A STUDY OF DEGRADATION AND LIQUEFACTION OF WASTE PLASTICS

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Abstract

With a view to the environment protection and reduction of non-regeneration resource, recycling technology for converting to oil from plastic waste has drawn much attention in the world. India has also witnessed a substantial growth in the consumption of plastics and an increased production of plastic waste. Hence, the basis theories and the technology for industrialization of plastic liquefaction is the broad area of research today. The variety in plastic waste composition and differences in thermal degradation behavior makes modeling, design, and operation of thermal conversion systems a challenge. The aim of this study is to obtain detailed information on the pyrolysis characteristics like degradation ability with and without catalyst, chemical kinetics and the nature of liquefaction of most important waste plastics. A thermogravimetric analysis (TGA) including determination of kinetic parameters was performed at different constant heating rates of 5, 10, 15, 20°C/min in an inert atmosphere. The plastics polystyrene, polypropylene, low-density polyethylene and high-density polyethylene except PVC was modeled as single reactions to describe the degradation of hydrocarbon polymer. Using a semi batch reactor the experiments conducted for testing the nature of liquefaction of plastic waste individually. The maximum temperature maintained in the reactor was about 700°C. The catalytic degradation of waste PE and PP with poly-olefinic structure exhibited the liquid yield of 80-86 % and the solid yield below 2%, where as that of waste PS with polycyclic structure produced much more liquid, solid products than gases. The PVC diverted from the other plastics with the more generation of gaseous streams which included the production of HCL and with much less liquid yield. The comparison made between thermal and catalytic degradation of waste plastics for their liquefaction into fuel oils.

Keywords: Liquefaction, degradation, plastic waste, TGA

1. Introduction

Plastics have become an indispensable part in today's world. Due to their light-weight, durability, energy efficiency, coupled with a faster rate of production and design flexibility, these plastics are employed in entire gamut of industrial and domestic areas [15]. Plastics have moulded the modern world and transformed the quality of life. There is no human activity where plastics do not play a key role from clothing to shelter, from transportation to communication and from entertainment to health care [16]. The ever increasing commercial importance of polymeric materials has entailed a continuous interest in their thermal stability. Plastics are non-biodegradable polymers of mostly containing carbon, hydrogen, and few other elements such as chlorine, nitrogen etc. Due to its non-biodegradable nature, the plastic waste contributes significantly to the problem of Municipal Waste Management.

Table 1.1: Consumption of Plastics in Some Selected Countries in the World.

Rank	Country	1988 (MMT)	Country	2000 (MMT)	Country	2010 (MMT)	2010/ 2000
1	USA	16.6	USA	27.3	USA	38.9	3.6%
2	Germany	6.4	China	14.4	China	31.3	8.1%
3	Japan	4.3	Japan	9.1	India	12.5	14%
4	China	3.7	Germany	6.4	Japan	11.5	2.3%
5	Italy	3.1	Korea	4.7	Germany	9.4	3.9%
6	CIS	2.4	Italy	4.7	Korea	7.4	4.8%
7	France	2.4	France	4.1	Italy	6.8	3.8%
8	UK	2.2	UK	3.5	Brazil	6.7	7.0%
9	Taiwan	1.9	India	3.4	CIS	6.2	9.1%
10	Korea	1.8	Brazil	3.4	France	6.1	4.1%
16	India	1.6	Taiwan	3.3	UK	5.2	4.0%

The production of plastics is significantly growing. Nowadays the plastic production is more than 200MT worldwide annually. [17] The per capita consumption of plastics from a last few decades increasing rapidly, reached 14% from 2000-2010. It is showed in the Table 1.1, the status of the consumption of

plastics in some selected countries worldwide [7]. The current growth rate in Indian polymer consumption (16% p.a.) is clearly higher than that in China (10% p.a.)[17] The per capita consumption of plastic in the country stood at 6 kg now and is expected to go up to 12 kg by 2011.[b] A logistic function of the form expressed has been used to estimate the per capita consumption figures for India in the coming years:

$$Y_t = Y_{max}/(1+e^{a-bt})$$

Where: Y_t is consumption level at time t; Y_{max} is saturation point for consumption for the time series considered; a and b are parameters, determined econometrically.[5]Waste Plastics are mostly land filled or incinerated; however, these methods are facing great social resistance because of environmental problems such as air pollution and soil contamination, as well as economical resistance due to the increase of space and disposal costs [4]. In a long term neither the land filling nor the incineration solve the problem of wastes, because the suitable and safe depots are expensive, and the incineration stimulates the growing emission of harmful and greenhouse gases e.g. NOx, SOx, COx etc [3].Plastic is derived from petrochemical resources. In fact these plastics are essentially solidified oil. They therefore have inherently high calorific value. The calorific values of some of the plastic materials along with coal and some of the petroleum products are shown in table1.2 [19]

