Methods for Recycling of Waste Polymer to Transport Fuel

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***Abstract*: **Plastic is a high molecular weight polymer which has become an integral part of our modern life and is used in most of daily activities. As plastic is synthesized from non -renewable resources and are non- biodegradable so waste plastics are the cause of many of the serious environmental problems of in the world as huge amount of plastic waste material is dump in to the environment. According to recent study done by EPA (environmental protection agency) approximately 48 million tons of waste plastics are generated in the USA alone out of which 10% is recycled, 25% is incinerated and remaining 65% is dumped in landfills. Latest studies show that approximately 100 million tons of waste plastics are floating the Pacific ocean, creating an island that stretches over an area twice the size of Texas. This large amount of waste plastic floating on our oceans is seriously damaging the ecosystem and the environment. Traditional treatments for waste plastics were recycling, land filling or incineration. Landfill of the waste plastics has the potential problems due to limited land resource and non –biodegradability of plastics. Incineration if incomplete may generate poisonous substances such as polychlorinated dibenzo-p-dioxins, a carcinogen and may cause serious health problems (Vogler,2005). Established technologies such as depolymerisation, pyrolysis, thermal cracking can convert waste plastic into renewable source of hydrocarbon fuel such as petrol, kerosene, and diesel, lube oil etc. which can be used as an energy source for numerous purposes such as diesel engines, generators, vehicles etc. Thus, converting the waste plastic into oil will have two benefits i.e. the hazards caused due to plastic waste can be reduced and also we will be able to obtain some amount of oil from it. We know crude oil is used to make plastics. By recycling, the waste energy in the form of waste plastic can be recovered. Thus waste can be changed into useful resources. In this paper pyrolysis is discussed in detail.

***Index Terms*- Fuels, Plastic, Recycling, Polymer, Recycling Methods**

I. INTRODUCTION

Plastic is the general common term for a wide range of synthetic organic amorphous solid materials used in the manufacturing of industrial products, The word plastic is derived from Greek word plastikos meaning fit for moulding and plastos meaning moulded. Fuels derived from both plastics andpetroleum are hydrocarbons that contain carbon and hydrogen elements. The difference is that the plastic molecules contain long carbon chains as compared to those in LPG, petrol and diesel fuels. Therefore it is possible to convert waste plastic into fuels, by breaking its longer carbon chains into smaller carbon chains by pyrolysis i.e catalytic cracking which is economically and environmentally accepted methods because in this method the emission of hazardous gases to the environment is quite less (Pawar and Lawankar , 2013). The products of such processes are liquid mixtures of hydrocarbons boiling in temperature range 35- 360^{o} C, gaseous hydrocarbons as well as solid residue like wax and coke. The different types of catalysts, such as ZnO, CaO and K_2O can be used but these materials deactivate very quickly. However excellent results have been obtained from liquefaction of individual polymers polyethylene (P E), polystyrene (P S), polypropylene (P P) etc. and using solid acid catalysts with relatively clan mixed plastics. From the latest studies it is clear that there is an increase in the recycling operations compared to land filling due to strict regulations and growing awareness.

1.1. Recyclable Plastics

It has been observed that all plastics are not suitable for recycling. This may be due to the fact that plastics are generally made up of more than one kind of polymer and some sort of fibre may have been added to the plastic to give them additional strength which makes the recovery difficult. There are 4 types of plastic which are usually recycled i.e. both high density and low-density polyethylene (PE), Polypropylene (PP), Polystyrene (PS) and Polyvinyl chloride (PVC).(Brydson, 1999) Identification of different types of polymers present in a plastic can be done with simple tests so that they may be separated for processing. For example by putting in water polyethylene (PE) and Polypropylene (PP) floats whereas Polystyrene (PS) and Polyvinyl chloride (PVC) sink. On burning , PE burns with a blue flame having yellow tip with smell like candle wax, PP burns with a Yellow flame having blue base with weak candle wax like smell, PS burns with Yellow, sooty flame giving sweet smell and PVC burns with Yellow, sooty, Smoke only as long as it is kept in flame.

