURE ON LDPE

Effect of temperature on the yield of fuel oil from LDPE: 10008 low density polyethylene was cracked at the different temperatures and reaction time. The initial temperature before the start of heating was found to be 31°C.

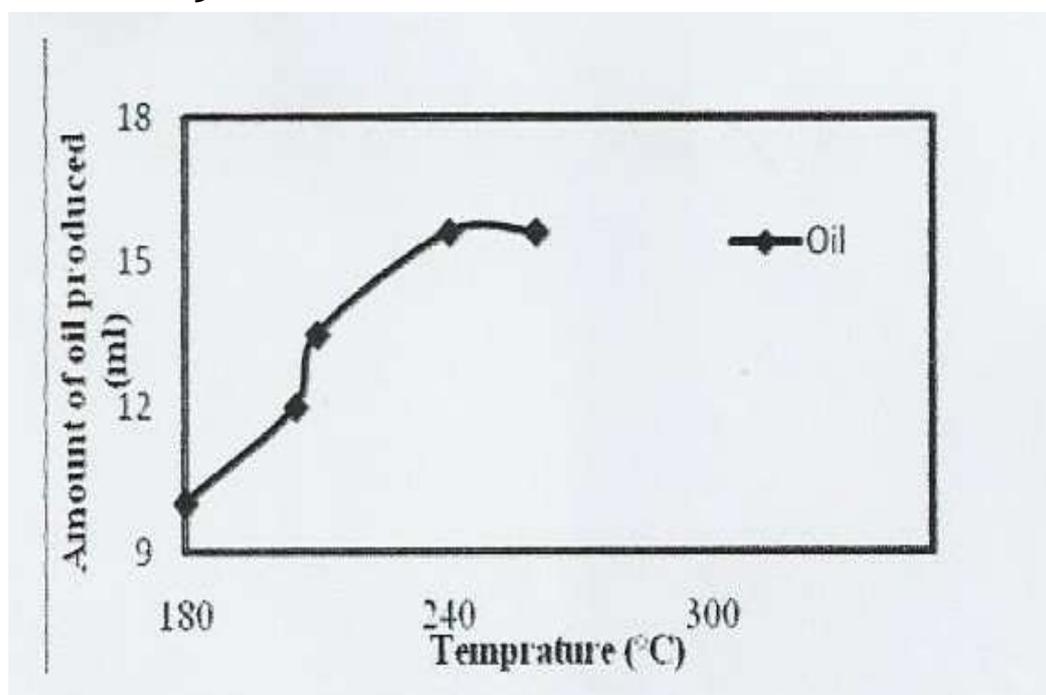


Fig. 2. Effect of temperature on the residue left and gas produced for LDPE.

Fig. 2 represents the production of gases at different temperatures and residue obtained at that temperature. Here, it was found that at the 180°C, they are just started to separate from each other and after that at 205°C the residue is reduced to 48.3% and gaseous product is increased to 50.5%. At 210°C residue is 46.8% and gaseous product is about 52%. Finally at the temperature 250 we find the residue 44.9% and gaseous product is 53%.

