International Journal of Current Engineering and Technology
ISSN 2277 – 4106

Research Article

Catalytic Degradation of Municipal Waste Plastics to Produce Fuel Range Hydrocarbons using Bentonite

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Abstract

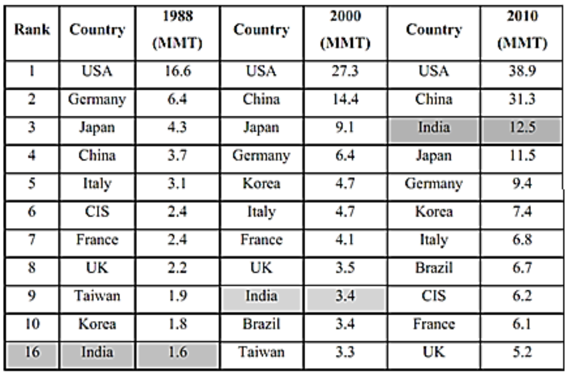
The aim of this project work is to convert waste plastics into useful fuel range hydrocarbon mixture. Catalytic cracking process using Bentonite as catalyst (1:4 ratios) is used to achieve the aforesaid aim. A Reactor is designed with dimension 300mm height and 150mm inner diameter, made of mild steel sheet (4mm thickness). Necessary equipments such as PID controller, contactor and a k-type thermocouple complete the required circuit. Heating of reactor is done by using a 3-phase band heater. Municipal waste plastics mainly consist of Low density polyethylene (LDPE),High density polyethylene(HDPE) and Polypropylene(PP).These are shredded, weighed and are loaded into the reactor. The reactor is gradually heated to attain temperatures as high as 430-450^0 C. Melting of plastics is observed at 121^{0}C (LDPE) 131^{0}C(HDPE) 150^{0}C(PP).The vapors arising due to subsequent heating of plastics quenched directly into ice cold water and oil is separated with the help of separating funnel. Physical properties like volume, density, viscosity, flash point and fire point of oil samples is determined. Chemical analysis of the oil samples is carried out by using FTIR and presence of paraffin's, olefins and naphthenes is observed in the liquid product. Simple batch distillation of oil is carried out between a temperature range 240-260^{0}C for about 20 minutes to obtain distillate and it's analysis using FTIR shows the presence of paraffin's, olefins and naphthenes.

Keywords: *waste plastics, catalytic degradation, Bentonite, municipal waste plastics, Polypropylene, LDPE, fuel range hydrocarbon, plastic to fuel, plastic degradation.*

Introduction

A marvel of polymer chemistry, plastics has become an indispensable part of our daily life. Although plastics are a newer discovery, they have become a part of everyday consumer life and its production and consumption have increased drastically. Plastic 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. 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,**(Sarthak Das et al 2007)** these plastics are employed in entire gamut of industrial and domestic areas. The production of plastics is significantly growing. Nowadays the plastic production is more than 200MT worldwide annually. 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), the status of the consumption of plastics in some selected countries worldwide. The current growth rate in Indian polymer consumption (16% p.a.) is clearly higher than that in China (10% p.a.) 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.

Table 1: Per capita consumption of plastics from a last few Decades **(Sarthak Das et al 2007)**



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

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

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point for consumption for the time series considered; a and b are parameters, determined econometrically. Plastics are non-biodegradable polymers 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. According to a nation-wide survey, conducted in the year 2009, approximately 10,000 tonnes (ten thousand tonnes) of plastic waste were generated every day in our country, and only 60% of it was recycled, balance 40% was not possible to dispose off. So gradually it goes on accumulating, thereby leading to serious disposal problems. 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 are shown in Table no 2

Table2: Calorific values of some of the Plastic along with coal **(Sarthak Das et al 2007)**

Material	Btu per pound	Kilojoules per kilo
Coal	11,500	27,000
Polyethylene	20,000	46,500
Polypropylene	19,300	45,000
Polystyrene	17,900	41,600
PET	9,290	21,600
PVC	8,170	19,000

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. 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. NO_x, SO_x, CO_x etc.

With a view to protect environment and reduce solid plastic waste **(Ramesh Babu et al),** conversion of waste plastics into energy yielding oil has gained a lot of importance. 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.

Many works have been carried out to crack plastics thermally to produce useful hydrocarbons. The thermal degradation process (M Sarker et al. 2012) applied with none coded waste plastics with muffle furnace and reactor without using catalyst or chemical. None coded polymer has been selected for the experiment 100% by weight. The temperature used for thermal degradation for muffle furnace at 420°C and for reactor temperature was 300- 420 °C and total experiment run time was 7-8 hours. The obtained products are liquid fuel 85%, light gas 9% and black carbon residue 6%. Various technique (Gas Chromatography and Mass Spectrometer, FT-IR) were used for produced fuel analysis. GC/MS analysis result is showing hydrocarbon compound ranges are C_3-C_{28} and light gas are present C_1-C_4. Fuel analysis result showing different carbon range and these produced fuel contain short to long chain hydrocarbon such as alkane and alkene. Produced fuel could be uses in combustion engine or as feed for feed stock refinery.

