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Research Article

CATALYTIC PYROLYSIS OF DAIRY INDUSTRIAL WASTE LDPE FILM INTO FUEL

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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, $NiMo/Al_2O_3$. 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}, ash content 0.02%, relative density 0.876, flash point greater than 45°C and sulphur content of 0.083%. The liquid can be used as a feed stock in the steam boiler.

Keywords: Polymers, LDPE, Pyrolysis, Dairy waste film.

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 prompted 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[1]. Primary recycling involves in the conversion of these products similar to the original product. Secondary recycle involves conversion into 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[2]. 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[3]. 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[4] 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[5].

Several problems are associated with the recycling of polyflims are associated with the presence of antioxidants and colorants[6]. 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[7]. Most of the researches deal with hydrolysis, methanolysis and aminolysis for condensation polymers (e.g. polyethylene terephthalate, polyurethane) and hydrogenation, pyrolysis, gasification liquefaction, coking, visbreaking and hydrocracking for addition polymers (e.g. polyolefins, 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[8]. Thermal cracking of polyolefins 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[9].

India is a number one producer of milk in the world. Around 150 million tones of milk were produced every year in India. The co-operative 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 posses 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 pyrolysis 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 study was NiMo/Al_2O_3 (2.72 wt% Ni and 13.16 wt% Mo). Before use, the catalyst was crushed, sieved through 160 mesh and dried in hot air oven.

Table 1: Physical properties of waste LDPE

Properties	Units	Values
Density	g cm^{-3}	0.920-0.922
Melt index	g 10 min^{-1}	1.8 – 2.4
Tensile strength	Mpa (Psi)	18
Average molecular weights	Daltons	80,000
Melting temperature	°C	118

Methods

Thermal Gravimetric Analysis (TGA)

The thermal degradation temperature of waste dairy LDPE, was measured using the Pyris-1 DSC from Perkin Elmer. A typical TGA instrument consists of a precision mass balance which records the initial and instantaneous mass of a sample and a furnace to increases the temperature in a linear relationship with time (the range of temperatures between 35 and 750 °C). A sample of about 10 mg was introduced into the appropriate position of the instrument and heated at a constant rate of 10 °C min^{-1} with a nitrogen purge rate of 20 mL min^{-1} at pan.

Experimental Setup

The thermal degradation of LDPE was carried out in an in-house designed stainless steel batch reactor (60 mL volume). A temperature controller was used to control the temperature of the furnace. The reactor was charged with 10 g of materials was mixed with 0.5 g of the catalyst powder and then charged into the reactor. The presence of catalyst lead to increased amounts of the liquid fraction accompanied by decreased gaseous fraction and residue. The reactor was completely purged with dry nitrogen to remove air. In this investigation, reaction products were classified into three groups: Gases, Liquid hydrocarbons and residue. Volatile products leaving the reactor were passed through a glass-fiber filter, followed by an ice-water condenser to collect condensable liquid product. The Tedlar bags were used to collect gaseous samples. The yield of liquid product was defined as the amount of liquid collected in a burette and the yield of residue as the solid waxy compounds remaining inside the reactor along with coke accumulated on the catalyst. The yield of gas was calculated from the difference between the loaded amount of polymer and catalyst, the yield of liquid and residue. The plastic conversion values were also calculated by considering only those products having boiling points low enough to leave the reactor. Heavier degradation products, remaining in the reactor were not considered in calculating the conversion.

The temperature profile of 10 °C min^{-1} was employed. The reactor was heated from room temperature to 550 °C. This temperature is sufficient for the full degradation of LDPE.

The percent conversion C, was defined according to the equation:

$$C = [(W_L+W_G)/W_O] \times 100$$

The yield, Y, of a certain species (gas or liquid) was calculated based on the following equation:

$$Y = (W_S/W_O) \times 100$$

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_S 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[10].

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.

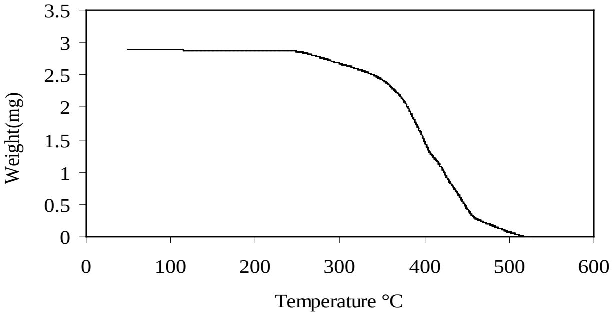

Fig. 1: Thermo gravimetric curve for thermal degradation of waste LDPE

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[11]. It was also observed that the presence of catalyst, NiMo/Al_2O_3 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[12]. 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.

