

Conversion of into Liquid Hydrocarbons

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Abstract: Various methods of degradation of polymeric material polyolefin waste, polystyrene, waste wax, PVC, rubbers, PET bottles etc are reported in the literature. There are two types of catalytic degradation of plastics, one is liquid phase catalytic degradation and other method is where hydrocarbon vapours are passed over catalyst bed to decompose the long chain hydrocarbons into small ones. We have done both type of work but in the present paper catalytic plastic degradation was done in the liquid phase only. The purpose of our research was to catalytic degradation of waste plastics. We found that polyolefins gave the maximum yields of the fuel oil. Aluminosilicates with different cations were used as catalysts and were activated before putting them in the reactor and then waste plastics was added. In some cases combination of the two or more catalysts was used for degradation of the plastics. In most of the cases the conversion of waste plastic to fuel oil remained between 95 – 100 % ml liquid / 100 gm of plastic waste. We carried out repeated experiments using the same quantity of waste plastic and the catalyst and found that similar quantities of the oil was obtained. In case of waste plastic containing paper stickers and heated to 300 to 460°C, very low quantity of liquid oil collected which was blackish in colour. Non condensable gases were formed in good quantity. Black carbonaceous residue was also obtained. Carbonaceous residue was pressed into pellets. The pellets when ignited by flame burned till completely turned into ash. Calorific value, ASTM Distillation and complete GC-MS analysis of liquid obtained from product carried out. We used the oil to run the scooter as well as house generator. No problem was arisen in running both of them.

Keywords: catalysts, liquid hydrocarbons, waste Plastics

I. INTRODUCTION

India has been a favoured dumping ground for plastic wastes mostly from industrialized countries like Canada, Denmark, Germany, UK, the Netherland, Japan, France and the United States. According to the Government of India import data more than 59000 tons and 61000 tons of plastic waste have found its way into India in the years 1999 and 2000 respectively¹. Though plastics have opened the way for a plethora of new inventions and devices it has also ended up clogging the drains and becoming a health hazard.² Catalytic degradation of polymers have many advantages like reducing the temperature of degradation, uniformity of products, better process controls etc as described in a review article³. Y Sakata⁴ et al showed comparison of catalytic effect on polymer degradation on silica-alumina and non acidic meso porous silica catalysts. FSM catalysts accelerates the degradation of polythene and polypropylene. Dummersdorf et al⁵ in their patent disclosed a plasma process to convert waste plastic to into power. Paul R Stapp⁶ obtained a patent for obtaining high quality synthetic crude oil from waste plastics in hydrogen atmosphere at moderate temperature and pressures.

Crude oil could be separated into gasoline, diesel fuel & gas oils. Point J et al⁷ in a patent worked a process for degrading plastic material waste by pyrolysis for transformation into hydrocarbon mixture to be used as fuel. Polymers waste contained PE, PET, PS and PVC. Nitrogen gas was used as an inert medium. The melt plastics was dechlorinated before pyrolysis. There are patents where waste plastics were combined with other chemicals like Fischer – Tropsch wax⁸, or plastic waste with refinery waste⁹. In some cases¹⁰ solvent were used which dissolved the waste plastics partially to obtain lower molecular weight stream. There are papers and patents where catalysts were used for converting waste plastics to oil. Kwak¹¹ used Nickel or nickel alloy to the plastic melt for dehydrogenation of oil during the process. Vladil Stankevitch¹² carried out catalytic cracking technique to convert waste plastics to oil. Patent¹³ mentions the catalyst used belong to ZnNiHSM-5, zeolite REY, mercerised zeolite & ZnO or compounds containing Zn, Pb, Cu, Ni, Pt or Fe. Catalytic cracking is done simultaneously for gaseous products. The products are separated to give the desired products. Stankevitch¹⁴ in his patent discloses a process for the conversion of waste plastics to produce hydrocarbon oils. Shredded waste plastic is delivered to the top of a tubular reactor which comes in contact with the granular inert heat carrier which is pored from the top of the reactor. Thus pyrolysis of waste plastic proceeds at the temperature between 300 – 600°C. In India serious work on degradation of waste plastics was started from the year 1995 on wards. When I started my research in the year 1969, zeolite field was very new in India. During my research work on Zeolites for my Ph.D. degree, I found many research papers mentioning use of zeolites as cracking catalyst and I decided to work on catalytic cracking of Plastics. Meanwhile my colleague at defence lab was working on preparation of high melting wax by degradation of virgin plastic using activated charcoal as catalyst. After the process was over he would dissolve the wax in some solvent. The desired wax would be recovered by distilling of the solvent. There I tried the catalytic degradation of the virgin plastic using the same equipment. After the reaction was over the contents were allowed to cool slightly so that molten wax could be decanted leaving the catalyst in the reactor. The experiment was successful because of saving man hours and the cost of solvent. This lead me to work on degradation of waste plastics which could be started only in the year 2000.

II. EXPERIMENTAL

Catalytic degradation of waste plastic was carried out in a Pyrex glass reactor round bottom flask with standard joints having suitable arrangement for electrical heating, temperature measuring devices & set of air & water condenser, liquid oil collecting arrangement etc fixed on the metallic stand with the help of clamps.