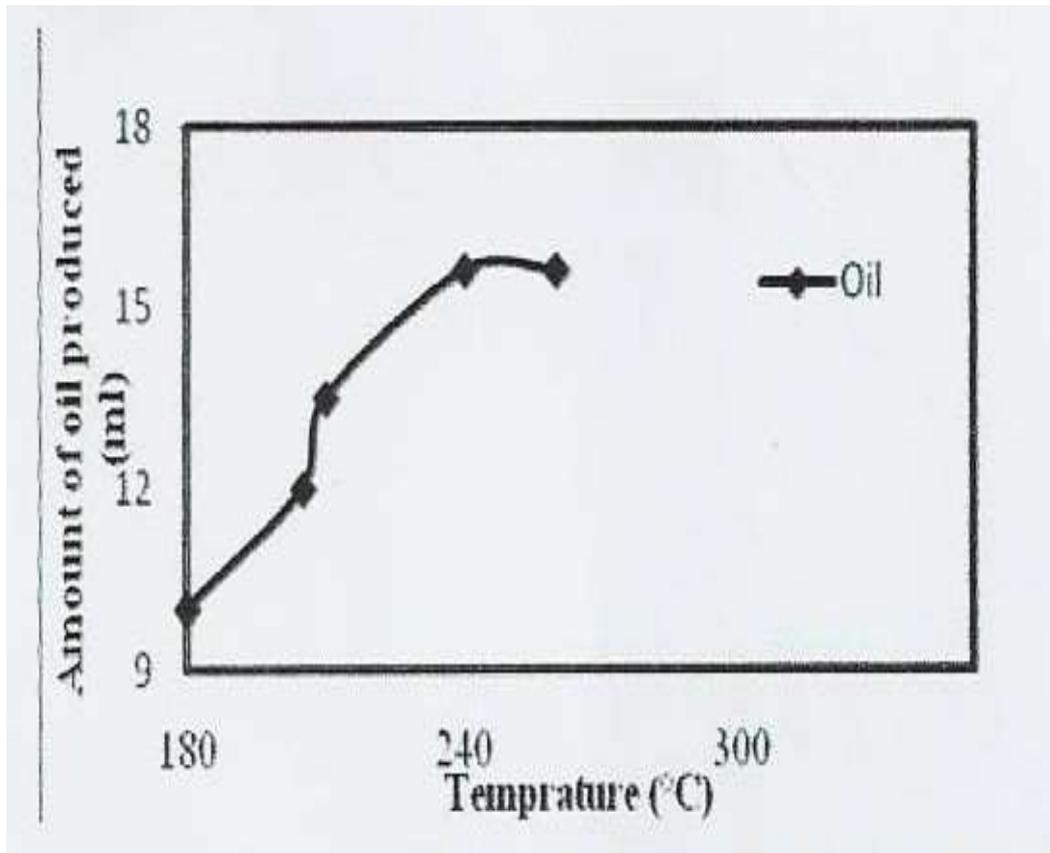


Fig. 3. Effect of temperature on the amount of oil produced from LDPE. Fig. 3 shows that the amount of crude oil produced with respect to temperature. With increases of the temperature the amount of oil produced is increasing up to 15ml. Finally it remains constant even if temperature is increasing.

Effect of temperature on fuel oil from HDPE

1000g of high density polyethylene was measured and cracked at different temperatures. At the different temperature the amount of oil produced and residue left after the reaction is completed was collected. The initial temperature before cracking was found to be 31°C. Fig. 4 shows the effect of temperature on the amount of oil produced from **HDPE**.

First the amount of oil is increasing as the temperature is increasing up to 185ml.

Finally, the amount of oil produced is remaining constant which indicates the consumption of the raw materials (plastics).

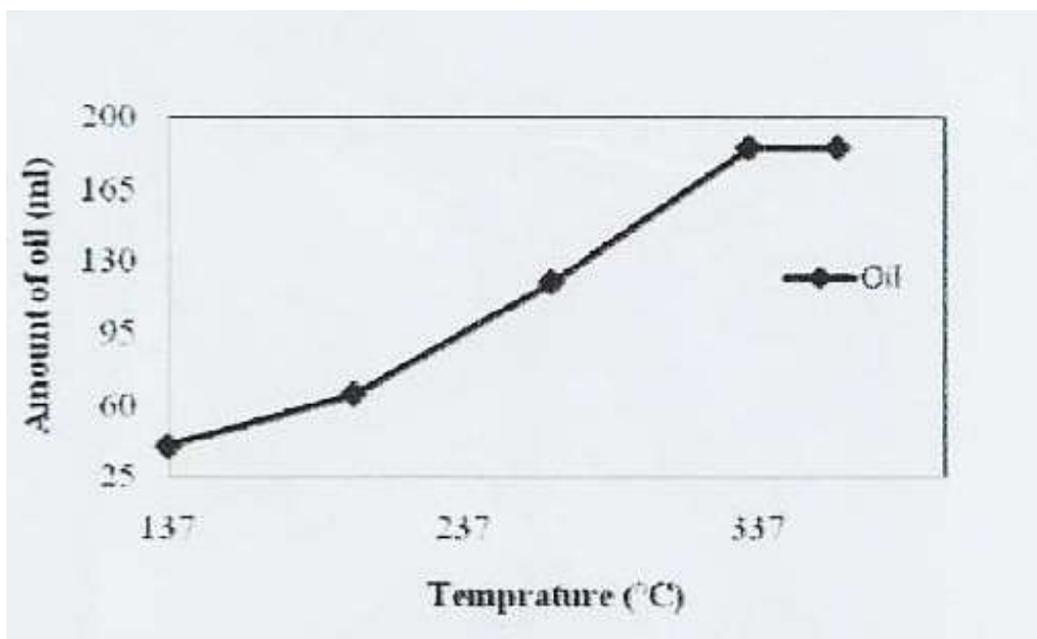


Fig. 4. Effect of temperature on the production of crude oil from HDPE.