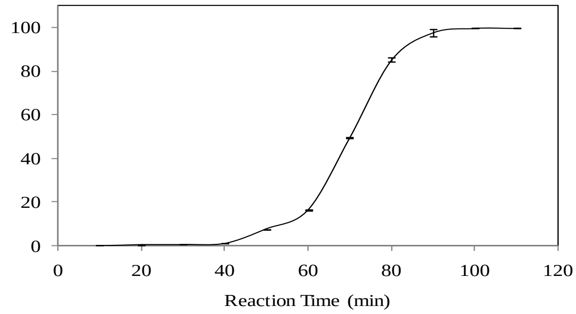

Fig. 2: Conversion of LDPE as a function of reaction time

Table 2: Product distribution for thermal degradation of LDPE

Product	Percentage
Conversion	93.8
Gas yield	8.5
Liquid yield	85.3
Solid residue	6.2

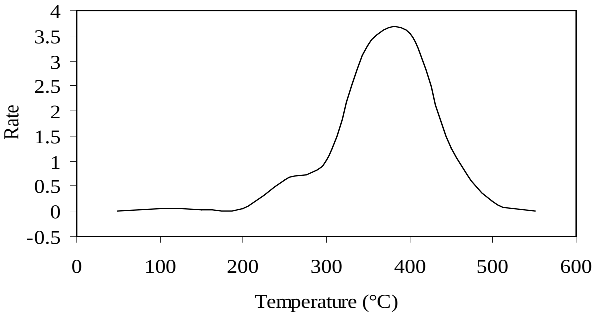

Fig. 3: Variations of instantaneous reaction rates at different temperature for the pyrolysis of LDPE

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.

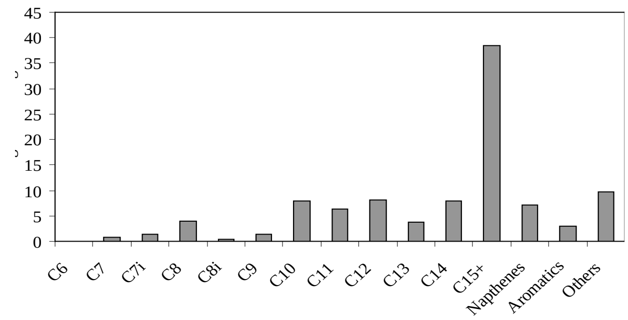

Fig. 4: Composition of the liquid fractions from the catalytic pyrolysis of LDPE

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.

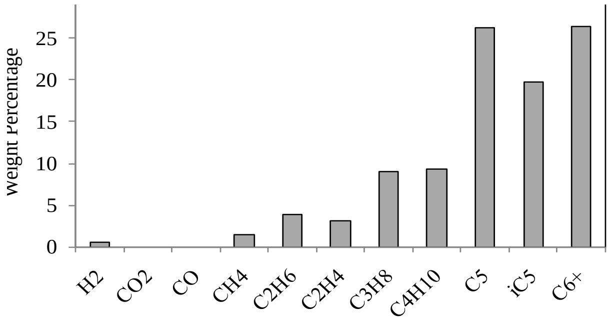

Fig. 5: Composition of the gaseous fractions from the catalytic pyrolysis of LDPE

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 3: Comparison of fuel properties of MV2 fuel oil and Liquid fraction

Characteristic	Test methods	IS : 1593-1982 standard for MV2 fuel oils	Liquid fraction
Acidity, inorganic	IS : 1448 [P : 2]	Nil	Nil
Ash, percent by mass	DIN EN 7	Maximum 0.1	0.002
Gross, calorific value cal g^{-1}	IS : 1448 [P : 6]	Report (Normally 10,000)	10,810
Flash point	ASTM D 93	66 °C	45 °C
Kinematic viscosity in centistokes at 50 °C	IS : 1448 [P : 25]	Maximum 180	147
Sediment, percent by mass	IS : 1448 [P : 30]	Maximum 0.25	0.001
Sulphur, total, percent by mass	IS : 1448 [P : 33]	Maximum 4.0	0.083
Water content, percent by volume	IS : 1448 [P:40]	Maximum 1.0	0.0001

The gaseous fraction can be recycled. This can be used for heating furnace which reduces the energy requirement of the waste LDPE pyrolysis process. The solid residue leftover can be purified and used as activated carbon. The purified carbon has wide applications as an additive to rubber and plastic products. Profitability can be considerably increased by high quality activated carbon. Activated carbon has various applications in filtering processes, gas purification, water purification etc.

CONCLUSION

In the present investigation, successful catalytic pyrolysis of waste LDPE was studied. Under this experimental conditions, LDPE degradation in the presence of $NiMo/Al_2O_3$ catalyst resulted in liquid fraction contained mainly of iso and straight chain hydrocarbons (85.3 wt%), Gas product predominantly composed of C5 and C6 hydrocarbons(8.5 wt%) with small quantity of solid residue (6.2 wt%). It was observed that the products obtained have the high economic values. Specifications were established for liquid fraction which serves as a superior quality fuel oil. Promising results for application of gaseous and solid residue for use as fuel or as a source of chemical was also obtained.

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