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Thermo-catalytic conversion of waste polyethene bags into value added products

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An integrated and sustainable approach has been proposed for materials management for waste polythene bags(WP). In this context, a thermo catalytic degradation of WP yields liquid and solid residue at optimised conditions. The obtained liquid product (LP) and solid residue(SR) has been characterized for structural and different physical properties like flash point, viscosity(dynamic and kinematic), molecular weight, etc using ASTM methods. Thus, obtained results of LP is flash point 265°C, dynamic viscosity 11.99 cp and kinematic viscosity 10.55 cp. These results were compared with existing literature data and suitable application has been projected. Further, SR has also been also characterised as carbon materials with high adsorption capacity along with some metallic impurities. In net conclusive findings of this piece of works expedite the sustainable use of waste plastic with effective ways as a source of value added products.

Keywords: Waste polyethene, Thermolytic degradation, Value added products, Fuel, Charcoal.

The bombastic accumulation of plastic wastes from industries and households have been posed a serious theft to entire atmospheric components since last few decades. These plastic wastes are producing several toxic pollutants, which are seriously deteriorating the quality of water, air and living beings[1,2]. The degradation of plastic wastes also produces several carcinogenic chemicals, which are taken by aquatic organism. Further, life of these organism becomes highly miserable and also they spread to other living being. According to an estimate, worldwide plastics production of plastic is growing by an average of about 4% each year, which is an indicator for generation of equivalent amount of plastic wastes. The important consumers of plastics are agriculture, automobile, medical, electronic industries and household items. Among the all potential users of plastics, the collections and segregation of households are very seemingly difficult due to scattered nature of consumption as well wide range of plastics. Generally, main plastic used in household are polyethylene (low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE)), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyethylene-terephthalate (PET), which constitute around total 74% of all plastic wastes. Among these different plastics, polythene bags are rarely collected for reprocessing because of several social and technical reasons[3,4].

Furthermore, plastics wastes are non biodegradable in nature and thus generates serious problems in their waste management. The dumping of plastic causes depletion of natural resources, environmental conditions, and landfill space. However, the novelty of plastic is recyclability for repeatedly use after reprocessing. But, recycled plastics deteriorate its valuable properties and not possible below certain dimensions (thickness). In this regards several discrete reports are available for conversion waste plastics into several value added products like small hydrocarbons(fuel) after chemical and physical treatments beyond its life. The conversion waste plastic into fuel is based on depend on degradation by thermal, catalytic and hydrocracking[5,8]. However, the basic problem is development of suitable reactors and depolymerisation conditions for conversion efficiency and complete materials management[9,10]. Another drawback is reproducible conversion route, scale up possibility, residual products and economy. However, the conversion of waste plastic into value added product is future prospective for recycling of plastic for different value added products[11,12]. In continuation to above development present paper reports a laboratory scale reactors for thermolytic dissociation of polyethene waste into value added products. Thus, obtained products has been separated and characterised for their physical and chemical properties for suitable applications. Further, on the basis of properties and chemical composition a protocol is designed for scale up possibility for future suitable applications.

Experimental Section

Materials and methods

Polyethene bags were collected from Bhalsawa Landfill of Delhi on 10.10.2017. Further, KNO_3 (99.5 %) , $NaNO_3$ (99. 8 %), Zinc sulphate (98.5%), were procured from LOBA chemicals. The double distilled water deionised water and AR grade solvents were used in entire investigation.

Pretreatment

The collected polyethylene bags were shredded into small pieces with approximate size of 4 to 5 mm. Further, the pieces were washed thoroughly with double distilled water and then dried in hot air oven for 2 h at 60°C. Thus, obtained polythene waste were kept in air tight container for further use.

Thermolytic degradation

The thermolytic experimental set setup was consists of an exclusively designed semi batch reactor (SBR) borosil glass with internal diameter 20 cm, length 40 cm and capacity 1.25 L. It also contains two outlets, one outlet is fitted with reflex condenser (300 mm length and 40 mm diameter), while other end is attached to gas monitoring systems. An electric heater was attached externally to heat it at requisite temperature. The temperature of SBR was measured by a Cr-Al: K-type thermocouple fixed inside the reactor, while temperature was controlled by external PID controller.