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A known quantity of plastic waste was charged to the glass reactor along with the activated cationic catalyst aluminosilicate (0 to 30 % by weight of waste plastics). As the temperature starts increasing to about 80 – 120 °C , the plastic material starts melting and at the same time hydrocarbon vapours are seen .As temperature rises all the plastic gets melted. Hydrocarbon vapours formed are refluxed for a period of 1-3 hrs of with the help of water condenser. Period of refluxion depends upon the type of plastics used. Liquid oil was obtained by distillation and collected in bottles. We started working out on many type of plastic wastes like polyolefins , polystyrene, electronic items and converted them into useful products. Most interesting results were obtained from Polyolefins , PS and their blends. We developed a process to convert plastic wastes in to gaseous products and liquid fuel oils. We obtained gaseous hydrocarbons that could be stored for end use as fuel. In an experiment 5 gm activated N catalyst and 500 gm of waste plastic was used After refluxion period of 2 hours at 350 °C.500 ml fuel oil was obtained .In another experiment 500 gms of PS waste was taken in which 3% activated N catalyst from the above experiment was used.515 ml of oil was obtained in a shorter period of refluxion of 1.3 hours at 250°C,This showed that same catalyst could be used again without affecting the yields irrespective of the type of polymer. To confirm the activity of the catalyst 6 gm of the catalyst was taken in RBF and 300 gm of polypropylene was added. Refluxing the material for 2 hrs oil was obtained. The experiment was repeated three times and and following results were obtained as shown in Table -1

Table – 1 Activity of the catalyst N

Expt. No.	Weight of PP	Refluxed at	Oil obtained
1	300 gm	360 °C	280 gm
2	300 gm	340 °C	295 gm
3	300 gm	360 °C	290 gm

In another experiment 375 gm of waste plastic was added to 125 gm of crude waste wax in the flask, to which 8 gm of activated C catalyst plus 2 gm of activated N catalyst was added. At 325 °C 455 ml of fuel oil was collected. 10 gm of activated N catalyst was added to 145 gm of waste plastic with cellulosic coating and refluxed at 450°C for one hour. Only 70 ml of black coloured liquid was obtained. 60gms of black carbonaceous residue was obtained. Carbonaceous residue was pressed into pellets .The pellets could be ignited by flame, and it burned till completely turned into ash. Various other type of waste plastics shown in Table -2 were tested to find the oil contents obtained and quantity the charcoal/solids obtained in the process.

Table – 2 Degradation of Various Plastics

Catalyst Type & weight	Type of plastic	Oil obtained	Carbon Char weight
C -- 25gm	350gm electronics plastic	143 ml	190 gm solid
	200 gm municipal waste	132 gm	
C-- 13gm	200 gm municipal waste	185 ml	32gm
		151 gm	

C— 13 gm	150 gm hm colored Bags washed	140 ml 108gm	41 gm
Reg. Cat-- .15 gm	265 gm LDPE grannuals	314 ml 243 gm	9 gm
C – 25 gm	310 gm HM plain plastic sheets	70 ml 51 gm	151.6 gm

gm of polyolefin waste plastic and 20 gm of N catalyst was heated to 400 oC . 190 ml liquid oil was obtained. The fuel oil was divided into two parts (1) Oil collected below 140 deg C and (2) oil collected above 140 deg.C to 290oC. GC analysis of first fraction showed 16 peaks on the chromatogram. Major peaks shown were only six possessing volume percent of the fuel as 5%, 11.6%, 5%, 12%, 21%, and 36% . High boiling fraction consisted of 44 peaks on the chromatogram. Major peaks shown were only seven, possessing volume percent of the fuel as 5.4%, 12.6%, 19.6%, 21.5%, 14.5%, 9.6% and 9.9%. In another experiment polyolefin plastic waste (1000 gm) was charged to the glass reactor along with the activated N catalysts metal aluminosilicate (10 % w/w) & C catalyst (2% w/w). One litre of liquid hydrocarbons was collected. Complete analysis of the liquid hydrocarbon was carried out by Shri Ram Research Lab, Delhi. Analysis of liquid fuel shown in Table – 3 was carried out by GCMS showing various hydrocarbons present in the fuel oil based upon number of carbon atoms present in a HC .Molecular weight of hydrocarbons was lying between 80 to 422. Calorific Value Of Fuel Oil = 10023 Kcal/ gm

Table -3 Analysis Of Fuel Oil

Carbon Atom Nos.	Cyclo HC %	Non Cyclo HC %	Trialkylsilane %	Total HC %
C6	0.0	2.17	0.0	2.17
C7	0.0	0.29	0.0	0.29
C8	0.7	2.50	0.0	3.27
C9	19.18	29.44	4.10	52.72
C10	4.12	0.13	0.0	4.25
C11	0.92	17.50	0.0	18.42
C12	0.49	8.56	0.0	8.56
C13	0.52	0.0	0.0	0.52
C18	0.0	0.19	0.0	0.19
C21	0.0	0.11	0.0	0.11
TOTAL	25.93	60.89	4.10	90.92

Table -4 Distillation Characteristic Of Fuel Oil

Distilled V/V	Temperature °C	Distilled V/V	Temperature °C
Initial	58	70 %	268
10 %	121	80 %	301
20 %	143	90 %	335
30 %	161	95 %	355
40 %	183	Final	364
50 %	211	99 %	Recovery
60 %	243	Residue	Nil

III. CONCLUSION

The results of liquid phase catalytic degradation of various types of waste plastics especially polyolefins were very satisfactory as far as conversions and the quality of the oils are concerned. The oil produced was found very suitable to run scooter and also generators. Electronic waste and certain other types of waste gave poor yields and lot of carbon char. We already have a patent. With these catalysts we carried out vapour phase degradation of plastic waste in a continuous plant. I have developed processes to purify fuel oil produced and regeneration of spent catalysts and how to reduce pollution in case of waste plastic containing PVC.

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