Table 1.2: Comparison of Calorific values of Plastics with Fossil fuels:[6]

Fossil Fuels	Calorific Value kJ/kg	Plastic	Calorific Value kJ/kg
Coal	27,000	Polyethylene	46,500
Diesel fuel	46,000	Polypropylene	45,000
Gas oil	46,000	Polystyrene	41,600
Kerosene	47,000	PET	21,600
Petrol	44,800-46,900	PVC	19,000

With a view to the environment protection and reduction of non-regeneration resource, recycling technology for converting to oil from plastic waste has drawn much attention in the world. Plastics pyrolysis, on the other hand, may provide an alternative means for disposal of plastic wastes with recovery of valuable liquid hydrocarbons. In pyrolysis or thermal cracking, the polymeric materials are heated to high temperatures, so their macromolecular structures are broken down into smaller molecules and a wide

spectrum of hydrocarbons are formed. These pyrolytic products can be divided into a gas fraction, a liquid fraction consisting of paraffins, olefins, naphthenes and aromatics (PONA), and solid residues.

The main objective of this study was to investigate the effect of reaction temperature, plastic type (especially HDPE) and weight ratio of waste plastic to catalyst, with a semi-batch reactor, based on the results of yields and yield distributions of liquid product as a function of lapsed time. And to study the product yields and their distribution with different types of catalysts (Silica- Alumina, Activated Carbon, Mordenite and a new catalyst) in the catalytic degradation of waste plastics with respect to time and temperature. The goal of these experiments was the developing of a waste free so-called green technology [3]. The ever increasing commercial importance of polymeric materials has entailed a continuous interest in their thermal stability.

1.1. Waste Plastics Liquefaction:

The waste plastics have been recycled by many ways with the view of the end product from the process. The two main alternatives for treating municipal and industrial polymer wastes are energy recycling, where wastes are incinerated with some energy recovery and mechanical recycling. The incineration of polymer waste meets with strong societal opposition. Mechanical recycling of waste plastics has been applied to achieve the secondary grade plastics. Then followed by many chemical conversion techniques like chemolysis (methanolysis, glycolosis and alcoholysis), partial oxidation/gasification and pyrolysis to recover some valuable chemicals from the waste plastics.

At present there are many options to recover the liquid fuels from waste plastics based on the mechanism of polymer degradation. Thermal pyrolysis is the process of breaking heavier polymers into smaller molecules by providing the higher temperatures under controlled conditions. Thermal degradation of polymers always leads to the presence of most of the gaseous streams in the product distribution. In the case of polyolefins like polyethylene or polypropylene, thermal cracking has been reported to proceed through a random scission mechanism that generates a mixture of linear olefins and paraffins over a wide range of molecular weights [1]. In other cases, like polystyrene and polymethylmetacrylate, thermal degradation occurs by a so-called unzipping mechanism that yields a high proportion of their constituent monomers [1]. Recent progress in converting plastic wastes into petrochemicals by means of pyrolysis in the absence of a catalyst has been reviewed by Kaminsky. Four types of mechanisms of plastics pyrolysis have been proposed: (a) End-chain scission or depolymerization: The polymer is broken up from the end groups successively yielding the corresponding monomers. (b) Random-chain scission: The polymer chain is broken up randomly into fragments of uneven length. (c) Chain-stripping; Elimination of reactive substitutes or side groups on the polymer chain, leading to the

evolution of a cracking product on one hand, and a charring polymer chain on the other. (d) Cross-linking: Formation of a chain network, which often occurs for thermosetting polymers when heated. Catalytic pyrolysis has the advantages of reducing the degradation temperature and also obtaining the better yield of the liquid products in the product distribution of all kinds of polymers. Hence, the basis theories and the technology for industrialization of plastic liquefaction is the broad area of research today. The variety in plastic waste composition and differences in thermal degradation behavior makes modeling, design, and operation of thermal conversion systems a challenge.

2. Materials and methods

Five Plastics types (HDPE, LDPE, PP, PS and PVC) were used in this work. The plastics were obtained from the various locations of the Rourkela, Orissa, India. The material that was collected was subjected to cutting by using scissors manually. This was done to increase the surface area of contact of the material during melting process. The material was then directly taken into the reactor.