As plastics have high heat of combustion and the high availability in local communities, waste plastics are one of the most capable resources for fuel production. Water content of plastics is much lower than the water content of biomass such as crops, paper, wood and kitchen wastes because plastics do not absorb much moisture. The methods to be used for the conversion of waste plastics into fuel depend on the types of plastics to be embattled and the characteristics of other wastes that might be present in the process. The feedstock of waste plastic to be converted into fuel requires should be non-hazardous and combustible (Jefferson, 2011). The each type of waste plastic conversion method requires specific feedstock suitable for it. The composition of the waste plastics used as feedstock generally is very different and sometimes plastic articles may contain additives such as bromine and antimony compounds or plastics containing nitrogen, halogens, sulphur or any other hazardous substances which are harmful to humans and to the environment. Thus the types of plastics and their composition will determine the conversion process, the pre-treatment requirements, the combustion temperature, the fuel quality, the fly ash and bottom ash composition, and the probability of chemical corrosion of the equipment.

II. Recycling Methods

2.1. Chemical Depolymerisation

This method involves the treatment of the used plastic with chemical reagents. Depending on the chemical reagents employed, different processes have been developed the most common are methanolysis, glycolysis, hydrolysis and ammonolysis (Aguado & Serrano, 2007). In India Rudhra Environmental Solutions factory set up at Pune, 2010 by two women Medha and Shirish Phadtare is based on thermos-catalytic depolymerisation

2.2. Gasification

In this process the partial oxidation of organic matter is done at high temperatures (1200-1500 ^{o}C) under mild oxidizing conditions for the production of synthesis gas which is mainly consist of carbon monoxide and hydrogen. This gas may be used in the synthesis of methanol and ammonia. It can be used to make synthetic diesel or may be used directly as a fuel (Belgiorno, 2003).

2.5. Hydrogenation

Hydrogenation of plastics is another method for breaking down the polymer chain. It results in the formation of extremely saturated products, with very little olefins present in the liquid fractions which may be used as fuels without further treatments. Also, during hydrogenation, hetero atoms, such as chlorine (Cl), nitrogen (N) and sulphur (S) are removed in the form of volatile compounds. But due to the high cost of hydrogen and the requirement to operate under high pressure hydrogenation is not favoured method.

2.3. Thermal Pyrolysis

Pyrolysis is economically and environmentally accepted method as it emits only an insignificant amount of hazardous gases to the environment. The word pyrolysis also called thermolysis is derived from Greek word: pur means fire; thermos means; warm. It involves the process of chemical and thermal decomposition, leading to smaller molecules. The name thermolysis is preferred to pyrolysis as pyro means fire which requires the presence of air (oxygen) leading to formation of many oxidised side products. So air is excluded in the process of pyrolysis to have greater quality of products and avoid accidents.

Wang Xu, of China, started experimenting with the processing of waste plastics in 1980s, and teamed up with Zeng Guangming of Hunan University doctoral tutor, who gave him scientific basic ideas on decomposing plastic waste. Wang Xu built a refinery in 1999.The first report of turning plastic waste into oil came in 2001 in china‘s English language newspaper, The People’s Daily. An oil refinery in Hunan province had succeeded in processing 30,000 tonnes of plastic wastes into 20,000 tonnes of gasoline and diesel oil that satisfied the provincible standards. Illinois microbiologist Paul Baskis of United States in 1980s modified the process to produce lighter, cleaner oil, but could not convince the investors until 1996, when a company named changing world technologies began development with Baskis and made the process commercially viable. The plants with running capacities of one thousand tonnes per annum have been running in many nearby cities in china (Zhang et al., 2007).

The thermal cracking involves the heating of polymeric materials in the absence of oxygen between 350 to 900^{o}C temperatures. This results in formation of solid residue (carbonized char) and a volatile fraction which is liquefied and separated by passing through condensing pipes. The hydrocarbon oil is consists of paraffins, isoparaffins, olefins, naphthalenes, aromatics, and a non- condensable high calorific value gas. The precise composition and relative proportion of each component depends upon the nature of the plastic waste and the conditions of the process involved (Zhang and Zhu, 2006). The liquids obtained from thermal cracking usually have low octane value and higher residue contents at moderate temperatures; hence it is an inefficient process for producing gasoline range fuels. The gaseous products obtained by thermal Pyrolysis require further refining to be suitable for use as fuel products.