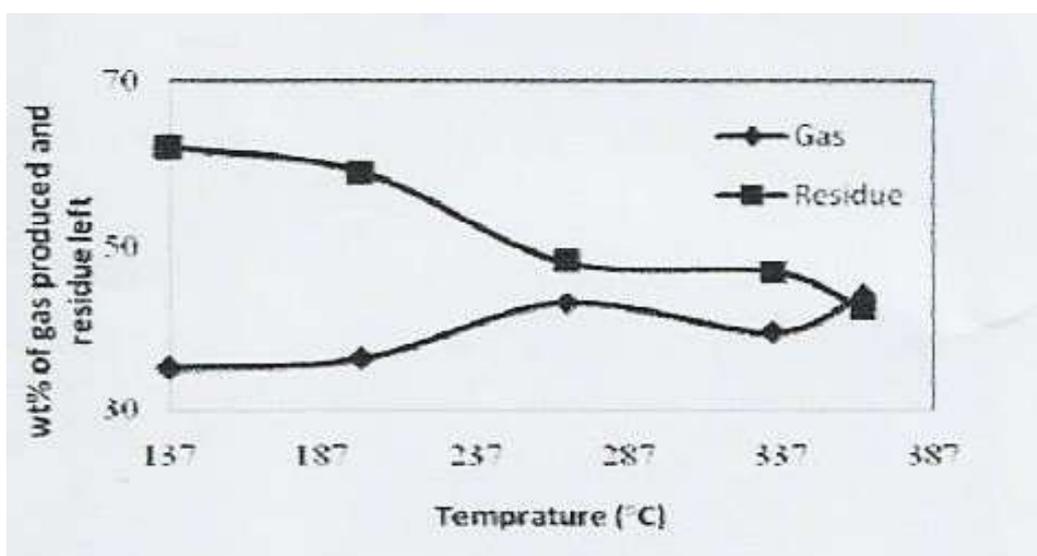


Fig. 5. Effect of Temperature on the distribution of residue left and gas produced

At a temperature of 137°C the percentage of gas produced and residue left were measured to be 35% and 62% respectively. As temperature is increasing, the value of the gas produced is increasing because the plastic is cracked more at higher temperature while the residue left was decreasing. As the temperature is increasing the amount of residue is close to zero.



SOLID FUEL PRODUCTION

A. Scope of solid fuel in this compendium

Solid fuel, as referred in this compendium, is prepared from both municipal and industrial non-hazardous waste. Additionally, the solid fuel outlined here excludes coal and coal derived fuels as well as solid bio fuels such as firewood and dried manure but it may contain bio fuels as a component. This compendium differentiates two types of solid fuel: refuse derived fuel (**RDF**), also called solid recovered fuel (SRF) and refuse-derived paper and plastic dandified fuel (RPF). RDF is mainly produced from municipal kitchen waste, used paper, waste wood and waste plastics. Due to the presence of kitchen waste, prior to the conversion to a fuel, a drying process is required to remove the moisture from such waste to allow the solidification of the waste in suitable shapes and densities.

This process is seen as a disadvantage due to the large amount of energy that the process requires. Solid recovered fuel (SRF) is defined in the European Committee for Standardization technical specification (CEN/TS 15359:2006). The components of RPFs are mainly sorted from industrial wastes and are sometimes also obtained from well-separated municipal waste. This type of solid fuel is set to be standardized in the Japanese Industrial Standards (HS).

Production method

The solid fuel production process usually involves two steps, pretreatment and pellet Production:

-Pre-treatment includes coarse shredding and removal of noncombustible materials.

-Pellet production comprises secondary shredding and pelletisation (<200°C).

Large-scale model (3 ton/hour). Industrial waste plastics, which have been separated and collected in factories, are ideal to be used for solid fuel production.