2.1. Catalyst Materials

The catalysts applied in the study of polyolefins were Silica Alumina (white amorphous powdery catalyst which consists of 87% SiO_2, 13% Al_2O_3) and Activated carbon, also called activated charcoal or activated coal, is a general term which covers carbon material mostly derived from charcoal.

2.2. TGA Procedure

Plastic samples were subjected to thermogravimetric analysis (TGA) of detector type DTG-60H in an inert atmosphere of nitrogen. Degradation of HDPE, PP, PS and PVC plastics performed at different constant heating rates of 5, 10, 15, 20°C/min. Nitrogen gas was used as an inert purge gas to displace air in the pyrolysis zone, thus avoiding unwanted oxidation of sample. A flow rate of 40ml/min was fed to the system. The polymer samples used were shredded into very small pieces and placed into platinum crucible and loaded on to the TGA weighing pan. In any case the total sample mass varied. The temperature maintained between 25 and 700°C; the precision temperatures was estimated to be +2/-2°C. The degradation ability of the plastics identified with varying temperatures for all types of plastics by using TGA.

2.3. Semi Batch Reactor

 The molten waste plastic pellets were taken into a cylindrical cast iron reactor of volume 0.3 lit (300 ml). The reactor was completely packed with the material. The reactor was perfectly sealed with M-Seal for the prevention of leakage of vapors. Then the reactor was put inside a furnace with the support of a stand. The furnace used was muffle furnace made by SHIMADEN CO. LTD, Japan coupled with SR1 and SR3 series

digital controller. With the help of controller we set the process at different temperatures for different experiments. The rate of increase of temperature is 25°C/min. The vapors that are coming from the reactor were passed through the pipeline connected to the top of the reactor. The vapors were allowed in to a glass condenser as show in the fig. Then the condensed liquids were collected. The non-condensable gases were very less and probably negligible in quantity.

Fig.1(a) SBR Experimental setup   **Fig.1(b)** Liquid fuels of PP with various catalysts to feed ratios.

2.4. SEM- Analysis of catalysts

JEOL, JSM-6480LV Scanning Electron Microscope was used to analyze the structure of the Si-Al, Mordenite and for activated carbon catalysts. The photographs were obtained at 350 and 6500 magnifications for Si-Al catalyst and for Activated carbon catalysts to observe the pore sizes of catalysts. The photographs showed in fig.2 & fig.3 is the photographs of Si-Al catalyst and Activated carbon Catalyst at 350 and 6500 magnifications shows their porosity to provide the maximum surface area for better degradation of polymers to influence on the yield of liquid products. These were employed in the liquefaction of waste PP.
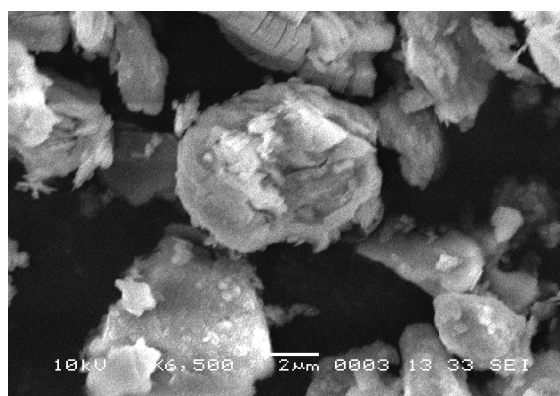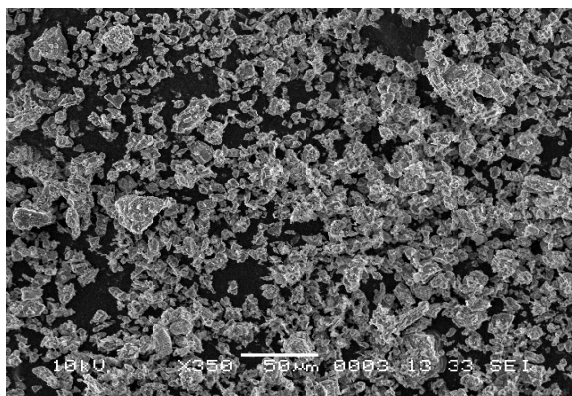