2.4. Catalytic Conversions

The addition of catalyst in poly pyrolysis considerably lowers Pyrolysis temperatures and conversion time thus results in an increase in the conversion rates at much lower temperatures than with simple thermal Pyrolysis. Catalytic pyrolysis also provides better control over the distribution of hydrocarbon products. It Increases the yield of gaseous products. For example under similar temperatures and reaction times, a much higher yield of gaseous product has been observed in the presence of a catalyst for polyethylene(Jerzy and Mieczyslaw, 2001).

III. General process involved in thermal pyrolysis

The general process involved in the conversion of plastics to liquid fuel is based on the pyrolysis of the plastics in a reactor followed by the condensation of the resulting hydrocarbons using a condenser. Collected waste plastic is cleaned using liquid soap and water. Then the plastics which are appropriate for the conversion are fed into a reactor where during pyrolysis the thermal decomposition of the matter takes place at 450 to 550^{o}C under the atmosphere of an inert gas like nitrogen. Depending on the type of the waste plastic, a variety of feeding methods may be used. The easiest one is to simply put the waste plastics into the reactor without any pre treatment. Soft plastics such as films and bags are often shredded and a melted before introducing them into the reactor as otherwise they would occupy a large space of the reactor. There are different types of reactors and heating equipments used. Both kiln-type and Screw-type reactors are proposed, also induction heating by electric power is developed as a substitute to a burner (Jenni, 2005). When the waste plastics in the reactor are decomposed enough so as to evaporate at reaction temperature, the resulting oil which is a mixture of liquid hydrocarbons is continuously distilled. The oil collected as distillate is further cracked with a catalyst (Nishmo et al.2008). Distillation equipment may be installed to perform fractional distillation and condense in a water-cooled condenser in order to separate hydrocarbons such as diesel, kerosene and gasoline with different boiling points (Ding et al., 1997). The liquid hydrocarbons are collected in a storage tank through a receiver tank and the gaseous hydrocarbons such as methane, ethane, propylene and butanes which cannot be condensed are incinerated in a flare stack. Some acids that form in the breakdown of some scrap plastics have to be removed because they may be corrosive to the PTF systems as well as the engines that will consume the fuel (Timothy, 2011). On an average, 79-80 percent of each pound of the plastic introduced into the system is converted to liquid hydrocarbons, coke and gas. Depending on the nature of the waste plastic used and the conditions of pyrolysis, carbonous matter produced slowly forms a deposit on the inner surface of the reactor which acts as a heat insulator, and has to be removed from the reactor after pyrolysis so as to maintain the heat conduction efficiency of the reactor (Zhang and Zhu, 2006). In some tank reactors the stirrer is used to remove the carbonous matter. After the distillation of the liquid product of the Pyrolysis, the carbonous matter is removed with a vacuum cleaner. Some reactors are equipped with a screw conveyor at the bottom of the tank reactor in order to remove the carbonous matter. The performance of the plant is evaluated on the basis of energy consumption and plant costs relative to the plastic treatment capacity. As highly flammable liquid fuels are formed in this chemical conversion so operating skill of the operators and safety considerations are very significant.

IV. Some commercial methods that produce fuel from plastic waste

4.1 Thermofuel Process

In this process the plastic waste is first melted and then cracked in a stainless steel chamber by heating at the temperature range 350-425^{o}C in inert atmosphere of inert gas. The hot gases obtained after pyrolysis are passed through a specially designed two stage condenser system. A liquid mixture consisting of straight and branched chain aliphatic, cyclic aliphatic and aromatic hydrocarbons is obtained as distillate. This mixture is equivalent to diesel.

Typical examples of waste plastics for thermofuel process are

1. Oil and detergent bottles.

2. Mixed post –consumer plastics like mineral water bottles, plastic plates, spoons, glasses etc. after use.

3. Caps, labels, rejected bottles from bottle recycling operations.

4. Plastic packaging scraps from material recovery facilities.

5. Mulch film and silage wrap.

6. Commercial stretch and shrink wrap.

Chemically suitable plastics for making fuel include polyethylene (PE), polypropylene (PP), polystyrene (PS) are very good, polyurethane (PUR), &PET are not suitable so should not be used. Fibre reinforced plastics can be used only after removal of fibre.