In a thermolytic experiment of shredded pieces of PE (20 g) waste sample were carried out two conditions: a) without catalysts and b) in the presence of catalyst in SBR. The nanosize ZnO was used as catalysts, which was prepared by earlier reported[13.] The heating was started at different temperature under static temperature and constant N_2 Flow of 50 cc per minute. After definite time condensable liquid products (LP) were collected SBR in a reagent bottle with the help condenser using water purification system. The solid residue left out inside the reactor was also collected weighed for sustainable material management. After that, weight of gaseous/volatile product was calculated from the material balance. The conversion yield has been also calculated by using the following equations

$$\text{Wt \% of liquid yield} = \frac{W_l}{W_f} \times 100\ \% \qquad \ldots(1)$$

$$\text{Wt \% of residue} = \frac{W_s}{W_f} \times 100\ \% \qquad \ldots(2)$$

$$\text{Wt \% of gas yield} = 100\ \% - \text{Wt \%} \ [\text{liquid yield + solid yield residue}] \qquad \ldots(3)$$

W_l = the weight of liquid yield

W_f = the weight of feed waste plastic

W_s = the weight of solid residue

Characterizations

The structural characterization of developed products were done by Bruker alpha model fourier transform infrared (FTIR) spectrometer in ATR mode from 600 to 4000 cm^{-1} range. The spectra were recorded with an accumulation of 16 scan and resolution of 2 cm^{-1}. The chromotagraphic study were made by Anatec gas chromatograph (GC) equipped with FID detector and a capillary column (30m × 0.5mm × 0.5µm) using acetone as solvent. The sample was operated in temperature programming mode, with injector and detector temperatures 210°C and 230°C respectively. The particle phase, size and structure of the synthesized materials were studied using Rigaku Rotaflex, RAD/Max-200B model X-ray powder diffractometer with CuKα (λ=1.5405 Å) radiation at a scanning rate of 2° per min.

Fuel behaviour

In order to evaluate the application of LP as fuel, kinematic viscosity, dynamic viscosity, calorific and flash points were determined. Kinematic viscosity was recorded by brookfield viscometer (ASTMD 2393), while dynamic viscosity was determined with uphold viscometer. Initially, sample was preconditioned by placing it at constant temperature. The R2 spindles was used to rotate the samples upto 2 min before recording. The calorific value was determined by bomb calorimetric methods using recommended standard parameters. The flash point of collected liquid was determined by reported ASTM methods[14] using parameters prescribed as per recommendation standard.

Results and Discussion

Thermolytic degradation

The basic observations during degradation experiment are listed in Table 1

The result indicates that the results of S.N.2 is more efficient for conversion of plastic wastes to fuel. It appears that at lower temperature plastic unable degrade as well as higher at temperature more volatile products is produced. The thermolytic conversion are also studied in the absence of ZnO but the reaction started after 90 min and completed in 180 min along with very less products. This indicates the suitability of ZnO as an efficient catalyst for thermolytic degradation of PE. Further, the physical properties of LP are given Table 2 along with commercially used fuels. The parameter are quite identical with commonly used liquid fuels.

Chemical characterisation of liquid

GC spectra of LP shows several peaks at different retention times 2.52, 2.64, 3.29 min before solvent peak at 4.14 min. These peaks reveal the presence of components of different molecular masses. The polymers after cracking at drastic condition of temperature undergo fragmentation of different masses. These mass of products decides its combustions behaviour, ignition temperature to use as fuel. Thus, above GC data indicates its mass in the range of used petroleum fuels. In continuity, IR spectrum of LP is shown in Fig. 1. The results are very much supporting to our expectation that fragmented products of polyethenes.

The peaks observed at about 2900 cm^{-1} and 2800 cm^{-1} are due to C-H stretching band and at about 1470, 1380 cm^{-1} are due to C-C stretching and C- H bending bands respectively. The C-H stretching band at 3000 cm^{-1} or slightly above this frequency is characteristic of un-saturation. Further the C=C stretching band in alkenes is also at a higher wave number (1600 – 1700 cm^{-1}) than in alkanes and this band is weak to medium[15]. Absence of these two bands in IR spectrum reveals that there is no un-saturation in the compound.

Non volatile components:

The IR and XRD spectra of SR of polyethene are shown in Fig. 2 a and b.

