ABSTRACT

Disposal of commonly used plastic wastes to landfill was becoming more undesirable due to environmental concerns, rising costs and poor biodegradability. Therefore, recycling through mechanical or chemical method seems to be the only route of plastic waste management. Polyfilms, mainly Low Density Poly-Ethylene (LDPE) is a major type of thermoplastic used for packing milk throughout India. In the present investigation the recycling dairy waste LDPE film is examined via catalytic pyrolysis. Pyrolysis of LDPE was investigated with the use of catalyst, NiMo/Al2O3. Experiments were carried out in a laboratory conditions. High yields of liquid fraction in the boiling range of 65-380°C and gases were obtained along with a small amount of coke. The liquid and gaseous products were analyzed using Gas Chromatograph Mass Spectrometer (GC MS) and Gas Chromatograph (GC) respectively. It is found that the derived liquid products were hydrocarbons, consist of alkanes and alkenes. The pyrolysis liquid has a calorific value 10810 Cal g⁻¹. As far as recycling is concerned, plastic wastes after several methods for waste plastics, catalytic degradation to fuel oil and primary recycling, separation of these waste plastics for primary recycling and processing waste plastic particularly in areas distant from centers of population. Most of the researches deal with hydropyrolysis, methanolysis and amination for condensation polymers (e.g. polyethylene terephthalate, polyurethane) and hydrogenation, pyrolysis, gasification liquefaction, coking, visbreaking and hydrocracking for addition polymers (e.g. polystyrene, polyacrylnitrile chloride). Thermochemical recycling techniques like pyrolysis have been proposed as process of producing series of refined petrochemical products and particularly of liquid fractions similar to that of commercial fuels. Thermal cracking of polystyrenes are usually carried out either in high temperature to produce an olefin mixture (C1-C4) and aromatic compounds (benzene, toluene and xylene) or in low temperature process where three fractions are received, a high calorific value gas, condensable liquid hydrocarbon and solid waxes.

INTRODUCTION

During last few decades, the increase in world population increased the consumption of polymers (mainly plastics). In recent years there has been a worldwide growing concern over the disposal of various types of wastes originating due to plastics. The increased consumption of plastics in a modern society is inevitable due to their versatile utilities, functional values and economical when compared with other materials. These trends result in plastic waste generation and disposal problems which gradually prompt researchers to refocus on plastics recycling technology. This new initiatives was driven by both environmental concerns and economic factors.

The plastic waste recycling can be categorized into four modes. Primary recycling involves in the conversion of products towards the original product. Secondary recycling involves in the conversion of products of different forms for less demanding applications. Tertiary recycling converts wastes into basic chemicals or fuels. Quaternary recycling retrieves energy through incineration. Today, secondary recycling is a more common practice for many plastic products through grinding, re-melting and re-forming them into lower-value products such as fillers and fibers. Its application is somewhat limited. Only 20% of plastic waste can be handled this way. As far as recycling is concerned, plastic wastes after several primary and secondary recycling will eventually have to be treated in the tertiary or quaternary mode. Although burning plastics for energy is a more mature and established technology but there is strong public opposition to incineration. Further, sighting a new incinerator will be very difficult which faces public sensitivity. In contrast, tertiary recycling of plastic wastes are gaining momentum as petroleum and petrochemical companies begin to realize that this technology can be integrated into their daily operations.

Now a day the increased amount of waste plastics, mainly polyfilms, has not only produced serious environmental problems but also caused huge waste of resources. Among the various recycling methods for waste plastics, catalytic degradation to fuel oil and valuable chemicals are regarded as the most promising method to realize commercial use. Waste plastic, a common petroleum-based waste material, is a source of hydrocarbon that is not being used effectively. Only 2 % of the waste plastics are currently being recycled and the remaining being disposed of in landfills. An increase in the usage and consumption of plastics is considered to be inevitable because of their versatility, their numerous uses and the relatively small amount of energy required for their production compared to that of other materials.

Several problems are associated with the recycling of polyfilms are associated with the presence of antioxidants and colorants. The difficulty of persuade consumer households regarding the necessity to recycle, separation of these waste plastics for primary recycling and processing waste plastic particularly in areas distant from centers of population. Most of the researches deal with hydropyrolysis, methanolysis and amination for condensation polymers (e.g. polyethylene terephthalate, polyurethane) and hydrogenation, pyrolysis, gasification liquefaction, coking, visbreaking and hydrocracking for addition polymers (e.g. polystyrenes, polystyrene, polyvinyl chloride). Thermochemical recycling techniques like pyrolysis have been proposed as process of producing series of refined petrochemical products and particularly of liquid fractions similar to that of commercial fuels. Thermal cracking of polystyrenes are usually carried out either in high temperature to produce an olefin mixture (C1-C4) and aromatic compounds (benzene, toluene and xylene) or in low temperature process where three fractions are received, a high calorific value gas, condensable liquid hydrocarbon and solid waxes.