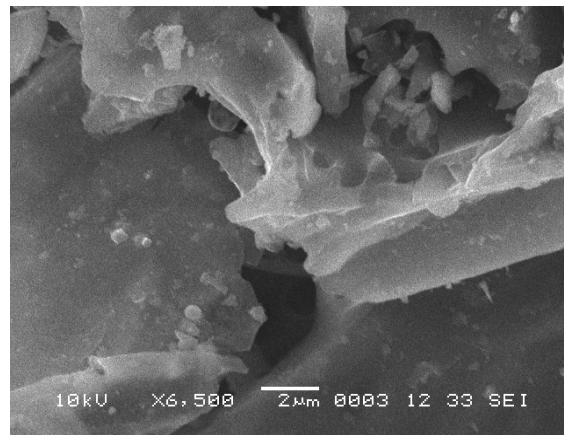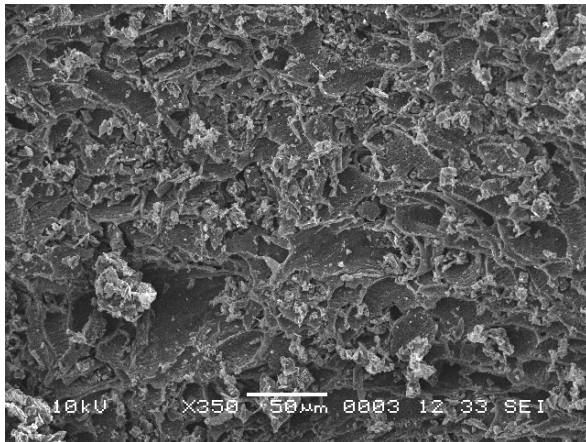**Fig.2**. SEM photographs of Si-Al catalyst at 350 and 6500 magnifications

Fig.3. SEM photographs of Activated carbon catalyst at 350 and 6500 magnifications

3. Results and Discussions

3.1. Degradation ability and kinetic study of individual plastics:

To model the decomposition study of any waste plastic mixture, knowledge of decomposition kinetics of the individual components is needed. The thermal stability of all the samples was studied with TGA. Figure 4(a), 4(b), 5(a) and 5(b) shows the mass-loss behavior as a function of temperature for the waste PS, HDPE, PP and PVC control samples. By thermo-gravimetric analysis test of waste polystyrene sample it was known that pyrolysis, both thermal and catalytic, should be done in the temperature range of 450-550 ^{o}c as shown in fig4(a). For HDPE waste plastics the mass loss first identified at $268^{o}C$ and the 90% of mass lost obtained at $474^{o}C$ as shown by the TGA graph in fig 4(b). Degradation ability of waste HDPE is more in this temperature range. Thermogravimetric analysis of PVC shows that degradation range of waste polyvinyl chloride was 100-$300oC$ as shown in fig 5(b). Polypropylene waste plastics showed their rapid degradation ability in the temperature range of $230-700^{o}C$ as showed in fig5(a).
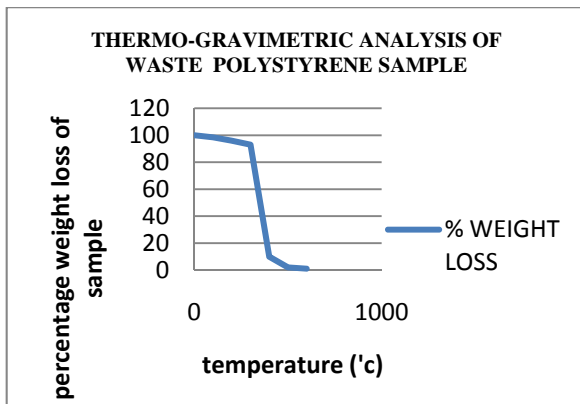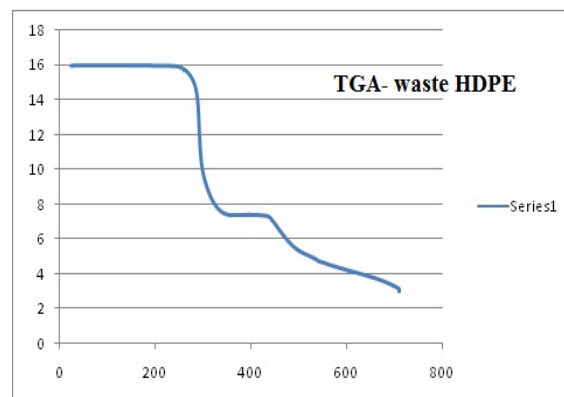