Means And Method

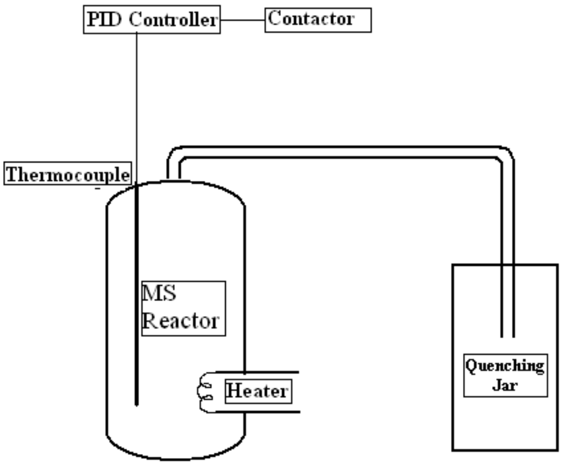

Figure 1. Flow sheet of the process

Experimental setup

A reactor is designed for catalytic degradation of waste plastics. The reactor is designed for a capacity of 1kg of feed for every batch trial. Using density data of plastics the volume of the reactor required is calculated. Suitable ID and height (150 x 300 mm) are selected. The maximum design pressure build up in the reactor is assumed to be 10 bar. Mild steel is selected as the material of construction. The thickness of the shell is determined to be 4mm (without allowance for corrosion). An asbestos gasket and a mild steel head complete the reactor set up. Delivery pipes made of GI pipes and a quenching jar complete the experimental set up.

The heart of the process is a mild steel reactor where the cracking reaction occurs. The reactor is loaded with feed mixed with catalyst in the desired ratio and sealed off from the external environment by tightly screwing the head with an asbestos gasket in between the reactor and head. The reactor is uniformly heated across its surface by using a band heater. The temperature within the reactor is measured with the help of a thermocouple which is connected to a PID controller and contactor as explained in the previous section. As the temperature within the reactor rises the feed present in the reactor melts. Vapors are generated rapidly as cracking temperature is attained. The generated vapors are removed from top of the reactor through opening provided on the head of the reactor.

The vapors then pass through a series of GI pipes interconnected to form two 90^0 bends. The open end of the pipe connections is immersed in a quenching jar with ice cold water. The vapors pass through the GI pipes into the quenching jar where they are met by ice cold water and are condensed to form an oil layer which separates above the water layer due to density difference. Oil is separated from water by using a separating funnel to obtain the oil.

Materials

Segregated waste plastics like Polypropylene, Low density polyethene (LDPE), High density polyethene (HDPE) are collected from municipal waste and shredded into small pieces by shredder in SembCorp shredding unit.

Catalyst used

Bentonite is used as catalyst in present work.it is an absorbent composed of aluminium phyllosilicate, essentially impure clay consisting mostly of montmorillonite. There are different types of bentonite, each named after the respective dominantelement, such as potassium (K), sodium (Na), calcium (Ca),and aluminium (Al). In our catalyst dominant element is sodium.

Operating condition

Two trials are carried out with different feed like only polypropylene and combination of LDPE and polypropylene. In both trials the catalyst to feed ratio is maintained as 1:4(weight basis). The reactor is gradually heated to attain temperatures as high as 430-450^0 C. Melting of plastics is observed at 121^{0}C (LDPE) and 150^{0}C (PP). Total time duration of processes is 6 hrs. The vapors obtained are directly quenched in quenching jar containing ice cold water.

Analysis

Oil obtained is inspected and various tests are carried out to determine the physical properties like specific gravity, density, viscosity (Redwood viscometer), flash point (Penske martin Apparatus), and fire point (Penske martin Apparatus).

FTIR is used to determine the functional group in the oil. Fourier Transform Infrared Spectroscopy (FTIR): The Instrument is from BRUKER with Attenuated Total Reflectance (ATR) facility by which solid (crystal, amorphous), liquid and gels samples can be analyzed. The spectral range will be from 500 to 20000 /Cm with scan rate of 32. The major advantage of this instrument is samples can be analyzed without making pellets. The medium infra- red range of 400-4000/cm has been used for our sample

Result and discussion

Physical Analysis

The oil samples were analyzed for their physical properties and the results obtained are listed below.

Table 3: physical properties of oil samples

Physical Property	Oil from Polypropylene	Oil from LDPE+ Polypropylene
Color	Yellow (turns dark with time)	Dark Brown
Density(kg/m^3)	779.77	790.82
Flash Point(^{0}C)	46	60
Fire Point(^{0}C)	56	82
Kinematic Viscosity (centistokes)	1. 35 (at 40^{0}C)	1. 34 (at 40^{0}C)
Dynamic Viscosity (Poise)	10.53 (at 40^{0}C)	10.597 (at 40^{0}C)

FTIR results:

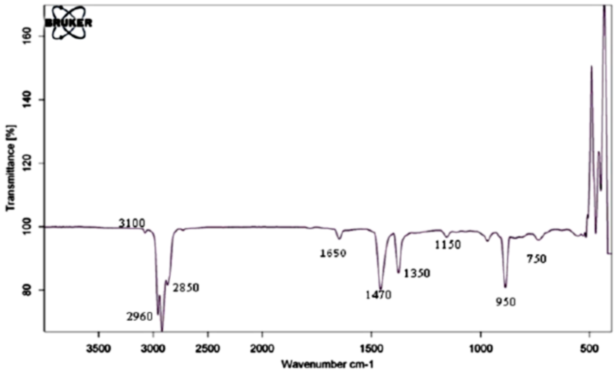

Figure 2: FTIR spectra for Polypropylene oil sample

Table 4: Data of Peaks in Figure 2 and the representative functional groups

Peak	*Wave no(cm^{-1})*	*Functional Groups*
1	3100	H-NH
2	2960	C-CH_3
3	2850	C-CH_3
4	1650	Amines
5	1470	CH_3
6	1350	CH_3
7	1150	Acetates
8	950	CH=CH(Trans)
9	750	CH=CH (cis)
10	650	CH=CH (cis)

Table 5: Data of Peaks in Figure 3 and the representative functional groups

Peak	*Wave no(cm^{-1})*	*Functional Groups*
1	2915.01	C-CH_3
2	2919.05	C-CH_3
3	1647.07	Amines
4	1457.07	CH_3
5	1378.3	CH_3
6	1156.28	Acetates
7	988.02	Secondary cyclic alcohols
8	888.72	C=CH_2
9	734.51	CH=CH (cis)
10	522.99	CH=CH (cis)

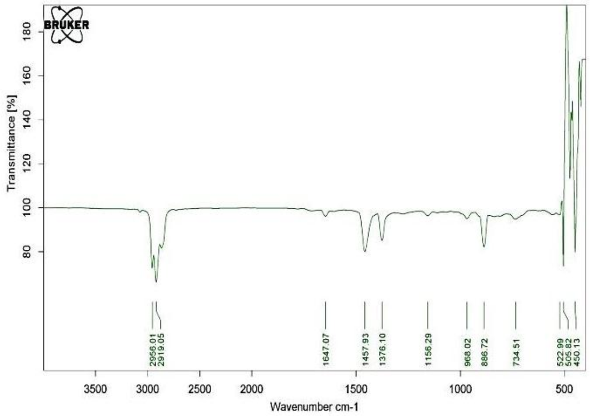

Figure 3: FTIR spectra for LDPE+PP oil sample

From the figure 2 FTIR analysis for the Polypropylene oil sample, different functional groups showed response at unique wavenumber ranges. The results confirms that the oil sample contains NH_2, C-CH_3, CH_3, CH=CH (Trans) and CH=CH(cis) groups. Transmittance Vs Wavenumber for LDPE & Polypropylene mixture (figure 3) showed the presence of C=CH_2, Acetates, Amines, Sec. cyclic alcohols, CH_3, C-CH_3, CH=CH (cis) groups.

To verify the oil fraction present in the oil obtained from Polypropylene was distilled by the method of Simple Distillation. The distillate is obtained at 240-260^{o}C. This is tested for physical properties using similar method mentioned above. And FTIR results for Distillate obtained from Polypropylene (figure 4) shows the presence of C-CH_3, Amines, CH=CH (Trans), CH_3 groups.

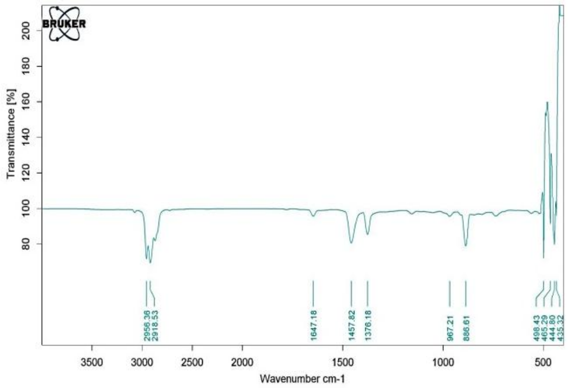

Figure 4: FTIR spectra for distillate of polypropylene oil

Table 6: Data of Peaks in Figure 4 and the representative functional groups

Peak	*Wave no(cm-1)*	*Functional Groups*
1	2958.38	C-CH_3
2	2918.53	C-CH_3
3	1647.18	Amines
4	1457.82	CH_3
5	1376.18	CH_3
6	957.21	CH=CH(Trans)
7	888.81	C-CH_2

Conclusion

From the above experiments, it can be concluded that –

- Waste plastic can be reduced significantly due to its convertibility to several other forms
- Bentonite can be used for the process as a catalyst.
- Polypropylene and its mixture with LDPE can be degraded catalytically to produce significant amount of oil with the yield of 60% (wt basis)
- The FTIR analysis confirms the presence of Paraffins and Olefins in the oil samples obtained

Acknowledgement

Author acknowledges the KSCST SPP for funding and the Department of Chemical Engineering, DSCE for the support. Author thanks to Mr. Shreyank Hampi for the significant contribution in the project work.

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