The IR spectra is indicating very low C-H vibration at 3000 cm^{-1} in comparison to obtained LP. However , C=C bands in between 1500 to 1600 cm^{-1} are very prominent. It indicates that the non volatile residual parts of polyethene has been converted into carbon containing product rather hydrocarbon due to unavailability of oxygen, while other volatile fractions are converted into liquid products[16]. Further, XRD of SR is indicating sharp due crystalline nature of materials, while polyethene does not show any XRD peak due to amorphous nature. The morphology of obtained charcoal was also studied by SEM and micrograph is shown in Fig. 3. The photograph is indicating the formation of round shape carbon nano particles.

However, the optical micrograph in Fig. 4 indicates the formation of porous micro sized materials with high surface area of 684 m^2 g^{-1}. Such materials with high surface area are used for removal of different water pollutants like heavy metals[17].

Table 1 — The experimental observation during thermolytic degradations

S.N.	Conditions		Initiation time	Completion time	% Product yields	
	Amt (g)	Temperature (°C)			lP	SW
1	40	250	20	40	75	20
2	40	300	15	25	82	15
3	40	350	12	28	71	20

Table 2 — Different physical properties LP along with commercial fuels

S.N.	Viscosity		Calorific value(Kj/g)	Specific gravity	Flash points
	Kinematic	Dynamic			
Fuel	18.766	5.86	1.18	0.75	41
Petrol	16.36	4.70	1.34	0.80	30
Diesel	17.27	6.20	1.25	0.72	43