Fig 4(a).TGA of waste PS
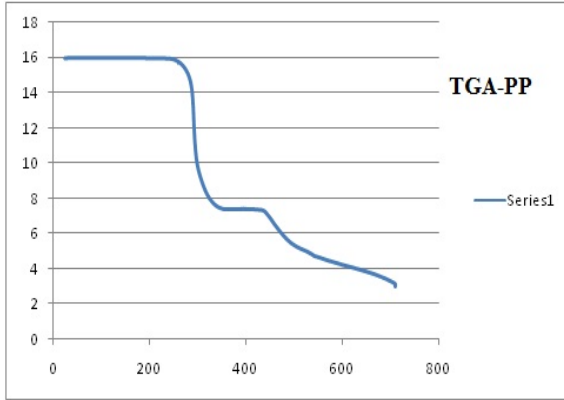

Fig 4(b). TGA of waste HDPE
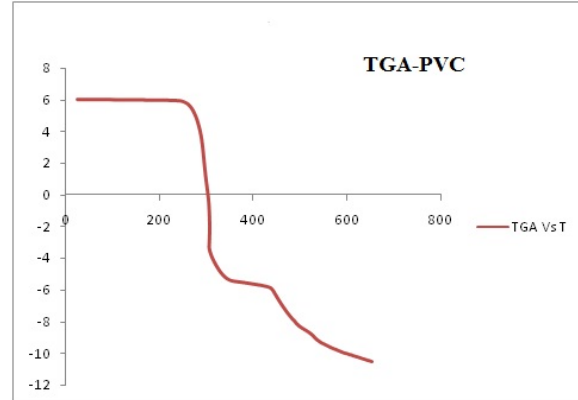
Fig5(a). TGA of waste PP

Fig5(b). TGA of waste PVC

For a closer analysis of these thermogravimetric data, the kinetics of each degradation process was studied with the Broido integral method. The kinetics of a system undergoing chemical changes is usually expressed in the following form:

$$\frac{d\alpha}{dt} = f(\alpha)k(T)$$

Where the rate of the change of the conversion with respect to time t, is equated to separable functions of and the absolute temperature T. The conversion or reacted fraction can be defined as the weight loss at time t divided by the weight loss at infinite time or total weight loss:

$$\alpha = \frac{\omega_0 - \omega}{\omega_0 \quad \omega_\infty}$$

Where ω_0, ω and ω_∞ are the sample weight initially, at time t, and at infinite time, respectively. Polymer degradation often involves a series of reactions. Therefore, $f(\alpha)$ represents the net result of a number of elementary steps. Each elementary step has its own activation energy, and so the rate constants of each have different temperature dependencies. The temperature dependence of the rate of reaction is generally expressed with the Arrhenius equation. The temperature dependence of the rate of reaction is generally expressed with the Arrhenius equation:

$$k(T) = A \ \exp\left(\frac{-E}{RT}\right)$$

Where R is the gas constant, T is the absolute temperature, E is the activation energy, and A is the pre – exponential factor. There are many models to describe the kinetic parameters but the models which are possible to write in constant heat rate will be applicable to establish the kinetics by using the thermo-gravimetric analysis.[14]

3.2. Liquefaction of Waste Plastics:

Liquefaction of polypropylene was studied with different kinds of catclysts by varying feed composition and as well as thermal pyrolysis also conducted to study the distribution of products. Using a semi batch reactor the

experiments conducted for testing the nature of liquefaction of plastic waste individually. The maximum temperature maintained in the reactor was about 700°C. The catalytic degradation of waste PP with poly-olefinic structure exhibited the liquid yield of 80-86 % and the solid yield below 2%, where as that of waste PS with polycyclic structure produced much more liquid, solid products than gases.
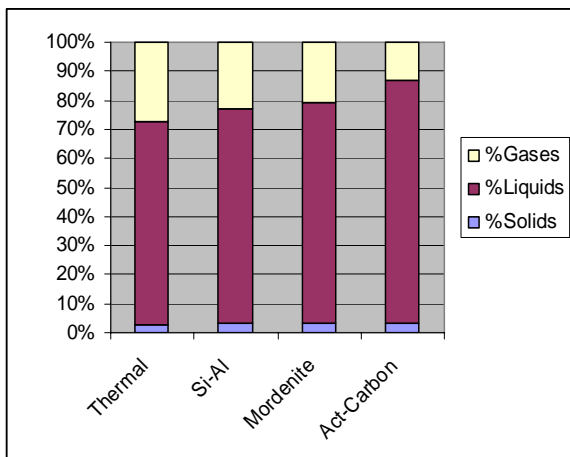

Fig. 6 Product distribution of PP by thermal and catalytic degradation.

4. Conclusions

Thermo-gravimetric analysis was very much helpful to determine the degradation ability of waste plastics. The polypropylene plastics require higher temperature range for degradation when compared with other kind of waste plastics. If the degradation of all waste plastics assumed as single order reactions then the kinetic parameters establishment will be easier by taking any mathematical models. The liquefaction of polypropylene is more in catalytic degradation when compared with thermal degradation.

5. References

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