The various steps in the thermofuel pyrolysis of plastics are

1. Removing oxygen from pyrolysis chamber.

2. Evenly heating the plastic to a narrow range of temperature without much temperature variations.

3.Ensuring that the plastic is homogeneous and stirred to prevent hot spots.

4. Pyrolysing the plastics.

5. Catalytic conversion of the gases to required carbon chain length.

6. Regularly removing the carbonaceous char by product, so that it does not act as a thermal insulator and lowers the heat transfer to plastic.

7. Careful condensation and fractionation of pyrolysis vapours toproduce fuel of good quality and consistency.

8. Removal of sulphurs and residual contaminants.

4.2 Sumuda Process

In Sumuda process given by I. Sumuda in 2004, the mixed plastic feedstock is continuously fed from an extruder into a pyrolysis chamber where it is continuously stirred and heated. Extruder exclude oxygen, acts as airlock, preheat and melt the plastic so less energy input is required in the main chamber. The process is performed in the inert atmosphere of nitrogen. The pyrolysis vessel is filled with plastic only up to 60% and 5-10% by volume is added a layered silicate catalyst to the molten plastic, the rest of the space is filled with nitrogen gas. The process involves catalytic cracking reaction.The fuel obtained in Sumuda process is transportation grade diesel (85%) and gasoline (15%) (Sumuda, 2004).

4.3 Hitachi Process

In this process Hitachi Zosen has developed a stirred tank (kettle) for performing pyrolysis process of waste plastic. It is characterized by the following features.

1. The ability to handle mixed plastic waste.

2. Pyrolysis can be performed at lower temperature.

3. The char and extraneous matter is automatically removed.

4. Double or triple condensers.

5. Production of kerosene and gasoline fractions.

4.4. Rudra Environmental Solutions

In Maharashtra's Pune, in India Medha Tadpatrikar and her friend Shirish Phadtare have also achieved significant success in converting plastic waste to fuel, using the mechanism of thermos-catalytic depolymerisation. They have founded Rudra Environmental Solutions and set up the first plastic to fuel conversion machine in Pune in 2010. In the process the collected plastic waste is shredded and fed into a reactor, then a catalyst is added and the plastic is heated at 150 ^{o}C. The gases methane and propane emitted are stored in a separate gas tank to be used as heating source for the machine to function. The oil obtained is filtered, stored and dispatched. In this process one tonne of plastic produce about 600 to 650 litres of fuel, 20 to 25 per cent synthetic gases and 5 to 10 per cent of residual char, which is used as road filler with bitumen. Today, the organisation collects plastic waste from almost 15,000 households from Pune, and encourages people from all over India to send plastic waste via courier for conversion to fuel.

India's Dehradun based Indian Institute of Petroleum (IIP), a constituent laboratory of the Council of Scientific and Industrial Research (CSIR) in 2014, has developed an exclusive process of converting plastic waste like polyethylene and polypropylene, to either gasoline or diesel. Their technology is proficient in converting 1 kg of plastic to 750 ml of automotive grade gasoline.

In Goa two plants Bicholim and Sonsoddo have been setup under the public private partnership (PPP) model with Bangalore-based M K Aromatics Ltd. and are functional since 2016, in converting plastic waste to fuel. Goa which generates nearly 66 metric tonnes of plastic waste every day, which is sufficient to be converted to fuel (Thorata, 2016).

In Hyderabad, the waste to energy company Ventana has also announced the setting up of multiple waste to fuel plants, in collaboration with Ramky Environment, a waste management service in January 2017.

V. CONCLUSION

The thermal pyrolysis of polymer waste leads to the production of fuel oil, valuable resource recovery of waste problem. So it is a truly sustainable waste solution, diverting plastic waste from landfills, utilizing the embodied energy content of plastics and producing very useful commodity which because of its cleaner burning characteristics, is environmentally friendly. At the end of the process, the waste obtained can be used in road construction. SO_2 produced at the initial stage is useful to produce sulphuric acid. However further studies are necessary to utilize oil as liquid fuel. In India also progress is being made in the field of the waste to fuel conversion. The processes used to convert plastic waste to fuel are not complicated and can be replicated on a large scale, to help in solving the growing issue of plastic waste and the demand for fuel.

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