India is a number one producer of milk in the world. Around 150 million tones of milk were produced every year in India. The cooperative dairies are handling majority of milk in India. After processing and standardization this milk is supplied to the consumer in milk sachets, i.e. in polyfilm bags. During milk packing and after consumption of milk these empty film sachets are thrown out as a waste. These polyfilm possess several environmental problems. Accumulation of this film on the ground prevents the entry of the rain water into top soil. Ignited film emanates dioxin into the air. If it is eaten by the stray animals cause immediate death to the animals. Hence most of the zoos banned the entry of plastic bags for the safety of the animals. Accumulation of these polyfilms in water bodies like lake, river and ponds prevents the entry of sun light and atmospheric oxygen into the water resulted in death of water animals such as fishes, crabs, prawns and plants. Because of all the above problems most of the states in India have banned the usage of polyfilm.

Therefore, catalytic pyrolys of these waste LDPE (polyfilms) in the dairy industry gained more important. This study forms part of research program for recycling of waste plastic to fuels.

MATERIALS AND METHODS

Materials

The plastic used in this study was thin clear film of waste LDPE (used milk packets and packing films). The physical properties of LDPE observed were shown on Table 1. The catalyst used in this
The yield, \( Y \), of a certain species (gas or liquid) was calculated based on the following equation:

\[
Y = \left( \frac{W_L + W_G}{W_O} \right) \times 100
\]

Where, \( W_L \) is the weight of liquid products, \( W_G \) is the weight of gaseous products, \( W_O \) is the initial loading weight of LDPE and \( W_i \) is the weight of certain species.

**Product Analysis**

**GC Analysis:** Gases collected were analyzed using a Varian Analytical Instruments CP-3800 series gas chromatograph. The types of detectors employed were the Flame Ionization Detector (FID) and thermal conductivity detector.

**GC MS Analysis:** Liquid product identification and quantification were determined using a SHIMADZU-QP 2010 series GC MS with FID, equipped with a VF-5ms column (Length: 30.0m, Diameter: 0.25mm, Film thickness: 0.25μm). The carbon number distribution of the liquids was determined by NP-gram method.[49]

**Fuel Properties**

**Water:** The water content was determined by Karl Fisher titration. In the titration the sample was dissolved in solvent (Chloroform: methanol, 3:1) and titrated with Karl Fisher reagent.

**Ash:** Ash content is measured according to DIN EN 7. The sample is ignited and burnt in a crucible in a crucible (platinum). A residue remaining after ignition at 770 °C was measured gravimetrically.

**Sulphur:** The sulphur content of the pyrolysis liquid was evaluated by using Inductively Coupled Plasma-Optical Emission Spectroscopy, (PerkinElmer Optima 7000 DV).

**Density:** The density measured by a digital density meter. A small volume of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency was used to determine the density.

**Viscosity:** Viscosity is a measure of resistance to flow. The viscosity of the pyrolysis liquid was determined using glass capillaries.

**Flash Point:** The flash point was determined according to ASTM D 93. The sample was heated in a Pensky-Martens Closed-cup tester at a slow and constant rate with continual stirring. A small flame is introduced into the cup at regular intervals. The flash point is the temperature at which the flame ignites the vapor above the sample.

**Calorific Value:** The heating value is measured in a Parr adiabatic bomb with a Parr Calorimeter Controlled 1720 is used. The heat of combustion is determined by measuring the increase in temperature differences and then calculated from the energy balance for the system.

**RESULTS AND DISCUSSION**

**Thermal Gravimetric Analysis**

The TGA curve shows the variation of weight with respect to temperature was presented in Figure. 1. As observed, the weight change of the pyrolysis (Thermal degradation) begins about 250-275 °C and finished at 500-525 °C. No residue remained after the analysis. Generally, this will result in a lower residual mass fraction in lab scale experiments. This result shows that the waste LDPE can be converted into fuels by pyrolysis.
Product Yield

Catalytic pyrolysis involves in the thermal degradation of the polymeric material in the absence of oxygen (Nitrogen atmosphere). Catalytic pyrolysis can improve the product selectivity and reduce the energy input. It was also observed that the presence of catalyst, NiMo/Al2O3, lead to increased amount of the liquid fraction. The relative amounts of gas are less when compared to liquid fraction. The conversion of thermal degradation increases with increase in reaction time, as shown in Figure 2.