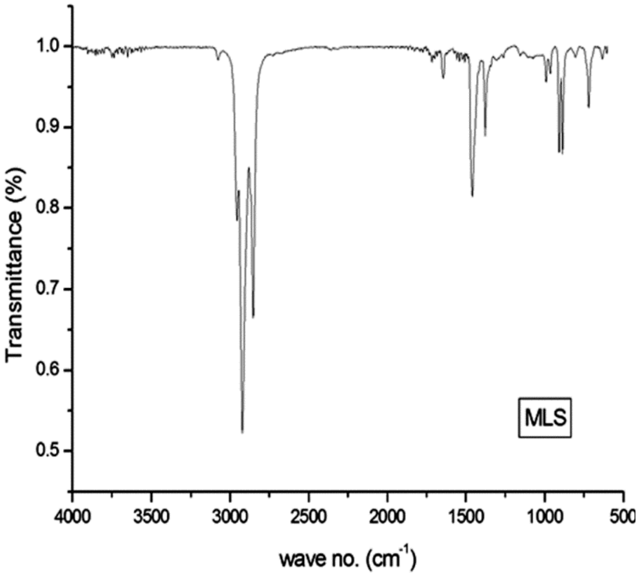

Fig. 1 — FT-IR spectra of LP

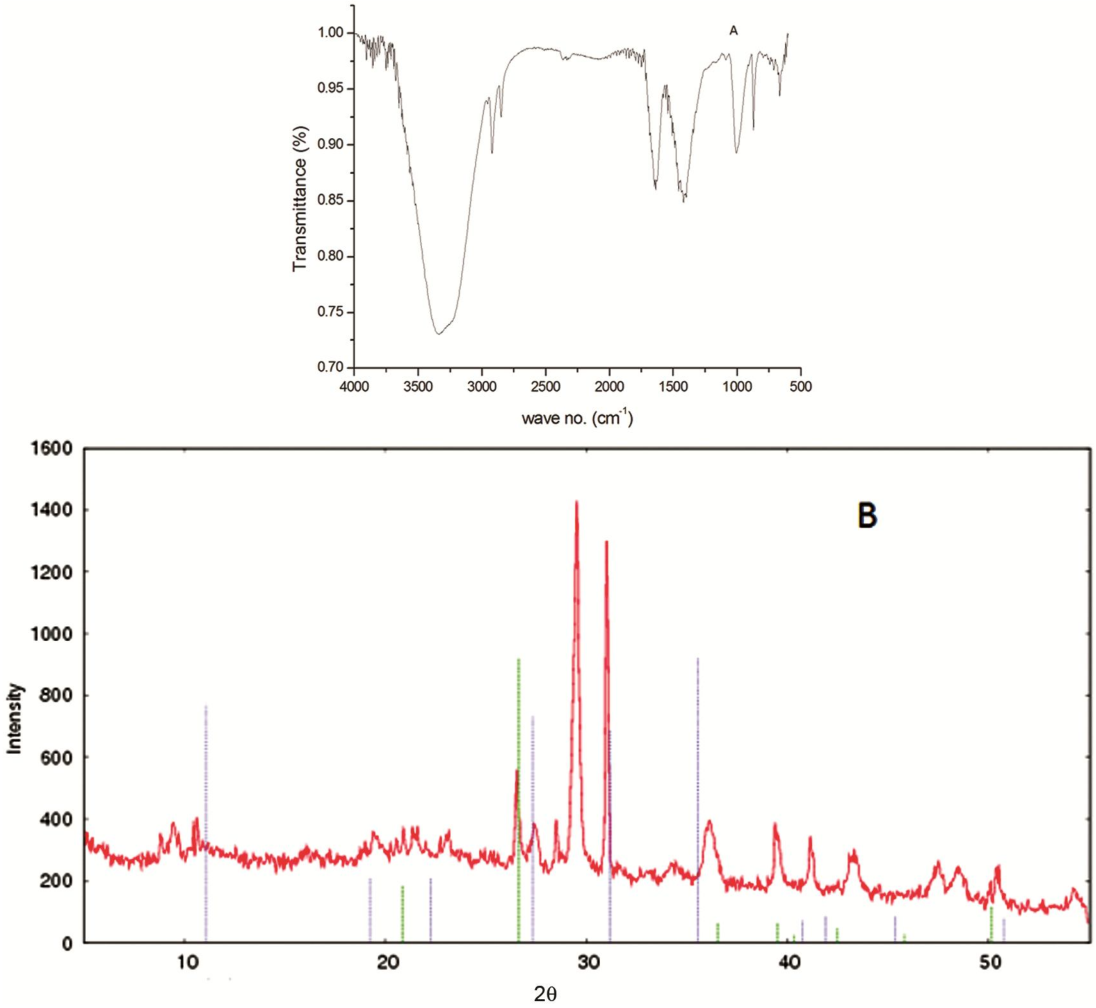

Fig. 2 — A) IR spectra and B) XRD spectra of SW

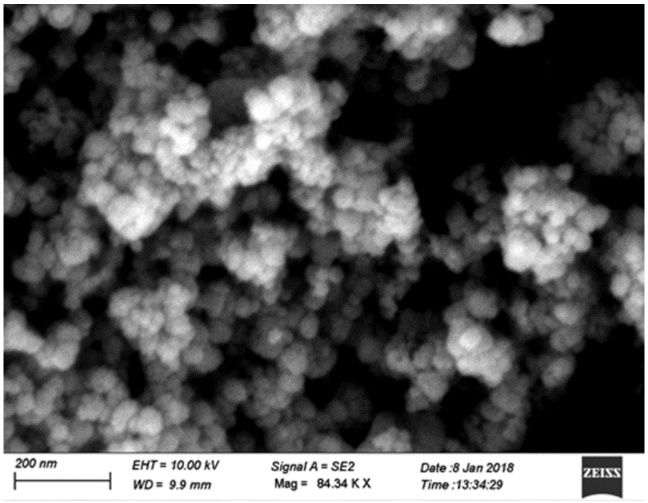

Fig. 3 — SEM photograph of SW

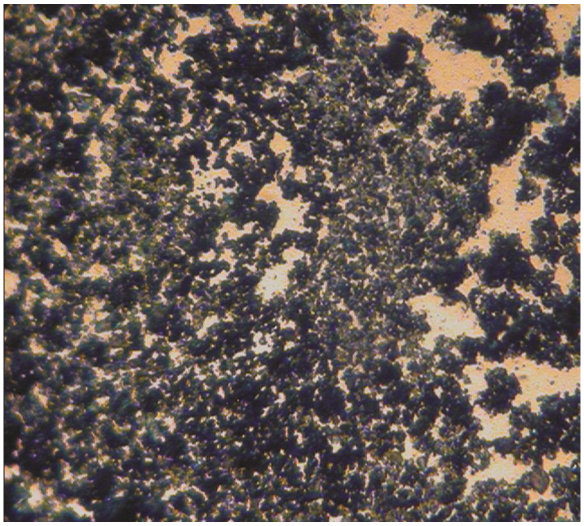

Fig. 4 — Optical photograph of SW

Conclusion

The thermal chemical process is reported for conversion of waste polyethene bags into value added products liquid as fuel and solid as adsorbent. The analytical results indicated that the formation of value added products i.e. high volatile hydrocarbon compounds and charcoal. The calorific value and flash point of obtained liquid confirms its utility as fuel and charcoal for water purifications.

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