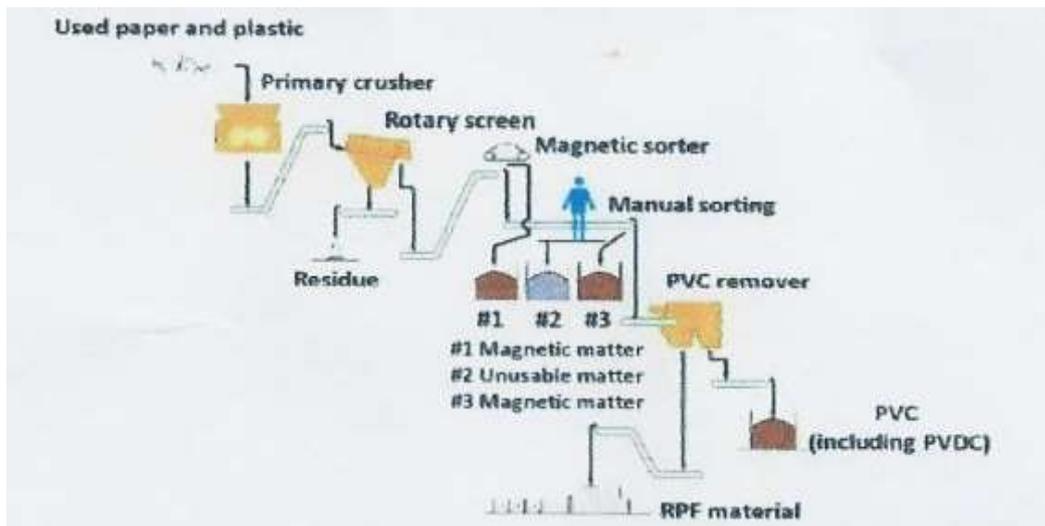


Fig. 6. Schematic diagram of pre-treatment process.

A fuel production facility consists of a waste unloading area, stockyard, pre-treatment Equipment, Pelletizing equipment and solid fuel storage. The pre-treatment process includes crushing and sorting for the removal of unsuitable materials from incoming wastes.

Small-scale model (150 kg/hour)

This small-scale model is a system for solid fuel production with a 150-kg/h capacity. In this case the facility does not have a pretreatment process, (as aforementioned, a sorting process is no required if properly segregated waste can be collected) so the combustible wood, paper and plastic waste is directly fed into the crusher of the facility. This is carried out by using a handling machine where the operator must control and feed into the crusher a suitable ratio of each type of waste in order to maintain the fuel qualities such as the heating value. After crushing the materials, they are transported through a pipe conveyor and are introduced into a twin-screw pelletizer.

Figure shows the entire process (the crusher, the pipe conveyor and the pelletizer).

Gasification of granulated waste plastic

Manufacturers of plastic equipment's leads to generation of plastic waste sometimes these waste are granulated before being sent to landfills thus companies are not paying to dump airspaces. This process involves gasification, the granulated plastic is sent to burner, converted from solid to a liquid and into a gas and immediately into combustion chamber. The



emissions testing evaluated the burner fuel with pelleted No. 4 low-density polyethylene (LDPE) from Korea; granulated No. 2 high-density polyethylene from discarded plastic barrels; and granulated, dirty No. 4 LDPE mulch film. Three main categories of pollutants were tested: particulate matter; gases (sulphur dioxide, nitrogen oxide and carbon monoxide); and dioxins/furans. Test results proved that this is an extremely dean-burning system.

CONCLUSION

Plastics present a major threat to today's society and environment. Over 14 million tons of plastics are dumped into the oceans annually, killing about 1,000,000 species of oceanic life. Though mankind has awoken to this threat and responded with developments in creating degradable bio-plastics, there is still no conclusive effort done to repair the damage already caused. In this regard, the catalytic Pyrolysis studied here presents an efficient, clean and very effective means of removing the debris that we have left behind over the last several decades. By converting plastics to fuel, we solve two issues, one of the large plastic seas, and the other of the fuel shortage. This dual benefit, though will exist only as long as the waste plastics last, but will surely provide a strong platform for us to build on a sustainable, clean and green future. By taking into account the financial benefits of such a project, it would be a great boon to our economy. So, from the studies conducted we can conclude that the properties of the fuel obtained from plastics are similar to that of petrol and further studies on this field can yield better results.

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