During pyrolysis at increased temperatures, depending on polymer type, either end chain or random breakdown of the macromolecules occurs. In LDPE the amount of monomer produced is very low lead to increased amount of the liquid fraction. The relative amounts of gas are less when compared to liquid fraction. The conversion of thermal degradation increases with increase in reaction time, as shown in Figure 2.

After 100 minutes of reaction time, the conversion reached around 93.8% and no significant change was observed on further increase in reaction time. This suggests that little additional conversion can be achieved for very long reaction times at this temperature. The products can be divided into three fractions; gaseous, liquid and solids (Residues), respectively. It was observed that the yields of these fractions behaved differently. The values measured for the products yield appear in Table 2.

The degradation rates of LDPE were given in Figure 3. The maximum rates occurred at a reaction temperatures of 375-400 °C. It is clear that the thermal degradation reaction in the presence of catalyst follows first order kinetics with respect to the reacting component concentration.

Product Analysis

According to the data of chromatogram, the different fraction formed in the pyrolysis of LDPE contains more than 275 individual compounds of different classes. However, fractions of many compounds are insignificant because their summation is less than 0.5 wt%. The compounds which have significant value was discussed.

<table>
<thead>
<tr>
<th>Product</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>93.8%</td>
</tr>
<tr>
<td>Gas yield</td>
<td>8.5%</td>
</tr>
<tr>
<td>Liquid yield</td>
<td>85.3%</td>
</tr>
<tr>
<td>Solid residue</td>
<td>6.2%</td>
</tr>
</tbody>
</table>

Table 2: Product distribution for thermal degradation of LDPE

Product Analysis

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Fig. 2: Conversion of LDPE as a function of reaction time

Fig. 3: Variations of instantaneous reaction rates at different temperature for the pyrolysis of LDPE

Fig. 4: Composition of the liquid fractions from the catalytic pyrolysis of LDPE
The compounds identified in the liquid fraction were illustrated in the Figure 4. A mixture of hydrocarbons was determined. The main part consisted of aliphatic compounds (normal alkanes, iso-alkanes and alkenes) with only a small portion of aromatic substances. The existence of the catalyst increased the amount of liquid fraction in the region of C7 to C13 and decreased the higher than C15 compounds. As observed, the product distribution showed that most aliphatic compounds appeared in the region of C15+.

Lower molecular weight species were found in gaseous fraction was within the carbon numbers C1 to C6. As shown in (Figure 5) the most dominant product was C5 and C6. However, the percentage of lighter alkenes (with carbon numbers less than five) was relatively low. The yield of the gaseous fraction was observed to be increased with respect to reaction time.

Fig. 5: Composition of the gaseous fractions from the catalytic pyrolysis of LDPE

Fuel Properties
Pyrolysis thermally decomposes waste LDPE into gas, liquid and solid (residue) products at moderate temperatures in an inert atmosphere, each of which has a potential as a fuel.

From the (Table 3) it was clear that the liquid fraction from waste LDPE has the superior quality than that of the MV2 fuel oil. The liquid fraction had the high calorific value (10,810 cal g\(^{-1}\)) compared with fuel oil, hence by using less quantity of the same, in house steam can be generated. The flash point is lesser than the prescribed level due to the presence of small quantity of C6 and C7 compounds. This can be considerably reduced by blending with fuel oil. The presence of trace quantity of sulphur may be from the printing inks used for naming and coding the milk packets. Carbon credits can be increased by those organizations, which reduce the usage of fossil fuel. It is additional earnings to the organization.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Test methods</th>
<th>IS : 1593-1982 standard for MV2 fuel oils</th>
<th>Liquid fraction</th>
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</thead>
<tbody>
<tr>
<td>Ash, percent by mass</td>
<td>IS : 1448 [P : 2]</td>
<td>NIL</td>
<td>NIL</td>
</tr>
<tr>
<td>Gross, calorific value cal g(^{-1})</td>
<td>IS : 1448 [P : 6]</td>
<td>Maximum 0.1</td>
<td>0.002</td>
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<tr>
<td>Flash point</td>
<td>ASTM D 93</td>
<td>66 °C</td>
<td>45 °C</td>
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<tr>
<td>Kinematic viscosity in centistokes at 50 °C</td>
<td>IS : 1448 [P : 25]</td>
<td>Maximum 180</td>
<td>147</td>
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<tr>
<td>Sediment, percent by mass</td>
<td>IS : 1448 [P : 30]</td>
<td>Maximum 0.25</td>
<td>0.001</td>
</tr>
<tr>
<td>Sulphur, total, percent by mass</td>
<td>IS : 1448 [P : 33]</td>
<td>Maximum 4.0</td>
<td>0.083</td>
</tr>
<tr>
<td>Water content, percent by volume</td>
<td>IS : 1448 [P :40]</td>
<td>Maximum 1.0</td>
<td>0.0001</td>
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